

# Tropospheric ozone.

## 4. Photochemical formation of tropospheric ozone: the role of solar radiation

B.D. Belan<sup>1,2</sup> and T.K. Sklyadneva<sup>1</sup>

<sup>1</sup>*V.E. Zuev Institute of Atmospheric Optics,  
Siberian Branch of the Russian Academy of Sciences, Tomsk*  
<sup>2</sup>*Tomsk State University*

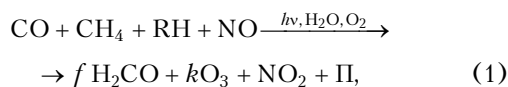
Received October 22, 2007

The factors determining mechanisms of photochemical formation of ozone in troposphere are considered. Principal factors are found on the base of estimation of tropospheric ozone budget. The ozone formation in background and smog conditions is considered. Other photochemical sources are described. Ozone formation in striking, ionic cycle, and ozone transport from stratosphere to troposphere are analyzed.

### Introduction

As it follows from the previous review,<sup>1</sup> the photochemical component of tropospheric ozone is the most significant and variable. In view of complexity and variety of ozone formation processes in troposphere, factors, determining the mechanism of photochemical formation of O<sub>3</sub> and components of ozone cycle, are considered in this work.

When studying this problem, many researchers tried to describe such processes in the form of schemes joining both direct and back bonds and reactions. Several such schemes are given in Ref. 1a. Such representation is convenient for specialists in this region of science. For other specialists it is not clear, because it combines many ozone cycles, characteristic for different atmospheric conditions. Therefore, let us represent the photochemical process of tropospheric ozone formation in the form of brutto-equation:



where  $f$  is the stoichiometric coefficient of hydrocarbon transformation;  $k$  is the factor of the ozone yield depending on the concentration of nitric oxides, which switches the chain of ozone generation; II are the products of photochemical reactions, i.e., aerosol particles resulting from interaction of gas components.

The physical sense of Eq. (1) is clear: reaching the real atmosphere, which contains water vapor (H<sub>2</sub>O) and oxygen (O<sub>2</sub>), primary admixtures (CO, CH<sub>4</sub>, RH – non-methane hydrocarbons, NO) are transformed under the action of UV solar radiation into more toxic compounds (H<sub>2</sub>CO, O<sub>3</sub>, NO<sub>2</sub>, and aerosol (II), often even into peroxyacetyl nitrates (PAN) etc.). Equation (1) does not reflect the role of intermediate compounds, i.e., hydroxyl groups HO,

and the switching role of nitrogen oxides. However, it clearly shows the components, forming tropospheric ozone, and factors, determining the process. The ozone yield evidently depends on two factors: the concentration of initial compounds (gas-precursors) and the intensity and spectrum of solar radiation. The part of solar radiation in O<sub>3</sub> formation is the topic of this work.

### 1. The role of solar radiation in tropospheric ozone formation

Describing the mechanism of ozone generation in pure conditions [Ref. 1, Sec. 2.1], we have noted that the process begins with photolysis of ozone residing in air. The appearing oxygen atom in O<sup>1</sup>D state interacts with water vapor and forms a hydroxyl group OH, which begins to oxidize gas-precursors. Thus, ozone photolysis is a key act for the beginning of the process. Photolysis of ozone itself and its mixtures was studied in many laboratory experiments. Their review is given in Ref. 2 in detail. Since not all *in vitro* results can be expanded to atmospheric conditions; consider only the data applicable to troposphere.

### 2. Photolysis of tropospheric ozone

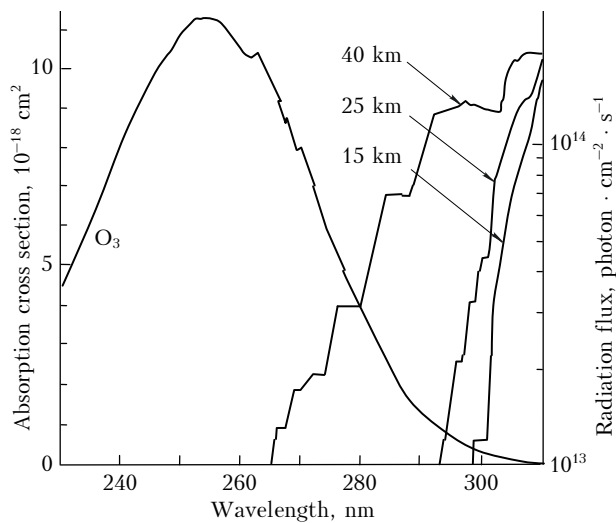
The photodissociation rate of a compound, undergone to the photolysis, can be calculated by the equation<sup>3</sup>:

$$J = \int_{\lambda_1}^{\lambda_2} F(\lambda) \sigma(\lambda, T, P) \varphi(\lambda, T, P) d\lambda, \quad (2)$$

where  $F_\lambda$  is the spectral irradiance;  $\lambda$  is the radiation wavelength;  $\sigma$  is the gas molecule absorption cross section at the wavelength  $\lambda$ , depending on the air

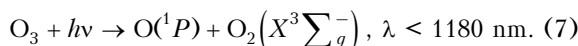
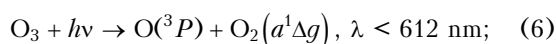
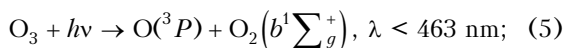
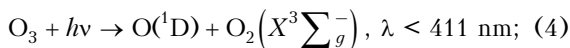
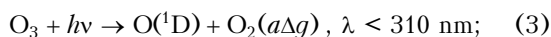
temperature and pressure;  $\phi_\lambda$  is the quantum yield, characterizing the probability of the molecule dissociation after photon absorption at the wavelength  $\lambda$ .

The spectral irradiance in troposphere is formed by the direct solar flux, attenuated by the absorption and scattering in the upper atmospheric layers, and radiation, scattered by the atmosphere, underlying surface, and clouds. The wavelength range between 295 and 1200 nm is the most important for photochemistry in troposphere. The lower boundary is determined by attenuation in higher atmospheric layers and does not exceed 295 nm already at an altitude of 15 km (see Fig. 1).



**Fig. 1.** O<sub>3</sub> absorption spectrum in the Hartley band at 263 K [Ref. 4] and spectral flux as a function of height at a zenith angle of 40° [Ref. 5].

The upper boundary is determined by the energy of quanta of a longer wave radiation sufficient for breaking bonds in ozone molecules. When analyzing ozone photolysis in troposphere, the following chain of reactions is usually considered<sup>6</sup>:



O(<sup>3</sup>P) is rapidly retrieved into ozone [Ref. 1, Sec. 2.1 and Eq. (3)]; hence, reactions (3) and (4) are basic in generation of excited oxygen atom O(<sup>1</sup>D).

