# Variation of tropospheric ozone concentration depending on solar radiation intensity

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We analyze the rate of the ozone generation depending on the solar radiation intensity within the near-ground air layer. The radiation absorption for formation of a unit of the ozone concentration is shown to range from 15 to 120 $W/m^2$ for 1 $\mu g/m^3$ and varies in different seasons. It is greater in cold seasons when the ozone concentration is minimum and lower in warm seasons when maximum ozone concentration is observed. This reflects the peculiarity in the ozone generation in the atmosphere that starts from photolysis of the ozone present in the atmosphere. Empirical relations are obtained connecting the ozone concentration and total solar radiation.

The increase of the ozone ($O_3$) concentration in the lower troposphere is now one of the urgent problems. It is caused by increasing emissions of the ozone producing gases of anthropogenic origin. The ozone generated in the troposphere exclusively in photochemical reactions is, on the one hand, a greenhouse gas which makes a significant contribution to heating the air. On the other hand, it is a biologically dangerous substance, which is related by biologists to the first class of danger. So the data on the peculiarities of its generation in the atmosphere are of interest in revealing the tendencies of $O_3$ concentration and assessing the consequences of its effect on the environment that can result from the possible increase of its concentration in the nearest future.

The full and sufficiently detailed diagram of physical processes, during which the ozone is generated in the atmosphere, is presented in Ref. 1. However, it is too complicated and does not provide for clear understanding of the principal affecting factors. So it is more convenient to use the gross equation of the balance of photochemical processes[2] in making quantitative analysis

$$RH + CO + NO \xrightarrow{\;I(h\nu),\ O_2,\ H_2O\;} NO_2 + fH_2CO + kO_3 + P,$$
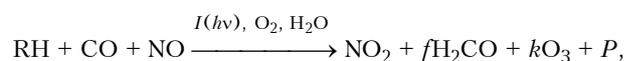
where RH denotes the hydrocarbons of different origin, CO is carbon monoxide, NO and $NO_2$ are nitrogen oxide and dioxide, respectively, $O_2$ is oxygen, $H_2O$ is water vapor, $I(h\nu)$ is the intensity of solar radiation, $H_2CO$ is formaldehyde, $O_3$ is ozone, $P$ is the aerosol product of photochemical reactions, $f$ and $k$ are the stoichiometric coefficient of ozone and hydrocarbon transformations.

It is seen from this gross equation that when the primary (ozone producing) admixtures, including hydrocarbons of different origin, RH, and carbon and nitrogen oxides come to the atmosphere where oxygen, $O_2$, and water vapor, $H_2O$, are present, they transform into nitrogen dioxide $NO_2$, formaldehyde $H_2CO$, and ozone $O_3$ during the photochemical processes under the effect of solar radiation $I(h\nu)$. The non-gaseous (aerosol) products can also appear in the photochemical reactions, but they quickly sink from the atmosphere. Obviously, the determining factor for the beginning and development of the photochemical reactions in the real atmosphere is the presence of solar radiation and the aerosol producing gases. However, as we know, there are no estimates of the contribution of solar radiation to the ozone generation in the atmosphere.

It was revealed in Ref. 3, on the basis of experimental data obtained under laboratory conditions in special chambers, that the yield of the products of reactions at different intensity of illumination of the primary mixture in the chamber depends on the type of reactions occurring there. Namely, photochemical generation of a substance occurs resulting from the direct transformation during the primary reactions, or it occurs in intermediate cycles during the secondary reactions.

If the substance has been generated during the primary cycle, the yield of the products is

$$dN/dt \sim I(h\nu).$$

If the intermediate mechanisms work, then

$$dN/dt \sim I^{1/2}(h\nu).$$

However, the dependences $dN/dt \sim f\,(I(h\nu))$ presented in Ref. 3 were obtained under laboratory conditions, i.e., under conditions when both the initial substances and the products of photochemical reactions were known. The limited amount of substances were used in the limited volume, as well as the processes were controlled. So we have certain doubts on whether one can transfer the features from Ref. 3 to the conditions in real atmosphere which is an open system with variable composition and unknown concentrations.

The aim of this paper is to estimate the contribution of solar radiation into the ozone generation in the near-ground layer of the troposphere from the data of measurements conducted in the

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atmosphere. The hourly data on the ozone concentration and total solar radiation obtained at the TOR-station[4] in the vicinity of Tomsk during 1996–1998 were used.

The proportionality relationship

$$dO_3/dt \sim I^X (h\nu)$$

similar to that obtained in the photochemical chambers[3] is quite readily seen in synchronous measurements carried out in the atmosphere. If one considers the data on the diurnal behavior of the total solar radiation and ozone concentration recorded during a day (Fig. 1a) or a monthly average (Fig. 1b), one can see that the increase in the intensity of solar radiation is accompanied by practically simultaneous increase in the ozone concentration. The decrease in the solar radiation influx in the afternoon causes a decrease in the ozone concentration. The rate of the ozone concentration fall off is a little bit lower than that of the solar radiation intensity. Obviously, this is caused by the fact that the ozone destruction is less determined by the photochemical processes.

