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Influence of Solar Radiation on the Variation of the Ozone Concentration in the Ground Atmospheric Layer

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ABSTRACT

A rate of the ozone generation within the ground air layer depending on the solar radiation intensity is considered in the paper. The radiation consumption for formation of a unit of the ozone concentration is shown to range from 15 to 120 W/m^2 for 1 mkg/m^3 and to vary in different seasons. It is greater in cold seasons when the ozone concentration is minimum and less in warm seasons with maximum ozone concentration. This reflects a peculiarity of the atmospheric ozone generation which starts from photolysis of the ozone available in the atmosphere. Empirical relations are obtained connecting the ozone concentration with total solar radiation.

Keywords: solar radiation, ozone concentration, ground atmospheric layer.

Increase of the ozone (O_3) concentration in the lower troposphere is now one of the urgent problems. It is caused by increase of emission 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 in the air heating. On the other hand, it is a biologically dangerous substance, related by biologists to the first class of danger. So the data on peculiarities of its generation in the atmosphere are of interest for revealing the tendency for the O_3 concentration and assessing the consequences of its effect on the environment which may result from possible increase of the ozone 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 complicated and does not give an obvious idea of basic affecting factors. So, for quantitative analysis, it is more convenient to use the gross equation of the balance of photochemical processes [2]

$$\mathrm{RH} + \mathrm{CO} + \mathrm{NO} \xrightarrow{I(h\nu),\ \mathrm{O_2},\ \mathrm{H_2O}} \mathrm{NO_2} + f\mathrm{H_2CO} + k\mathrm{O_3} + P,$$

where RH are the hydrocarbons of different origin, CO is the carbon oxide, NO and NO_2 are the nitrogen oxide and the dioxide, respectively, O_2 is the oxygen, H_2O is water vapor, I(hν) is the intensity of solar radiation, H_2CO is the formaldehyde, O_3 is the ozone, P is the aerosol product of photochemical reactions, f and k are the stoechiometric coefficients of the ozone and the hydrocarbon transformation.

It is seen from this gross equation that, when the primary (ozone-producing) admixtures. including hydrocarbons of different origin RH as well as the carbon and the nitrogen oxides, occur in the real atmosphere, where oxygen O_2 and water vapor H_2O are present, they are transformed into nitrogen dioxide NO_2, formaldehyde H_2CO, and ozone O_3 during the photochemical processes under exposure to solar radiation I(hν). The non-gaseous (aerosol) products can also appear in these photochemical reactions, but they are quickly washed out from the atmosphere. Obviously, the determining factors for initiating and proceeding the photochemical reactions in the real atmosphere are solar radiation and the aerosol-producing gases. However, as we know, there are no estimates of the solar radiation contribution into the ozone generation in the real atmosphere.

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

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

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

If the intermediate mechanisms are present, then

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

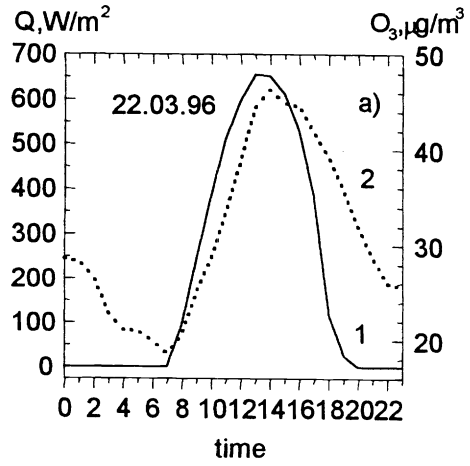
However, the dependencies $dN/dt \sim f(I(h\nu))$ presented in Ref. 3 were obtained under laboratory conditions, i.e. when both the initial substances and the products of photochemical reactions were known. The limited amounts of substances were used in the limited volume, as well as the processes were controlled. So we doubt whether one can extend the regularity from Ref. 3 to conditions of the real atmosphere, which is an open system with variable composition and unknown concentration of components.

The aim of this paper is to estimate the contribution of solar radiation into the ozone generation in the ground layer of the troposphere from the measurements in the real atmosphere. The hourly data on the ozone concentration and total solar radiation obtained at the TOR-station [4] in the neighborhood of Tomsk during 1996-1998 were used by us.