The radiation flux, determining the photodissociation at the level  $z$  can be described by the equation<sup>7</sup>

$$F_\lambda(z) = F_\lambda^0 \exp[-(\tau_n + \tau_p)] + F_\lambda^p(z, A), \quad (8)$$

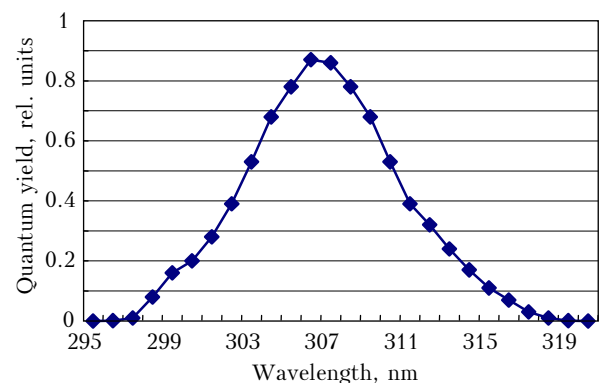
where  $F_\lambda^0$  is the flux of extraterrestrial solar radiation;  $\tau_n$  and  $\tau_p$  are optical depths of the absorption and scattering along a light beam;  $F_\lambda^p$  is the flux of radiation, scattered by molecules of atmospheric gases, aerosol particles, and underlying surface with the albedo  $A$ .

Though it is supposed that the integral flux of the extraterrestrial radiation is sufficiently accurately determined (1.5–2%) and slightly variable in time, data for separate spectral ranges are insufficiently unambiguous. The ambiguity is 15% for  $295 < \lambda < 400$  nm and 8% for  $\lambda > 550$  nm.<sup>8</sup> Therefore, when studying processes of the ozone photolysis, the authors take into account both the spectral interval and the presence of aerosol, water vapor, and clouds in the atmosphere, attenuating the flux  $F_\lambda(z)$ ; variations of the quantum yield  $\phi(\lambda, T, P)$  are of their primary interest in this case.

Models for calculating photolysis rates and quantum yield of photodissociation products have been developed.<sup>9–14</sup> Validation of 29 such models, carried out within the International Photolysis Frequency Measurement and Modeling Intercomparison (IPMNT) program in Boulder,<sup>15</sup> has shown that estimates of the photolysis rate could be calculated with an error not worse than 10% when measuring the solar radiation flux with an accuracy of about 5% at high Sun, clear weather, and low aerosol concentration. As it follows from the comparison of calculated and measured results, the calculated coefficients of quantum yield of O<sub>3</sub> and NO<sub>2</sub> are significantly higher than the observed ones.

To precise the photolysis parameters in the actual atmosphere, dozens of experiments were carried out; they are partly described along with the used equipment in Refs. 16–28. It has turned out that the ozone photolysis rate lies within  $10^{-2}$ – $10^{-5}$  s<sup>-1</sup> limit, and a wavelength of 360 nm, at which the maximum quantum yield is observed, can be accurately distinguished. As it is evident from Fig. 2, the rate decreases below this wavelength due to a sharp drop of incoming solar radiation intensity; and above it the ozone absorption cross section decreases.

Therefore, the range of wavelengths longer than 306 nm has been studied in a number of works.

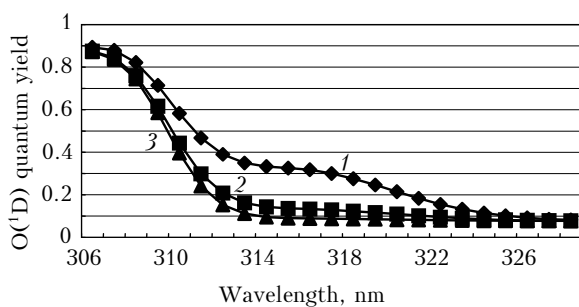


**Fig. 2.** The normalized quantum yield of O(<sup>1</sup>D) relative to the maximally possible as a function of the wavelength.

**Table 1. O(<sup>1</sup>D) quantum yield of ozone photolysis at 298 K**

$\lambda$ , nm	[Ref. 24]	[Ref. 29]	[Ref. 30]	[Ref. 31]	[Ref. 32]	[Ref. 33]	[Ref. 34]	[Ref. 35]	Average
306	0.85	0.85	0.89	—	0.86	0.90	0.84	0.91	0.87
307	0.85	0.84	0.89	0.87	0.83	0.91	0.80	0.85	0.86
308	0.78	0.79	—	0.83	0.81	0.73	0.79	0.74	0.78
309	0.67	0.71	0.75	0.72	0.62	0.66	0.70	0.61	0.68
310	0.55	0.56	0.60	0.51	0.40	0.52	0.62	0.48	0.53
311	0.40	0.42	0.39	0.42	0.32	0.37	0.44	0.38	0.39
312	0.33	0.35	0.30	0.32	0.26	0.31	0.35	0.32	0.32
313	0.27	0.32	0.26	0.24	0.24	0.29	0.34	0.28	0.28
314	0.22	0.30	0.22	0.22	0.22	0.29	0.27	0.27	0.25
315	0.21	0.29	—	0.23	0.24	0.25	0.22	0.26	0.24
316	0.25	0.27	0.21	0.21	0.22	0.22	0.28	0.24	0.24
317	0.23	0.26	—	0.21	0.22	0.23	0.26	0.21	0.23
318	0.19	0.23	0.18	0.16	0.21	0.21	0.24	0.20	0.20
319	0.21	0.26	—	0.14	0.22	0.20	0.27	0.22	0.22
320	0.15	0.21	0.12	0.13	0.15	0.19	0.19	0.09	0.15
321	0.14	0.20	—	—	0.14	0.09	0.17	0.07	0.14
322	0.11	0.15	0.11	—	0.11	—	0.15	0.03	0.11
323	0.09	0.13	—	—	0.09	—	0.13	0.04	0.10
324	0.08	0.13	0.09	—	0.09	—	0.13	0.04	0.09
325	0.09	0.10	—	0.06	0.08	0.07	0.11	0.01	0.07
326	0.09	0.11	0.13	—	0.08	—	0.10	—	0.10
327	0.09	0.12	—	—	0.07	—	0.10	—	0.10
328	0.08	0.09	0.11	—	0.06	—	0.12	—	0.09

The results are generalized in Table 1. It is evident that there is a spread in O(<sup>1</sup>D) quantum yield obtained by different authors, reaching 3 times at individual wavelengths. Near the maximum of O(<sup>1</sup>D) quantum yield, the difference is significantly less. Many authors notice the air temperature dependence of the O(<sup>1</sup>D) quantum yield.<sup>29,32,34</sup> A detailed analysis of laboratory experiments in Ref. 36 allowed authors to develop a corresponding model of the dependence and obtain explicit data for building Fig. 3.



