Long-term variability of tropospheric ozone in Tomsk as a reflection of solar activity

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In this paper we compare a many-year behavior of the surface ozone concentration (SOC) and solar activity (radio-frequency emission at $\lambda = 10.7$ cm). It is revealed that the behavior of SOC retraces the solar activity with a 2 to 3 years time lag. Analysis of possible causes of such a lag calls for a conclusion that it can be due to transient process of the vegetation response to the variations in the UV-B radiation income. It is known that vegetation produces up to one third of the ozone-forming substances. Therefore the comparison of long-term behavior of SOC and normalized vegetation index (NVI) was done that showed a good correlation between their dynamics.

Introduction

Studies of the tropospheric ozone carried out during recent decades significantly change the statement on its role in the atmospheric processes and environmental impact. Thus, for example, it was considered for a long time that ozone is nearly an indicator of the air purity. The results of recent studies indicate numerous negative consequences of the ozone concentration increase.[1] In the atmospheric surface layer the ozone relates to the greenhouse gases, its contribution yields only to carbon dioxide and methane. An increase of the surface ozone concentration depressively affects the vegetation that leads to the crop capacity reduction by 10 to 15% (Ref. 2). Also it can oxidize several materials right up to platinum group.[3] Therefore, in recent decades, many countries have performed monitoring of the ozone concentration to determine a tendency in its variation.

Authors started SOC monitoring in September 1989 and it continues until present time at TOR Station[4] of the Institute of Atmospheric Optics. Measurements of the ozone concentration are being made with the use of chemiluminescence ozone gas-analyzer designed and manufactured by OPTEC Corp. (St. Petersburg, Russia). In this paper the long-term variability of the surface ozone concentration and possible causes of the variation are discussed.

Earlier, authors performed similar investigation of long-term variability of aerosol number density and it was shown that since 1983 until 2000 the aerosol concentration decreased twice during the period by a considerable factor.[5] Temporal behavior of aerosol number concentration was similar to solar activity with 2 or 3 years lag depending on the number of 11-year solar cycle. Analyzing relation between the variability of aerosol concentration and other parameters we showed in Ref. 6 that during the period when measurements of ozone and aerosol coincided their variations occurred in phase. However, it was not correct to draw an unambiguous conclusion about their interrelation because when Refs. 5 and 6 were written the data array on SOC compiled did not cover full 11-year cycle of the solar activity. Following measurements enabled us to verify this preliminary conclusion.[5,6] Possible causes of the long-term variability of the surface ozone concentration (Fig. 1) are analyzed bellow.

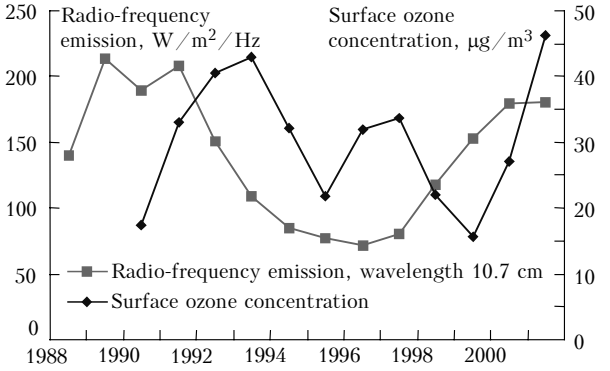

Fig. 1. Annual mean concentration of the surface ozone in Tomsk and annual mean radio-frequency emission ($\lambda = 10.7$ cm) from the entire solar surface.

As seen from Fig. 1, ozone concentration increased since 1990 until 1993 when two maxima of solar activity were observed. Since 1991 the solar radio-frequency emission ($\lambda = 10.7$ cm) that characterizes solar activity began to come down. The decrease of SOC was similar, but with a 2-year time lag. This synchronous behavior has lasted until 1995. In 1995 mean annual concentration of the surface ozone was unclearly anomalous.

To all appearances, some transient process had occurred in the atmosphere and, as a result, the behavior of the ozone concentration lagged by 3 years. Minimum of the ozone concentration was observed in

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1999, i.e., 3 years later than the solar activity. In 1997 solar activity became to increase. The increase of SOC began with a 3-year lag in 2000. Thus, as follows from Fig. 1, the surface ozone concentration follows the behavior of the solar activity during the entire 11-year cycle and demonstrates the same tendency in the beginning of the next one.

1. Possible causes of SOC variations

Against the background of the increasing global ozone concentration,[1,2] the data obtained nearby Tomsk, *prima facie*, seem to be contradicting the general tendency and call for some questions. First of all, whether such behavior of SOC is a reflection of local processes or not? If not, what is the scale of this process.