Because of the fact that the general ozone generation is determined  not only by solar radiation, but by the content of the ozone producing substances as well, especially at the air mass change, it is obvious that, in order to obtain  correct estimates of the contribution of solar radiation, one should select the situations in which the composition of air does not change strongly. In our  opinion, these  are  the  situations  when an anticyclone  center or a low-gradient  field is over the region. Then there are no intensive advection of air masses  to  the  observation  site,  and,  hence,  the composition of air does not change significantly.

We selected 88 such situations for data processing, each of them included a few days. Two of them are shown in Fig. 2 as an example. To separate out the contribution of solar radiation to the ozone generation, the following formulas were used:

$$Q = 1/2 \sum_{t=t_0}^{t=t_{max}} Q_i;$$

$$\Delta n_3 = n_3 (t_{max}) - n_3 (t_{min}),$$

where $Q$ is the half-sum of solar radiation for current day calculated from hourly values from minimum to maximum $Q_i$; $\Delta O_3$ is the ozone increase during the current day from morning minimum to daytime maximum. It is assumed that the greater is the intensity of solar radiation, the higher should be the ozone concentration, other factors being the same.



**Fig. 1.** Diurnal behavior of the total solar radiation (*1*) and the ozone concentration (*2*) on March 22, 1996 (*a*), mean of July 1998 (*b*).
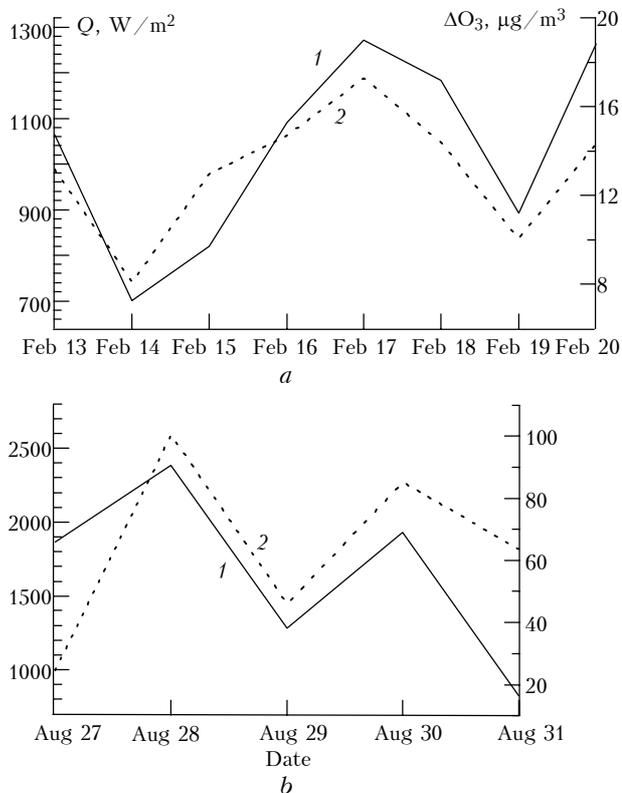


**Fig. 2.** The change in the influx of solar radiation $Q$ (*1*) and the increase of the ozone concentration $\Delta O_3$ (*2*) on February 13–20, 1996 (*a*) and August 27–31, 1996 (*b*).

It is seen in Fig. 2 that the change of the influx of solar radiation and the ozone concentration from day to day occurs quite synchronically in the selected situations. It is evidence of the fact that the ozone generation occurs in these situations proportionally to the intensity of solar radiation.

To estimate possible yield of ozone per a unit influx of solar radiation, let us use the following relationship:

$$\Delta I / \Delta n\,_3 = \left[\left(\sum_{t=t_0}^{t_{max}} Q_i - \sum_{t=t_0}^{t_{max}} Q_{i-1}\right)\right] \Big/ (\Delta n\,_{3i} - \Delta n\,_{3i-1}),$$

where the indices $i$ and $i-1$ denote the half-sums of solar radiation and daily amplitudes of ozone obtained for the current and previous day.