**Fig. 3.** Recommended<sup>36</sup> values of O(<sup>1</sup>D) quantum yield at  $T = 321$  (1), 253 (2), and 203 (3) K.

Figure 3 shows the rise of O(<sup>1</sup>D) quantum yield with the air temperature increase, especially in 310–320 nm wavelength range.

As it follows from the analysis of Eq. (8), the tropospheric ozone photolysis rate is influenced by aerosol particles, scattering the solar radiation. Many works are devoted to study of this process. Consider some of them.

The authors of Ref. 37, analyzing 14 tropospheric photolytic reactions, came to conclusion that in the absence of clouds at the average concentration of sulfates in urban air the photolysis rate decreases by 11–185 times. Similar calculations<sup>38</sup> with the ADIFOR model gave even higher value, namely, the photolysis rate in polluted air decreased by 70%. The study with the use of the 3D GEOS-CHEM model<sup>39</sup> has shown that the presence of aerosol decreases the photolysis rate in the ground air by 5–20% in the Northern Hemisphere. This value is to double in places of vegetation burning. Contribution of the mineral component was studied in Ref. 40. An increase of photolysis rate by 11% was obtained for average conditions and by 20% for increased air turbidity. A contribution of soot was distinguished<sup>41</sup> for polluted conditions of Huston, which could decrease the photolysis rate by 5–20%.

Clouds, especially cumulus, essentially change solar radiation flux, where spots appear and the photolysis is enhanced above clouds.<sup>42</sup> Similar results have been experimentally obtained in Ref. 43.

Simultaneous accounting for clouds and aerosol shows that the effects can change with height. Thus, it is shown in Ref. 44 that contribution of clouds in the change of the photolysis rate can vary from –90 to +200% relative to aerosol, which has a maximum of  $\pm 20\%$ . The authors of Ref. 45 have found out that the rate of photolysis decreases by 20% under clouds, observed in the 1–8 km layer, while grows by 30% above them. The global contribution into the decrease of photolysis rate has been estimated<sup>46</sup> as –20% by clouds (–30% in a storm zone), –10% by

soot in urban areas, +40% above clouds, up to -17% by the mineral aerosol fraction.

Thus, along with variations of the ozone photolysis rate, depending on solar radiation flux, it can vary due to external conditions, temperature, clouds, and aerosol as well.

### 3. Contribution of integral and UV radiation

As it follows from Eq. (2), the rate of ozone photodissociation, initiating photochemical processes in the atmosphere, depends not only on the quantum yield and gas absorption cross section, but on the solar radiation flux as well.

As it is evident from the data on daily variations of total solar radiation and ozone concentration for a certain date (Fig. 4a) and monthly mean data (Fig. 4b), the increase in solar radiation intensity is accompanied by the almost synchronous increase in the ozone concentration.

Figure 4 is built by the measurements at the TOR-station (Tomsk).<sup>46</sup> Attenuation of solar radiation in the afternoon results in a decrease in the ozone concentration; and the decrease in ozone concentration is slightly behind the decrease of the solar radiation intensity. This is evidently caused by the fact that ozone destruction is less influenced by photochemical processes.

On the base of experimental data obtained in laboratory conditions in special chambers,<sup>47</sup> it is established that the rate of chemical yield at different radiation intensity of the initial mixture in the chamber depends on the type of the proceeding reactions. Namely, some matter is photochemically generated as a result of direct transformation in primary reactions or in secondary reactions through intermediate cycles.

If a matter is generated in the primary cycle, the rate of chemical yield is

$$dN/dt \sim I(h\nu). \quad (9)$$

If there are some intermediate mechanisms, then

$$dN/dt \sim I^{1/2}(h\nu). \quad (10)$$

However, the relation  $dN/dt \sim f(I(h\nu))$  was obtained<sup>47</sup> in laboratory conditions, i.e., at known initial substances and products of their chemical reactions. A limiting amount of matters was used in a restricted volume, and the process was under control. Therefore, the extension of the regularities<sup>47</sup> to the real atmosphere seems unjustified, as it is an open system with variable composition and unknown concentrations of matters.

The contribution of solar radiation in ozone generation in the surface tropospheric layer was estimated in Refs. 48 and 49 from measurements in the real atmosphere, presuming the proportionality of UV solar radiation influx.<sup>50-53</sup> The results of hourly measurements of ozone concentration and total solar radiation near Tomsk at TOR-station in 1996-1998 were used.

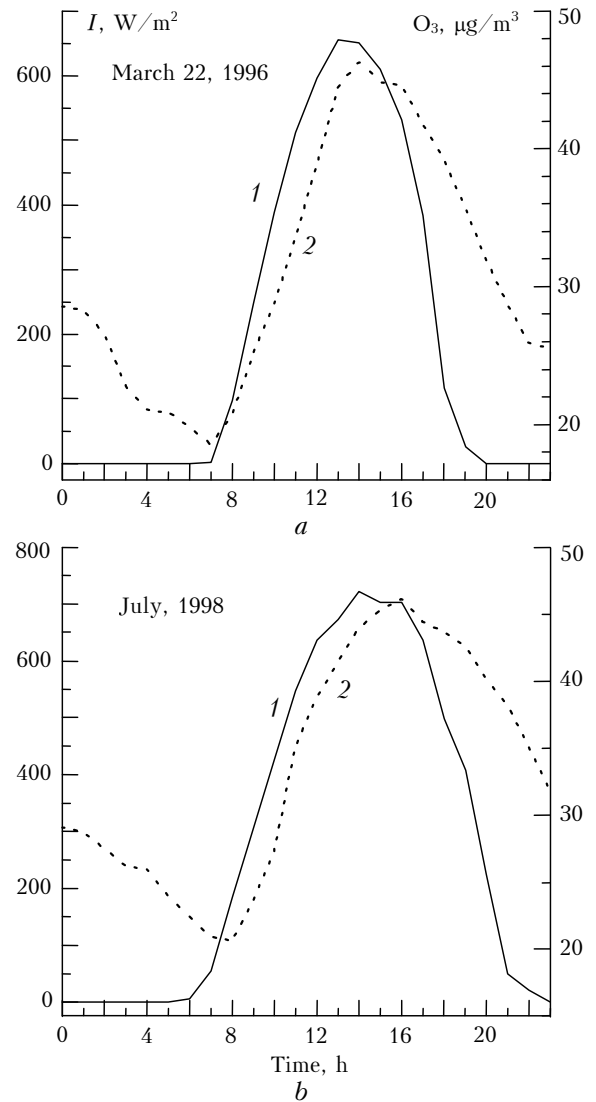


Fig. 4. Daily variations of total solar irradiation (curve 1) and ozone concentration (curve 2) on March 22, 1996 (a) and in July, 1998 on average (b).