The proportionality

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

similar to that obtained in the photochemical chambers [3] can be well seen in simultaneous measurements carried out in the real atmosphere. The data on the diurnal behavior of the total solar radiation and ozone concentration for some particular day (Fig. 1a) and monthly averaged (Fig. 1b) show that the increase of the solar radiation intensity is accompanied by practically simultaneous increase of the ozone concentration. A decrease of inflow of solar radiation in the afternoon causes some decrease of the ozone concentration. The decrease of the ozone concentration is behind the rate of the decrease of the solar radiation intensity. Obviously, it is caused by the fact that the ozone destruction is less determined by the photochemical processes.



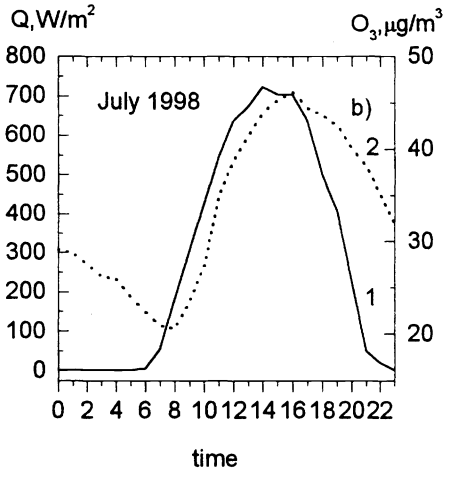


Fig. 1. Diurnal behavior of the total solar radiation (1) and the ozone concentration (2) in March, 22, 1996 (a), mean in July 1998 (b)

The total ozone generation is determined not only by solar radiation but also by the content of the ozone-producing substances, the amount of which significantly changes in the real atmosphere, especially at a change of air mass. So, it is obvious that, in order to estimate the contribution just of the solar radiation, one should select the situations, in which the air composition does not change significantly, i.e. when an anticyclone center or a small-rate field occur above some region. Then there will be no intensive advection of air masses in the point of observation, and, hence, the air composition will not change noticeably.

We have selected 88 such situations for data processing, each included a few days. Two of them are shown in Fig. 2 as an example.

To separate the contribution of solar radiation into the ozone generation, the following formulae were used:

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

$$\Delta O_3 = O_3 (t_{max}) - O_3 (t_{min}),$$

where Q is the half-sum of solar radiation for current day calculated by hourly readings from minimum to maximum Q_i; ΔO_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 greater should be the ozone concentration (at other factors being the same).

Figure 2 shows quite synchronous change of the solar radiation inflow and the ozone concentration in the selected situations from day to day. It is the evidence of the fact that the ozone generation is in these situations proportional to the intensity of solar radiation.

In order to estimate the possible yield of the ozone per unit of incident solar radiation, let us use the relationship

$$\Delta I/\Delta O_3 = [(\sum_{t=t_0}^{t\,max} Q_i - \sum_{t=t_0}^{t\,max} Q_{i-1})]/(\Delta O_{3i}-\Delta O_{3i-1})$$

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

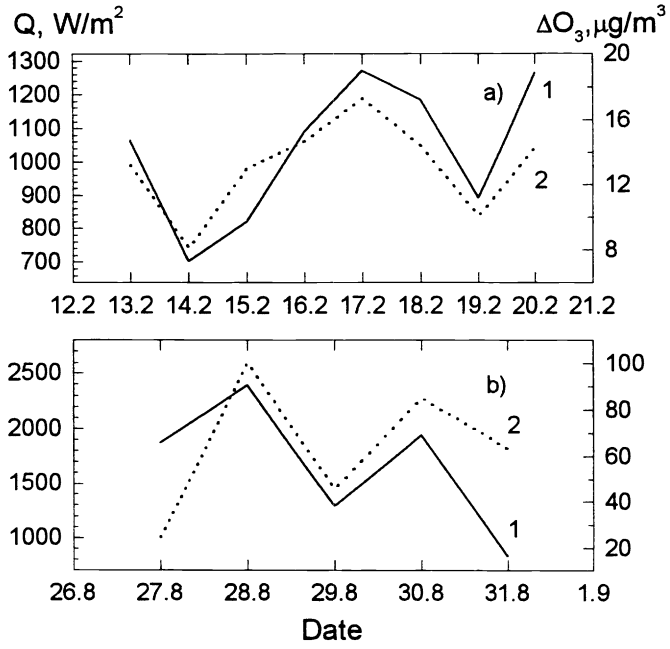


Fig. 2. The change of the inflow of solar radiation Q (1) and the increase of the ozone concentration ΔO_3 (2) in February, 13-20, 1996 (a) and in August, 27-31, 1996 (b)