Analysis of the results published during recent years[7–12] allowed us to draw a conclusion that this process is of a large-scale character. Thus, similar behavior of the SOC was observed in Kislovodsk,[7] Greece,[8] Finland,[9] and Denmark.[10] Really, taking into account that the results presented in Refs. 8–10 were obtained in urban regions, the amplitude of long-term variations of the ozone concentration is not that high as presented in Fig. 1 and Ref. 7. In addition to the trend of SOC, similar variations of ozone-forming substances have been obtained for the same period in Mexico City (NO_x and CO)[11] and in Norway (ethane, acetylene, and propene).[12] Consequently, the data presented in Fig. 1 are not of regional character and assignable. To all appearance, they represent processes that are typical of the Northern Hemisphere at least. More often the solar activity is denoted as the initial source of this process.

Considering possible direct mechanisms of the signal transmission from the sun to the troposphere, authors of Refs. 13 and 14 isolate three following processes. The first of them is condensational. It consists in the fact that, at the increase of the intensity of solar corpuscular emission, cosmic rays intensify condensation processes in the upper troposphere that leads to the additional formation of cirrus clouds. At present, there is no certain confirmation of this process. The second, ozone mechanism is determined by the increase of the intensity of UV-B radiation during the period of the reinforcement of solar activity. This radiation is absorbed in the upper troposphere that leads to the formation of the additional number of ozone molecules and, correspondingly, to the enhancement of total ozone content (TOC). This increase of TOC, in its turn, will cause an additional absorption of UV radiation (λ = 295–400 nm) that produces the ozone in the troposphere. In Ref. 15 there is a confirmation of this mechanism. And finally, the third mechanism consists in that the solar spectral luminosity can change in the UV spectrum. Thus from Refs. 13 and 14 it follows that the variations in SOC can be caused by many-year variations in the influx of solar UV radiation to the Earth's surface.

2. Role of UV radiation in the formation of tropospheric ozone

At present the data are available that confirm long-term variations of the UV-radiation influx[16–18] and those, which deny this fact.[19–20] In order to verify what a behavior of the UV influx was observed at the measurement site during the period under the study let us make use the spaceborne measurement data presented on the NASA web site.[21]

Figure 2 shows that influx of the UV radiation to the Earth's surface nearby Tomsk is close to the behavior of the solar activity within a long time. This shows that the UV radiation does not determine directly the ozone formation in the troposphere.

Periodicity of the UV-radiation variations close to 11-year cycle of the solar activity does not allow denying it possible relation to SOC.

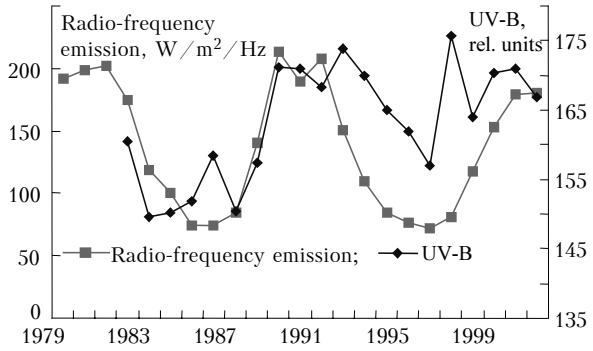

Fig. 2. Radio-frequency emission of the Sun (λ = 10.7 cm) and annual mean influx of the solar UV-B radiation.

As seen from Fig. 3*a*, a direct comparison of the UV-B radiation influx and surface ozone concentration reveals that relation between them is weak. It is possible to isolate some periods when they vary quite synchronously. Inasmuch as the behavior of ozone (Fig. 1) and aerosol[5,6] lags in respect to the solar activity, in Figs. 3*b* and *c* curves are shifted with respect to each other. It is seen from Fig. 3*c* that, at the 3-year shift, curve of SOC quite well follows up the variation of the UV-B influx. From our point of view, this shows that on the long-time scale UV-B radiation indirectly contributes to the generation of tropospheric ozone. Evidently, this is realized through some intermediate mechanism.

In order to reveal this mechanism let us write the following gross-equation of the ozone generation in the troposphere[22]:

$$RH + CO + NO \xrightarrow{h\nu, O_2, H_2O} NO_2 + f H_2CO + kO_3 + P,$$

where f and k are the stoichiometric coefficients of the formaldehyde (aldehydes) and ozone yield due to reactions; P is the reaction product (aerosol particles); RH denotes the hydrocarbons of different origin; CO is the carbon monoxide; NO and NO_2 are nitrogen oxide and dioxide, respectively; $h\nu$ denotes the UV influx; O_2 is oxygen; H_2O is water vapor.