The total ozone generation is determined not only from solar radiation, but also from concentrations of ozone-forming species, amount of which strongly varies in real atmosphere, especially at changing of air masses. Hence, to obtain the correct estimation, it is necessary to distinguish certain situations, when the air composition varies insignificantly. These situations realize, when the anticyclone center or a flat are set above the measurement region. In this case, an intensive mass advection is absent here and, hence, the air composition is invariable due to the absence of local sources of ozone-forming species.

To process the whole data array, 88 such situations were selected, each including several measurement days. To separate the contribution of the solar radiation in the ozone generation, we used the following equations:

$$I = \frac{1}{2} \sum_{t=t_0}^{t=t_{\max}} I_i, \quad (11)$$

$$\Delta O_3 = O_3(t_{\max}) - O_3(t_{\min}), \quad (12)$$

where  $I$  is the half-sum of solar radiation in a current day by hourly counts from minimum to maximum;  $\Delta O_3$  is the ozone increment during a current day from the morning minimum to day maximum. It is assumed that the higher the solar radiation intensity, the higher the ozone concentration (at other factors being equal).

To assess quantitatively the possible ozone yield per unit of the incoming solar radiation, we used the equation

$$\Delta I / \Delta O_3 = \left[ \left( \sum_{t=t_0}^{t_{\max}} I_i - \sum_{t=t_0}^{t_{\max}} I_{t-1} \right) \right] / (\Delta O_{3i} - \Delta O_{3i-1}), \quad (13)$$

where subscripts  $i$  and  $i-1$  designate half-sums of solar radiation and the daily ozone amplitude in a current and previous days.

Calculation for two seasons gave the following results:

$$O_3 = 0.089I^{0.75} \text{ (winter)}, \quad (14)$$

$$O_3 = 0.273I^{0.74} \text{ (summer)}. \quad (15)$$

It is seen from the above equations that the dependence of ozone generation on the intensity of solar radiation income in the real atmosphere has an intermediate form relative to photochemical chambers ( $I^1$  and  $I^{1/2}$ ) [Ref. 17] independently of the season. This is evidence of the fact that the ozone generation in natural conditions occurs simultaneously in direct and intermediate cycles.

Physical sense of the coefficients in the above empirical relations is the following. The proportionality coefficient reflects the annual variation of ozone concentrations and ozone-forming species at a particular point. It can be supposed that the coefficient varies significantly both in time and space. The exponent has more general physical sense and is determined by the dependence of photochemical processes on the intensity of solar radiation initiating these processes. This is more conservative parameter and its variability stronger depends on the ratio between primary and secondary photochemical cycles in the real atmosphere.

It follows from Section 2 that the influx of UV portion of the solar radiation  $\lambda = 290\text{--}320$  nm is more important for the ozone generation, than the influx of the solar radiation itself (see Fig. 2). Figure 5 shows variations of the surface ozone concentration and UV solar radiation near Tomsk in three central months of seasons.

The UV- $B$  radiation was measured at the TOR-station<sup>46</sup> with an UVB-1 piranometer (Yankee Environmental Systems, Inc.) and the ozone concentration – with a chemiluminescent ozonometer 3-02P (OPTEC, St. Petersburg).

A strong time modulation of the ozone concentration by the UV- $B$  solar radiation influx follows from Fig. 5. One-day shifts, observed in some periods, are rather caused by the fact that the plots present the daily-average data. Note that variation

amplitudes of ozone and UV- $B$  radiation are not synchronized in value, seemingly, due to the contribution of the air composition in the ozone formation, which is defined by the left part of Eq. (1) and reflected by the coefficients in Eqs. (14) and (15). This means that the rate and frequency of ozone formation in troposphere is determined by the UV- $B$  solar radiation income, while the concentration of the generated ozone – by content of gas-precursors in air.

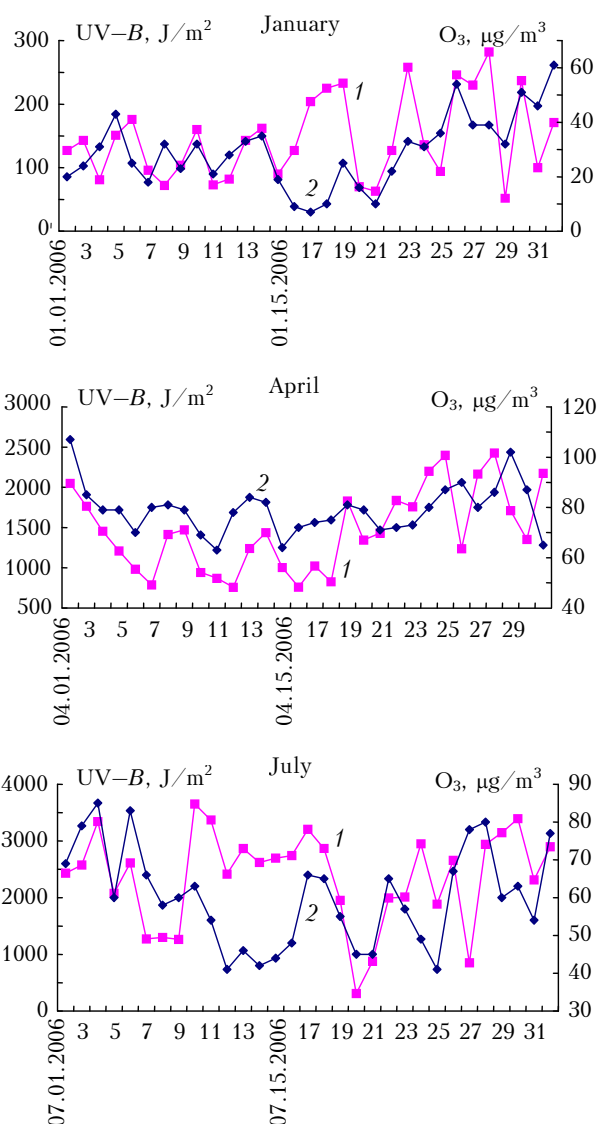


Fig. 5. Variations of UV- $B$  radiation (1) and ozone concentration (2) near Tomsk in 2006.