Our calculations show that the increase the ozone concentration by 1 $\mu g/m^3$ from one day to another can require from 15 to 120 W/m^2 of the total flux of solar radiation. The expense of energy for the ozone generation has well pronounced seasonal dependence. For confirmation, we present mean annual behavior of the parameter $\Delta I/\Delta O_3$ (Fig. 3) constructed over all selected cases.

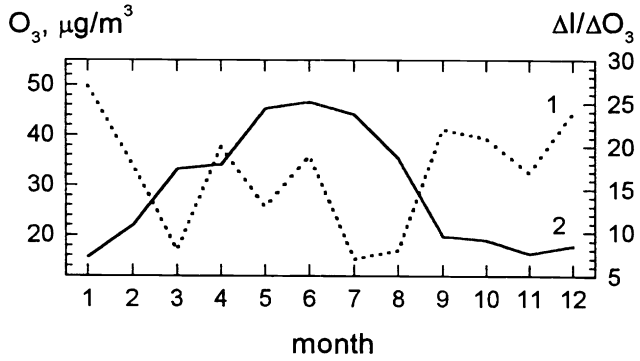


Fig. 3. Annual behavior of the ozone generation $\Delta I/\Delta O_3$ (1) and monthly mean ozone concentrations (2)

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

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

According to Ref.6, the initiation of photochemical processes in the troposphere is due to photolysis of the available ozone:

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

Then the process branches [7].

About 90% of oxygen atoms excited at the photolysis $O(^1D)$ pass to the lower state $O(^3P)$ when interacting with molecules of the air, and then they are again retransformed into ozone:

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

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

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

where M are the molecules of nitrogen or oxygen (N_2, O_2).

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

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

One should pay attention to the fact that the rate of the last reaction is 10 times greater than the rate of the ozone restoration. So the non-proportional branching of the processes at the beginning of the cycle gives the same yield of the product at its end.

Then the OH enters into reactions with atmospheric components and forms new cycles, in which it is restored again as well as the ozone is generated [8].

At the same time, the rate of photolysis of gases in the atmosphere is determined by convolution of the form [9]:

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

where $\Delta\lambda$ is the spectral range of photodissociation, $\sigma^A{}_\lambda$ is the absorption cross-section of the gas A, $q_\lambda{}^{A\rightarrow B}$ is the quantum yield of the reaction, and F_λ 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 the ozone. So, at other factors being the same, the ozone generation should be more productive in warm seasons when its concentration is enhanced. This fact can explain the mutually inverse behavior of the curves in Fig. 3.

The data used for constructing Fig. 3 were specially selected. Therefore they are not representative of all possible situations in the real atmosphere. So it would be expedient to check our conclusions using more extensive data without preliminary selection.

To do it, we calculated the monthly average values of total solar radiation and the monthly average daily ozone amplitudes for 1996-1998 years. The value of the solar radiation intensity required for generation of the ozone unit (1 $\mu g/m^3$) was determined.

One can accept such an approach due to the following reasons. More than a half of the data, generalized [10] over the region of measurements, are related to the situations similar to those, for which Fig. 3 was constructed. Another portion of data can be accepted as favorable for the tropospheric ozone generation.

In this calculation, contrary to the diurnal variability, daily mean sums of total radiation and daily mean amplitudes of the ozone concentrations averaged over a month were used. The calculations were performed by the formula

$$\Delta I/\Delta O_3 = [1/n \Sigma (\Sigma Q_i)]/1/n \Sigma (O_{3max} - O_{3min}),$$

where ΣQ_i is the daily sum of the total solar radiation for particular day, $\Sigma (O_{3max} - O_{3min})$ is the daily amplitude of the ozone concentration; n is the number of days in the month (see Table).