The calculations showed that the $1\ \mu g/m^3$ increase in the ozone concentration from one day to next can require from 15 to $120\ W/m^2$ of the total flux of solar radiation. The energy needed for the ozone generation has a well pronounced seasonal dependence. To confirm this, let us present the annual mean behavior of the parameter $\Delta I / \Delta O_3$ (Fig. 3) which has been constructed using data on all the cases which comprise the entire data set.
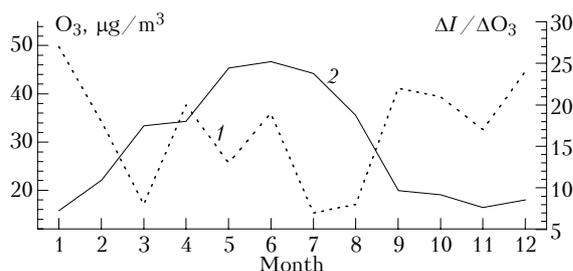


**Fig. 3.** Annual behavior of the ozone generation $\Delta I / \Delta n\,_3$ (*1*) and monthly mean values of the ozone concentration (*2*).

It is seen from Fig. 3 that the energy consumption for the ozone generation is greater in the cold season than in the warm. On the average, the annual behavior of the intensity of ozone generation and its monthly mean concentration are antiphased.

Such a change of the intensity of the ozone generation during a year is evidently caused by the peculiarities in the generation of ozone in the troposphere.[5]

According to Ref. 6, the beginning of photochemical processes in the troposphere is related to photolysis of the already available ozone:

$$O_3 + h\nu \rightarrow O(^1D) + O_2.$$

Then the process branches.[7]

Approximately 90% of oxygen atoms excited at the photolysis $O(^1D)$ take a lower energy state $O(^3P)$ due to interactions with the molecules of air and then transform to ozone again:

$$O(^1D) + N_2 \rightarrow O(^3p) + N_2,$$
$$O(^1D) + O_2 \rightarrow O(^3p) + O_2,$$

$$O(^3p) + O_2 + M \rightarrow O_3 + M,$$
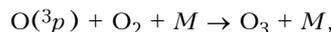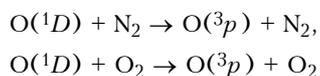
where $M$ are the molecules of nitrogen or oxygen ($N_2$, $O_2$).

Under normal conditions, the residual 10% of $O(^1D)$ react with water vapor thus yielding the hydroxyl:

$$O(^1D) + H_2O \rightarrow 2OH.$$

One should pay proper attention to the fact that the rate of the latter of these reactions is 10 times greater than the rate of the ozone reduction. So the non-proportional branching of the processes at the cycle beginning gives the same yield of the product by the cycle end.

Then OH enters into reactions with atmospheric admixtures and forms new cycles, in which OH is reduced again and ozone is produced.[8]

On the other hand, the rate of photolysis of gases in the atmosphere is determined by a convolution of the form[9]:

$$I_{A \rightarrow B} = \int\limits_{\Delta\lambda} \sigma_\lambda^A\, q_\lambda^{A \rightarrow B}\, F_\lambda\, d\lambda,$$

where $\Delta\lambda$ is the spectral range of photodissociation, $\sigma_\lambda^A$ is the absorption cross section of the gas $A$; $q_\lambda^{A \rightarrow B}$ is the quantum yield of the reaction, and $F_\lambda$ is the monochromatic radiation flux. Therefore, the intensity of the process of photolysis of the initially available ozone depends on the amount of the incoming solar radiation.

Thus, the greater is the initial concentration of $O_3$, the greater amount of new ozone is generated in the troposphere, and the less solar energy is needed for generation of $1\ \mu g/m^3$ of ozone. So, at other factors being the same, its generation should be more productive in a warm season when the ozone concentration is enhanced. This fact can explain the antiphased behavior of the curves in Fig. 3.

The data used for construction of curves depicted in Fig. 3 were specially selected and are not representative of all possible situations in the real atmosphere, so it is expedient to examine the conclusions on a more extensive data set without preliminary selection.

In so doing, we have calculated the monthly mean values of the total solar radiation and the monthly mean magnitudes of the ozone diurnal variation in 1996–1998. These values were then used to find the intensity of solar radiation needed to produce a unit amount of the ozone ($1\ \mu g/m^3$).

Such an approach can be accepted for the following reasons. More than a half of data, we have generalized in our previous paper[10] for the region of measurements, are related to situations similar to those for which Fig. 3 was constructed. Some more data from this set can also be accepted as representing situations favorable for the tropospheric ozone generation.

In contrast to calculations of the interdiurnal variation, these calculations used daily mean sums of the total radiation and monthly mean magnitudes of the ozone concentration diurnal variation. The calculations were performed by the formula

$$\Delta I / \Delta n_3 = [1/n \sum (\sum Q_i)]/1/n \sum (n_{3max} - n_{3min}),$$

where $\sum Q_i$ is the daily sum of the total solar radiation for a particular day, $\sum (n_{3max} - n_{3min})$ is

the magnitude of the ozone concentration diurnal variation; $n$ is the number of days in the month (see Table 1).

The conclusion that can be drawn from the table is similar to that from Fig. 3, namely: the amount of solar radiation needed for production of a unit amount of ozone is significantly greater in cold season than in the warm one. Note that the monthly mean values do not vary strongly from year to year.