We do not consider the UV- $B$  radiation mode here. Note only that the appearance of information about ozone holes over poles and possible biospheric backlash<sup>54,55</sup> made the study of this characteristic of solar radiation an urgent problem all over the world now. Monitoring networks have been developed in a number of countries to control probable enhance of UV- $B$  radiation.<sup>56–61</sup> Measurements are performed at many Earth's points; incomplete list of them is given

in Refs. 62–74. Satellite monitoring of UV radiation is carried out.<sup>75–79</sup>

The performed to date investigations allow one to find the dependence of UV-B solar radiation influx on geophysic factors<sup>80</sup>; albedo of underlying surface<sup>81–83</sup>; aerosol concentration together with its particle size distribution and chemical composition<sup>84–90</sup>; the presence and type of clouds.<sup>91–96</sup> All these factors undoubtedly affect significantly the UV solar radiation income. However, the main factor is the state of stratospheric ozone layer, which determines, like a filter, the amount of UV-B solar radiation, modified then by the above factors.

The stratospheric ozone layer is formed due to the absorption of the hard solar radiation.<sup>97,98</sup> The intensity of UV-B radiation, reaching the troposphere, also depends on the ozone concentration in this layer.<sup>99</sup> Hence, this layer should be the first, which reacts to processes on the Sun, usually characterized as “solar activity.”

An effect of solar activity on the stratospheric ozone layer was revealed long ago<sup>97–99</sup> and confirmed by later investigations.<sup>100–104</sup> There is a paradoxal situation, consisting in the fact that the total amount of energy, coming from the Sun to the upper boundary of the Earth’s atmosphere, varies within an error of 2% [Refs. 105–107]. The authors of Ref. 108 have found the manifestation of 11-year cycle even inside these 2%. Such situation is caused by the fact that main changes in solar energy occur in the UV and X-ray spectra, when changing the solar activity. When changing the solar activity index from its minimum to maximum, the radiation flux varies by 2.1–2.4 times near  $\lambda = 100$  nm and by 4.4–4.6 times – near 2–8 nm.<sup>109</sup> The longer wavelength, the weaker variation of the solar energy flux.

Changes of the stratospheric ozone layer undoubtedly affect the income of the UV-B radiation to the Earth’s surface. This is confirmed by Refs. 110–113, where inphase variations of the total ozone content (TOC) and UV-B radiation near the surface are shown on the base of long-term data. Hence, if the surface ozone concentration (SOC) is mainly determined by the photochemical component, it is expectable to be opposite in phase to TOC.

Such investigations are described in Ref. 114, where the authors analyze the data on TOC and SOC, measured near Tomsk since the beginning of 1990s. The TOC was measured with a M-124 ozonometer, regularly calibrated at the Main Geophysical Observatory (MGO) by Dobson spectrophotometer, and SOC – with a 3-02P meter designed by OPTEC and calibrated by a GS-2 ozone generator, certified and calibrated at D.I. Mendeleev VNIIM.

Time variations of SOC (top curve) and TOC (bottom curve) in 1993–1999 are shown in Fig. 6.

Clearly pronounced opposite trends in SOC and TOC are evident despite seasonal and long-term oscillations of the parameters. Thus, SOC decreases from 41.6 to 20.4  $\mu\text{g}/\text{m}^3$ , or by 50.7%, while TOC increases from 320 to 363 D.u., or by 11.8%, in that

period. Such mutual behavior of the trends allows us to assume that the decrease in SOC is caused by the increase in TOC.

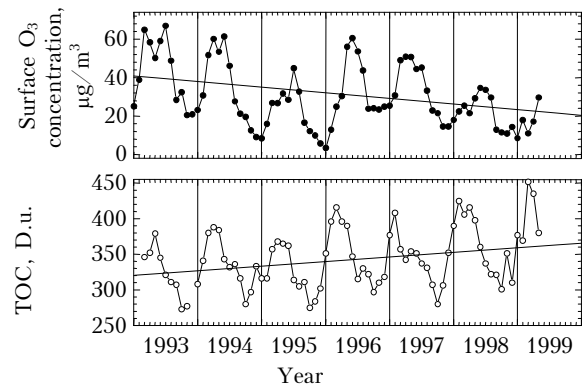


Fig. 6. Time variation of SOC and TOC near Tomsk.

Variations of photodissociation rate were calculated by Eq. (2) and compared with measurement data. The estimates are given in Table 2.

Table 2. Relative variations of TOC, %, ozone photodissociation rate ( $J$ ), and SOC ( $O_3$ ) near Tomsk in 1993–1999

$\frac{\text{TOC}_{99} - \text{TOC}_{93}}{\text{TOC}_{93}}$	$\frac{J_{99} - J_{93}}{J_{93}}$	$\frac{O_{3[199]} - O_{3[193]}}{O_{3[193]}}$
+11.8	-55.5	-50.9

It is seen that the increase in TOC by 11.8% can result in the decrease in tropospheric ozone photodissociation rate by 55.5% and, hence, in similar fall of the ozone generation. Factual data give a value of 50.9%, which is close to the estimated value with accounting for a number of assumptions.

To test this conclusion, the results<sup>115</sup> for the background Kislovodsk station were used, where similar trends were observed.

Table 3. Relative variations of TOC, %, ozone photodissociation rate ( $J$ ), and SOC ( $O_3$ ) for the Kislovodsk station in 1991–1995

$\frac{\text{TOC}_{95} - \text{TOC}_{91}}{\text{TOC}_{91}}$	$\frac{J_{95} - J_{91}}{J_{91}}$	$\frac{O_{3[195]} - O_{3[191]}}{O_{3[191]}}$
+4.9	-27.6	-22.2

As it follows from Tables 2 and 3, the increase in TOC results in the decrease in ozone photodissociation rate in a spectral range 295–310 nm and corresponding actual decrease in SOC, close in value.

Similar assessments of photodissociation rate were made for the period from 1979 to 1993. Close results for TOC and SOC comparison were obtained in Ref. 117 for Uzbekistan. Averaging of many tens of cases over all Uzbekistan stations for 10 years has shown that an increase in TOC answers a decrease in SOC and *vice versa*. Close modeling results have been obtained in Refs. 118 and 119.

## Conclusion

The above study allows a conclusion that the intensity of ozone formation in troposphere is proportionate to two factors, i.e., the intensity of incoming solar radiation at  $\lambda \sim 306$  nm and concentrations of gas-precursors. In the long-term sense, UV solar radiation flow is modulated by the total ozone concentration or its stratospheric component.