Table. Results of calculation of solar radiation (W/m^2 - hour/$\mu g/m^3$)

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 same conclusion follows both from the Table and Fig. 3, namely: the expense of solar radiation for the unit ozone generation is significantly greater in cold seasons than in warm. The monthly mean values change therewith insignificantly from year to year.

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.

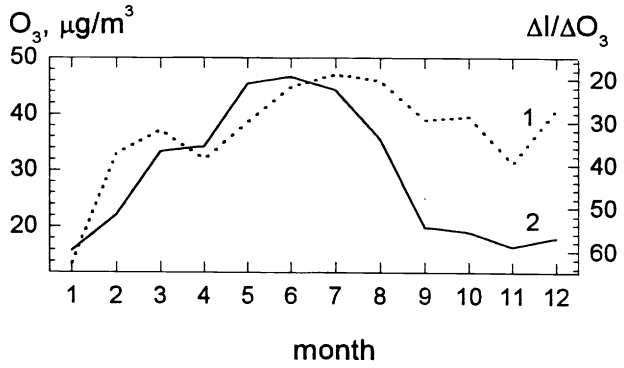


Fig. 4. Mean (1996-1998) intensity of the ozone generation (curve 1) and mean annual behavior of the ozone concentration (2).

It is seen there, that the greater is the ozone concentration, the less are the expenses of solar energy for generation of the unit ozone concentration. In addition, Fig.4 demonstrates synchronous behavior of the curves in the first half year and the partial similarity in the second half.

In our opinion, one can explain such a behavior of the curves by the following reasons. As the intensive generation of the ozone-producing substances takes place in the first half year, in spring and in the beginning of summer (growth of vegetation, evaporation), the dependence $\sim I^1$ is prevailing in the ozone generation. In the second half of summer, when the amount of the ozone-producing substances begins to decrease, the process follows to the scheme $\sim (I^1 + I^{1/2})$ or is close 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 least square method. The mean and maximum values were found by the formula

$$Y = a X^b.$$

In the beginning the sample included 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 for the photochemical chamber [3], what is little likelihood for the real atmosphere where numerous additional ozone sinks are present. Evidently, the aforementioned annual behavior of the ozone concentration affected the calculations.

In this connection, all array of data was divided into three portions: winter, summer and interseasons. The calculation for two seasons gave the following results:

$$O_3 = 0{,}089\ Q^{0{,}75} \qquad \text{(winter)},$$

$$O_3 = 0{,}273\ Q^{0{,}74} \qquad \text{(summer)}.$$

It is seen that the dependence of the ozone generation on the intensity of the solar radiation inflow in the real atmosphere has an intermediate form relative to the photochemical chamber (I^1 and $I^{1/2}$), independently of the season. This suggests that the ozone generation under field conditions occurs both in direct and intermediate cycles.

To check a reliability of the obtained estimates, the data array was added by the data obtained in 1995 and 1999. It became 20% greater at the expense of both enhanced and lowered ozone concentrations. The following coefficients were obtained for the resulting data array:

$$O_3 = 0{,}0092\ Q^{1{,}23} \qquad \text{(independently of the season)},$$

$$O_3 = 0{,}099\ Q^{0{,}73} \qquad \text{(winter)},$$

$$O_3 = 0{,}183\ Q^{0{,}83} \qquad \text{(summer)}.$$

Thus, at wide scatter of the proportionality coefficients in the obtained formulae, the exponents are less variable and lie in the range [3] determined from the laboratory data, except for the cases when the calculations were performed for all data array disregarding seasonal behavior of the ozone concentration. It indicates that the both mechanisms of the ozone generation in the real atmosphere take place simultaneously, in which primary and secondary cycles of reactions are present.

The coefficients of these empirical relationships have the following physical meaning. The proportionality coefficient shows the annual behavior of concentration of ozone and ozone-producing substances in some particular area. One can suppose that it will significantly change not only in time, but also in space. The exponent has more general physical meaning and determines the dependence of the photochemical processes' behavior on the intensity of solar radiation initiating such processes. It is the more conservative parameter, and its variability should depend more strongly on the relation of primary and secondary photochemical cycles in the atmosphere.

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