**Table 1. Calculated results of the solar radiation (W/m²·hour/μg/m³)**

| Year | Month | | | | | | | | | | | |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
|      | I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
| 1996 | 69 | 32 | 31 | 38 | 27 | 21 | 13 | 14 | 25 | 23 | 56 | 29 |
| 1997 | 62 | 35 | 35 | 32 | 25 | 17 | 15 | 24 | 32 | 24 | 35 | 29 |
| 1998 | 56 | 46 | 39 | 46 | 37 | 26 | 28 | 23 | 31 | 40 | 28 | 21 |

The three-year mean intensity of the ozone generation (in the inverse ordinate) and the mean annual behavior of the ozone concentration are shown in Fig. 4.
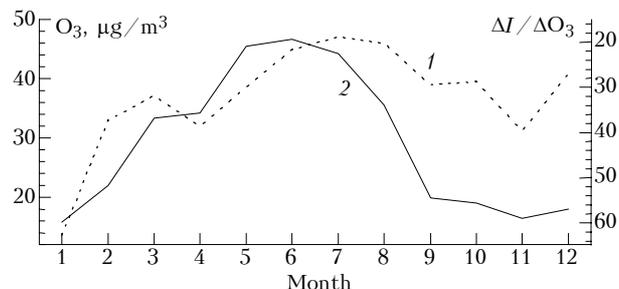


**Fig. 4.** Mean (1996–1998) intensity of the ozone generation (curve *1*) and mean annual behavior of the ozone concentration (curve *2*).

It is seen from Fig. 4 that the greater the ozone concentration, the less is the amount of solar energy needed for generation of a unit amount of ozone. Besides, this figure demonstrates the synchronous behavior of the curves in the first half of a year and partial similarity in the second half.

In our opinion, one can explain such a behavior of the curves as follows. As intensive generation of the ozone producing substances occurs in the first half of a year, in spring and the beginning of summer (growth of vegetation, evaporation), the dependence $\sim I^1$ is prevalent in the ozone generation. The ozone generation in the second half of a summer, when the amount of the ozone producing substances in the near-ground layer begins to decrease, occurs as $\sim (I^1 + I^{1/2})$ or similar to $\sim I^{1/2}$.

To test these suppositions, the rate of the ozone yield depending on the intensity of the total solar radiation was calculated by the method of least squares. The mean and maximum values were found by the formula

$$Y = a X^b.$$

First we made up the data sample from all data obtained in 1996–1998. The following coefficients of the sought formula were obtained:

$$O_3 = 0.0088 \, Q^{1.23}.$$

The exponent here is significantly greater than that obtained in the photochemical chambers,[3] that is hardly probable for the real atmosphere where the numerous additional ozone sinks occur. Evidently, the aforementioned annual behavior of the ozone concentration affected these calculations.

In this connection, the entire data array was divided into three parts: winter, summer, and transitional seasons. The calculation for two seasons gave the following results:

$$O_3 = 0.089 \, Q^{0.75} \quad \text{(winter)},$$

$$O_3 = 0.273 \, Q^{0.74} \quad \text{(summer)}.$$

It is seen that the dependence of the ozone generation on the intensity of the solar radiation influx in the real atmosphere has an intermediate form as compared with the photochemical chambers ($I^1$ and $I^{1/2}$), independently of season. This is an evidence of the fact that the ozone generation under field conditions occurs both in direct and intermediate cycles.

To examine the reliability of the obtained estimates, the data array was supplemented by the data obtained in 1995 and 1999 that made it 20% greater due to both enhanced and lowered ozone concentrations. The following coefficients were calculated for such a data array:

$$O_3 = 0.0092 \, Q^{1.23} \text{ (independently of a season)},$$

$$O_3 = 0.099 \, Q^{0.73} \quad \text{(winter)},$$

$$O_3 = 0.183 \, Q^{0.83} \quad \text{(summer)}.$$

Thus, at a wide scatter of the proportionality coefficients entering the obtained formulas, the exponents vary in a narrower range and lie in the

range[3] determined from the laboratory data, except the cases when the calculations had been performed using the entire data array without taking into account seasonal behavior of the ozone concentration. This is an evidence of the fact that the processes of ozone generation in the real atmosphere occur simultaneously by the mechanisms in which both primary and secondary cycles of reactions take part.

Physical meaning of the coefficients of these empirical relationships is the following. The proportionality coefficient shows the annual behavior of the ozone concentration and ozone producing substances at a particular site. One can suppose that it changes insignificantly not only in time, but also in space. The exponent has more general physical meaning and determines the dependence of the behavior of photochemical processes on the intensity of solar radiation initiating these processes. It is a more conservative parameter, and its variability should depend more strongly on the ratio between the primary and secondary photochemical cycles in the atmosphere.

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