## References

1. B.D. Belan, Atmos. Oceanic Opt. **21**, No. 7, 520–534 (2008).
- 1a. B.D. Belan, Atmos. Oceanic Opt. **9**, No. 9, 754–773 (1996).
2. V.V. Lunin, M.P. Popovich, and S.N. Tkachenko, *Physical Chemistry of Ozone* (Publishing House of MSU, Moscow, 1998), 480 pp.
3. S. Madronich, J. Geophys. Res. D **92**, No. 8, 9740–9752 (1987).
4. J. Malicet, J. Atmos. Chem. **21**, No. 3, 263–273 (1995).
5. B.J. Finlayson-Pitts and J.N. Pitts Jr., *Chemistry of the Upper Lower Atmosphere: Theory, Experiments and Applications* (Academic Press, San Diego, 1999), 485 pp.
6. G.K. Moorgat, Global Atmospheric Change and its Impact on Regional Air Quality. NATO Science Series: IV Earth and Environ. Sci. **16**, 115–120 (2001).
7. V.E. Zuev, *Propagation of Visible and IR Waves in the Atmosphere* (Sov. Radio, Moscow, 1970), 496 pp.
8. E.A. Makarova and A.V. Kharitonov, *Energy Propagation in Solar Spectrum and the Solar Constant* (Nauka, Moscow, 1972), 288 pp.
9. G.G. Palanear, R.P. Fernandes, and B.M. Toselli, Atmos. Environ. **39**, No. 5, 857–866 (2005).
10. D. Kim, Ch. Loughner, M. Wetrel, W. Goliff, and W. Stockwell, J. Atmos. Chem. **57**, No. 1, 59–71 (2007).
11. G. Bescer, J.-U. Groob, D.S. Mckenna, and R. Muller, J. Atmos. Chem. **37**, No. 3, 217–229 (2000).
12. C. Dimitroalopoulou and H.M. ApSimon, Atmos. Environ. **33**, No. 1, 147–154 (1999).
13. J. Landgraf and P.J. Crutzen, J. Atmos. Sci. **55**, No. 5, 863–878 (1998).
14. J.E. Walliams, J. Landgraf, A. Bregman, and H.H. Walter, Atmos. Chem. Phys. **6**, No. 12, 4137–4161 (2006).
15. Ch.A. Cantrell, J.G. Calvert, A. Bais, R.E. Shetter, B.L. Lever, and G.D. Edwards, J. Geophys. Res. **108**, D16, 8542, doi: 10.1029/2002JD002962 (2003).
16. E. Jakel, M. Wendisch, and B. Lefer, J. Atmos. Chem. **54**, No. 1, 67–87 (2006).
17. B. Bohn, R. Koppmann, and F. Rohrer, J. Geophys. Res. **111**, D12303, doi: 10.1029/2005JD006856 (2006).
18. A. Kylling, T. Danielsen, M. Blumthaler, J. Schreder, and B. Johnsen, Atmos. Chem. Phys. **3**, No. 2, 377–385 (2003).
19. B. Bohn and H. Zilken, Atmos. Chem. Phys. **5**, No. 1, 191–206 (2005).
20. S. Kazadris, C. Topaloglou, A.F. Bais, M. Blumthaler, D. Balis, A. Kazantridis, and B. Schallhart, Atmos. Chem. Phys. **4**, No. 8, 2215–2226 (2004).
21. A.R. Seroji, A.R. Webb, H. Coe, P.S. Monks, and A.R. Pickard, J. Geophys. Res. **109**, D21307, doi: 10.1029/2004JD004674 (2004).
22. B. Bohn, A. Kraus, M. Muller, and A. Hofrumahaus, J. Geophys. Res. **109**, D10590, doi: 10.1029/2003JD004319 (2004).
23. D. Jaffe, J. Herring, and S. Madronich, IGAC tiv. Newslett., No. 14, 8–10 (1998).
24. R.K. Talukdar, Ch.A. Longfellow, M.K. Gilles, and A.R. Ravishancara, Geophys. Res. Lett. **25**, No. 2, 143–146 (1998).
25. E. Putz, G. Pfister, D. Baumgartner, and R. Maderbacher, Ann. Meteorol. **1**, No. 37, 131–132 (1998).
26. A. Kraus and A. Hofzumahaus, J. Atmos. Chem. **31**, Nos. 1–2, 161–180 (1998).
27. H.-W. Patz, U. Corsmeir, K. Glaser, U. Vogt, N. Kalthoff, D. Klemp, B. Kolahger, A. Lerner, B. Neininger, T. Schmitz, M.G. Schultz, and A. Volz-Thomas, J. Geophys. Res. D **105**, No. 1, 1563–1583 (2000).
28. B.L. Lefer, S.R. Hall, L. Cinquini, and R.E. Shetter, Geophys. Res. Lett. **28**, No. 19, 3637–3640 (2001).
29. K. Takahashi, V. Matsumi, and M. Kawasaki, J. Phys. Chem. **100**, No. 10, 4084–4089 (1996).
30. S.M. Ball, G. Hancock, S.E. Martin, and J.C. Pinot de Moira, Chem. Phys. Lett. **264**, No. 3, 531–538 (1997).
31. W. Armerding, F.J. Comes, and B. Schulke, J. Phys. Chem. **99**, No. 10, 3137–3143 (1995).
32. D. Baner and L.D. D’Ottone, Phys. Chem. **2**, No. 7, 1421–1424 (2000).
33. M. Troler and J.R. Wiesenfeld, J. Geophys. Res. D **93**, No. 6, 7119–7124 (1988).
34. G.D. Smith, L.T. Molina, and M.J. Molina, J. Phys. Chem. **104**, No. 39, 8916–8921 (2000).
35. W.R. De More, S.P. Sander, C.J. Howard, A.R. Ravishancara, D.M. Golden, C.E. Kolb, R.F. Hampson, M.J. Kurylo, and M.J. Molina, in: *Chemical kinetics and photochemical data for use in stratospheric modeling JPL Pub.* (1997), pp. 97–104.
36. Y. Matsumi, F.J. Comes, G. Hancock, A. Hofzumahuas, A.J. Hynes, M. Kawasaki, and L.R. Ravishancara, J. Geophys. Res. **107**, D3, doi: 10.1029/2001JD000510 (2002).
37. H. Liao, V.L. Yung, and J.H. Seinfeld, J. Geophys. Res. D **105**, No. 19, 23697–23707 (1999).
38. S. He and G.R. Carmichael, J. Geophys. Res. D **104**, No. 21, 26307–26324 (1999).
39. R.V. Martin, D.J. Jacob, and R.M. Yantosca, J. Geophys. Res. **108**, D3, 4097, doi: 10.1029/2002JD002622 (2003).
40. H. Bian and Ch.S. Zender, J. Geophys. Res. **108**, D21, 4672, doi: 10.1029/2005JD003143 (2003).
41. G. Li, R. Zhang, J. Fan, and X. Tie, J. Geophys. Res. **110**, D23206, doi: 10.1029/2005JD005898 (2005).
42. A.-L. Brasseur, R. Ramarosan, A. Delannay, W. Skamarock, and M. Barth, J. Atmos. Chem. **41**, No. 3, 211–237 (2002).
43. P.S. Monks, A.R. Rickard, S.L. Hell, and N.A.D. Rickards, J. Geophys. Res. **109**, D17206, doi: 10.1029/2003JD004076 (2004).
44. B.L. Lefer, R.E. Shetter, S.R. Hall, J.H. Crawford, and J.R. Olson, J. Geophys. Res. **108**, D21, 8821, doi: 10.1029/2002JD003171 (2003).
45. Y. Tang, G.R. Carmichael, J.-H. Uno, G. Kurata, B. Lefer, R.E. Shetter, H. Huang, B.E. Anderson, M.A. Avery, A.D. Clarke, and D.R. Blake, J. Geophys. Res. **108**, D21, 8822, doi: 10.1029/2002JD003100 (2003).
46. M.Yu. Arshinov, B.D. Belan, D.K. Davydov, V.K. Kovalevskii, A.P. Plotnikov, E.V. Pokrovskii, T.K. Sklyadneva, and G.N. Tolmachev, Meteorol. Hidrol., No. 3, 110–118 (1999).
47. J. Calvert and J. Pitts, *Photochemistry* (John Wiley and Sons, New York, 1968).
48. B.D. Belan and T.K. Sklyadneva, Atmos. Oceanic Opt. **12**, No. 8, 695–699 (1999).
49. B.D. Belan and T.K. Sklyadneva, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1067–1068.

50. S. Hoffman, W. Sulkowski, and K. Krzyzanowski, *Pol. Acad. Ski.*, No. 42, 117–124 (1993).
51. C.P. Jacovides, F.S. Tymvios, D.N. Asimakopoulos, K.M. Theofilou, and S. Pashiardes, *Theor. Appl. Climatol.* **74**, Nos. 3–4, 227–233 (2003).
52. A. Zastawny, *Meteorol. and Atmos. Phys.* **85**, No. 4, 275–281 (2004).
53. J.H. Seinfeld and S.N. Pandis, *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change* (Wiley and Sons, New York, 1998), 1327 pp.
54. *Environmental Effects of Ozone Depletion: 1994 Assessment* (UNEP, 1994), 124 pp.
55. *Environmental Effects of Ozone Depletion: 1998 Assessment* (UNEP, 1998), 40 pp.
56. J. Grobner, A.F. Bais, S. Kazadris, P.C. Gorts, R.A. Tax, T. Kosnova, and A.R. Webb, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1088–1089.
57. A.F. Moise and R. Aynsley, *Int. J. Biometeorol.* **43**, No. 3, 128–138 (1999).
58. A.F. Bais, E. Kosmidis, A. Kazantzidis, S. Kazadris, C. Topaloglou, and C.S. Zerefos, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1065–1066.
59. G. Bernhard, C.R. Booth, and J.S. Eshamjian, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 259–260.
60. M.G. Kimlin, J.M. Samburg, A.V. Parisi, and R.S. Meltzer, *J. Atmos. and Sol.-Terr. Phys.* **65**, Nos. 16–18, 1401–1410 (2003).
61. N.S. Ivanova, G.M. Kruchenitskii, and A.A. Chernikov, *Atmos. Oceanic Opt.* **12**, No. 1, 1–5 (1999).
62. R.H. Grant and J.R. Slusser, *Theor. Appl. Climatol.* **74**, Nos. 3–4, 167–177 (2003).
63. H. Slaper, P.N. den Outer, J. Williams, A. Bais, J. Kaurova, T. Koskova, K. Lakkala, G. Seckmeyer, and Ph. Weihs, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 249–259.
64. C. Repapis, C. Philandras, A.G. Paliatsos, P. Zanis, C. Zerefos, P. Nastos, K. Eleftheratos, C. Meleti, and D. Balis, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 251–252.
65. K. Lakkala, E. Kuro, and T. Turunen, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1115–1116.
66. V.K. Semenov, N.I. Ignatova, V.N. Aref'ev, and F.V. Kashin, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1148–1149.
67. G. Bernhard, Ch.R. Booth, J.C. Eshamjian, R. Stone, and E. Dutton, *J. Geophys. Res.* **112**, D09101, doi: 10.1029/2006JD007865 (2007).
68. A. Daheback, N. Gelsor, J.J. Stamnes, and Y. Gjessing, *J. Geophys. Res.* **111**, D09308, doi: 10.1029/2006JD007700 (2006).
69. E. Gutierrez-Marco, E. Hernandez, J.L. Camacho, and A. Labajo, *Atmos. Res.* **84**, No. 4, 345–352 (2007).
70. G. Bernhard, C.R. Booth, J.L. Eshamjian, and S.E. Nichol, *J. Geophys. Res.* **111**, D11201, doi: 10.1029/2005JD005857 (2006).
71. P.N. den Outer, H. Slaper, and R.B. Tax, *J. Geophys. Res.* **110**, D02203, doi: 10.1029/2006JD004824 (2005).
72. M. Srivastava, S. Singh, A. Saha, U.C. Dumka, P. Hegle, P. Singh, and P. Pant, *J. Geophys. Res.* **111**, D08201, doi: 10.1029/2005JD006141 (2006).
73. A.Yu. Shalin, *Atmos. Oceanic Opt.* **15**, No. 11, 874–877 (2002).
74. E.V. Batueva, A.V. Bazarov, D.D. Darizhapov, M.V. Grishaev, V.V. Zuev, P.V. Zuev, and S.V. Smirnov, *Atmos. Oceanic Opt.* **14**, No. 12, 1058–1061 (2001).
75. P. Ciren and Zh. Li, *Agr. Forest Meteorol.* **120**, No. 1, 51–68 (2003).
76. A. Cede, E. Luccini, L. Nunez, R.D. Piacentini, M. Blumthaler, and J.R. Herman, *J. Geophys. Res.* **109**, D08109, doi: 10.1029/2004JD004519 (2004).
77. H. Nazaryan and M.P. McCormick, *J. Geophys. Res.* **110**, D17302, doi: 10.1029/2004JD005483 (2005).
78. A. Kazantzidis, A.F. Bais, J. Grobner, J.R. Herman, S. Kazadris, E. Kyro, P.N. den Outer, K. Garane, P. Gorts, K. Lakkala, C. Meleti, H. Slaper, R.B. Tax, T. Turunen, and C.S. Zerefos, *J. Geophys. Res.* **111**, D13207, doi: 10.1029/2005D006672 (2006).
79. E.G. Dutton, D.W. Nelson, R.S. Stone, D. Longenecker, G. Carlaugh, J.M. Harris, and J. Wendell, *J. Geophys. Res.* **111**, D19101, doi: 10.1029/2005JD006901 (2006).
80. J.B. Kerr, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 247–248.
81. A. Kylling, A. Dahlback, and B. Mayer, *Geophys. Res. Lett.* **27**, No. 9, 1411–1414 (2000).
82. A. Kylling and B. Mayer, *Geophys. Res. Lett.* **28**, No. 19, 3365–3368 (2000).
83. A. Pribullova, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1140–1141.
84. J.W. Krzyskin, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1111–1112.
85. K. Akagi, K. Nagata, K. Saito, Y. Kamata, T. Hashimoto, and T. Sasaki, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1103–1104.
86. O. Torres and N. Krotkov, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1163–1164.
87. A.M. Diaz, O.E. Garcia, J.P. Diaz, F.J. Exposito, M.P. Utrillas, J.A. Martinez-Lozano, L. Alados-Arboledas, F.J. Olmo, J. Lorente, V. Cachorro, H. Horvath, A. Labajo, M. Sorribes, J.M. Vilarlana, A.M. Silva, T. Elias, M. Pujadas, J.A. Rodrigues, and J.A. Gonzalez, *J. Geophys. Res.* **112**, D06213, doi: 10.1029/2006JD007348 (2007).
88. G.G. Palancar and B.M. Toselli, *Atmos. Environ.* **38**, No. 17, 2749–2757 (2004).
89. M.T. Pfeifer, P. Koepke, and J. Reuder, *J. Geophys. Res.* **111**, D01203, doi: 10.1029/2006JD006444 (2006).
90. A. Reinart, U. Kikas, and E. Tamm, *J. Geophys. Res.* **111**, D02205, doi: 10.1029/2005JD005726 (2006).
91. S. Wineski and J.F. Frederick, *J. Geophys. Res.* **110**, D22202, doi: 10.1029/2005JD006199 (2005).
92. Ch. Lovengreen, H.A. Fuenzalida, and L. Videla, *J. Geophys. Res.* **110**, D14207, doi: 10.1029/2004JD005372 (2005).
93. I. Foyo-Moreno, I. Alados, F.J. Olmo, J. Vida, and L. Alados-Arboledas, *Theor. Appl. Climatol.* **68**, Nos. 1–2, 41–50 (2001).
94. C. Kuchinke and M. Nunez, *Theor. Appl. Climatol.* **63**, Nos. 3–4, 149–161 (1999).
95. E. Luccini, A. Cade, and R.D. Piacentini, *Theor. Appl. Climatol.* **75**, Nos. 1–2, 105–116 (2003).
96. M.E.-N. Adam and S.M. Shazly, *Atmos. Environ.* **41**, No. 23, 4856–4864 (2007).
97. S.P. Perov and A.Kh. Khrgian, *Today's Problems of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1980), 288 pp.
98. E.L. Aleksandrov, I.L. Karol, L.R. Rakirova, S. Sedunov, A.Kh. Khrgian, *Atmospheric Ozone and Change in Global Climate* (Gidrometeoizdat, Leningrad, 1982), 168 pp.
99. K.Ya. Kondratyev and G.A. Nikolskii, *Issled. Zemli iz Kosmosa*, No. 5, 3–7 (1995).
100. J. Austin, L.L. Hood, and B.E. Soukharev, *Atmos. Chem. Phys.* **7**, No. 6, 1693–1706 (2007).
101. B.-M. Sinnhuber, P. von der Gathen, M. Sinnhuber, M. Rex, G. Konig-Langlo, and S.J. Oltmans, *Atmos. Chem. Phys.* **6**, No. 7, 1835–1841 (2006).
102. K. Labitzke, J. Austin, N. Butchart, T. Knight, M. Takahashi, N. Nakamoto, T. Nagashima, J. Haigh, and



- V. Willias, *J. Atmos. and Sol.-Terr. Phys.* **64**, No. 2, 203–210 (2002).
103. W. Steinbrecht, H. Claude, and P. Winkler, *J. Geophys. Res.* **109**, D02308, doi: 10.1029/2003JD004284 (2004).
104. A.N. Gruzdev and G.P. Brassyer, *Izv. Ros. Akad. Nauk, Fiz. Atmos. Okeana* **43**, No. 3, 379–391 (2007).
105. G.I. Marchuk, K.Ya. Kondratyev, A.E. Aloyan, and K.A. Varotsos, *Issled. Zemli iz Kosmosa*, No. 5, 12–30 (1999).
106. T. Egorova, E. Rozanov, T. Peter, M. Haberreiter, W. Schmutz, E. Manzini, and V. Zubov, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 742–743.
107. A. Larkin, J.D. Haigh, and S. Djavidnia, *Space Sci. Rev.* **94**, 199–214 (2000).
108. Yu.A. Sklyarov, V.A. Dvinskikh, Yu.I. Brichkov, and A.M. Katuma, *Issled. Zemli iz Kosmosa*, No. 6, 40–46 (1998).
109. A.A. Nusinov, L.A. Antonova, T.V. Kazachevskaya, V.V. Katushina, and P.M. Svidskii, *Geomagen. Aeron.* **39**, No. 6, 39–44 (1999).
110. S. Simic, P. Weihs, H. Kromp-Koeb, A. Vasec, and W. Laube, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 1154–1155.
111. R. Mc Kenzie, G. Bodeker, M. Kotkamp, and P. Johnston, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 257–258.
112. G. Palancar and B.M. Toselli, *Atmos. Environ.* **38**, No. 7, 1073–1082 (2004).
113. D.S. Balis, V. Amiridis, C. Zerefos, A. Kazantzidis, S. Kazadris, A.F. Bais, C. Meleti, E. Gerasopoulos, A. Papagannis, V. Matthias, H. Dier, and M.O. Andreae, *Atmos. Chem. Phys.* **4**, No. 2, 307–321 (2004).
114. B.D. Belan, V.V. Zuev, T.K. Sklyadneva, S.V. Smirnov, and G.N. Tolmachev, *Atmos. Oceanic Opt.* **13**, No. 10, 860–864 (2000).
115. G.S. Golitsyn, V.N. Aref'ev, E.I. Grechko, A.N. Gruzdev, N.F. Elanskii, A.S. Elokhov, and V.K. Semenov, *Atmos. Oceanic Opt.* **9**, No. 9, 774–786 (1996).
116. J.S. Fuglestvedt, J.E. Jonson, W.C. Wang, and I.S.A. Isaksen, in: *Atmospheric Ozone as a Climate Gas. NATO ASI Series* (Springer-Verlag, Berlin, 1995), V. 132, pp. 145–163.
117. A.A. Starovatov and V.L. Gartsman, in: *Abstr. of Reports on Intern. Conf. ENVIROIS-2004*, Tomsk (2004), pp. 58–59.
118. K. Sudo, M. Takahashi, and H. Akimoto, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 205–206.
119. I.S.A. Isacsen, C. Zerefos, K. Kourtidis, C. Meleti, S.B. Dabsoron, P. Zanis, D. Balis, and J.K. Sundet, in: *Proc. Quadren. Ozone Symp.*, Kos, Greece (2004), pp. 976–977.