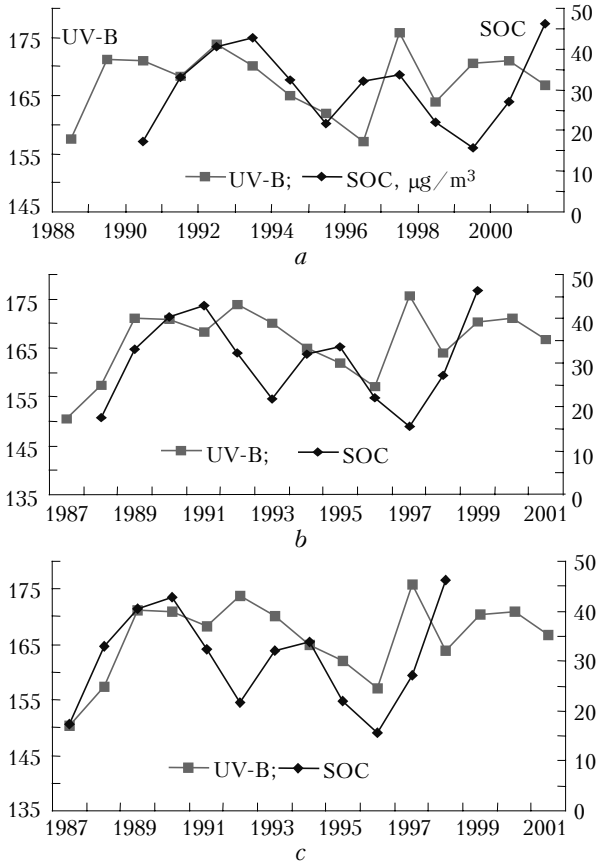

Fig. 3. Annual mean values of the surface ozone concentration (SOC) and influx of the solar UV-B radiation nearby Tomsk.

Physical meaning of this gross-equation is that, in the presence of UV radiation, oxygen, and water vapor, nitrogen dioxide and formaldehyde (or other aldehydes) are formed from the hydrocarbons initially incoming to the air. Then ozone and a part of other species transform into the aerosol phase. It is clear, that the content of ozone-forming substances (left-hand side of the equation) and UV-radiation influx will directly contribute to the ozone balance. The contribution of water vapor is indirect providing for formation of hydroxyl radicals in some cycles of the ozone generation.

The role of solar ultraviolet radiation can be clearly seen from Fig. 4 where the data published in Ref. 23 are plotted. As follows from Fig. 4*a*, all temporal variations of SOC depend on UV-radiation influx. However, the amplitude of these variations is not always in proportion to the increase or decrease of the UV-radiation intensity. This fact indicates that temporal variability of the SOC is determined by UV-radiation, and the magnitude of variations is governed by the ozone precursors or air composition. The same tendency can be seen in Fig. 4*b* for monthly mean values.

Consequently, the source of the long-term variation of SOC presented in Fig. 1 should be sought in the changes of the air composition or, more precisely, ozone forming components (left-hand side of the equation).

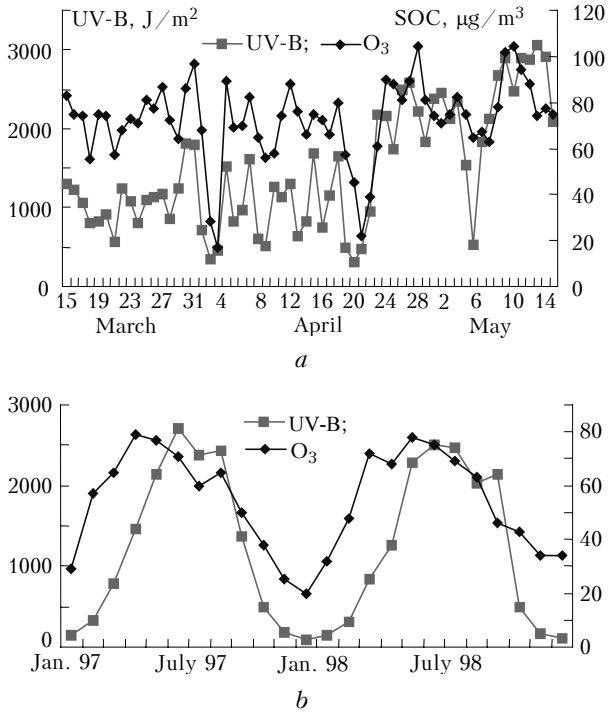

Fig. 4. Intensity of UV radiation and surface ozone concentration in Belsk (Poland): (*a*) daily average from 15th of March to 15th of May 1998; (*b*) monthly average for the period from 1997 to 1998.

3. Role of air composition in the ozone generation

In order to interpret unambiguously the role of the air composition in the process of the ozone formation, besides the UV radiation and ozone concentration, we need monitoring carbon and nitrogen monoxides, methane, and a lot of organic gases. Taking into account that significant part of organic gases is measured by means of gas chromatography or chromatomass spectrometry, theoretically, it is possible to organize the on-line monitoring of ozone cycle components, but, in practice, it is almost impossible. Therefore, we will estimate the contribution of independent components with the exclusion method.

During monitoring performed at our site we measured continuously only carbon and nitrogen monoxides,[4] and, episodically, methane. Also we have continuous data on some resulting gases such as NO_2 and O_3. Comparison of the data on the ozone concentration with other gases showed that there is no persistent relation between them. Furthermore, there are no persistent variations in the long-term behavior of NO, NO_2, and CO. Our measurement data are also confirmed by the data of global network published in Ref. 24. Therefore, there is a reason to suppose that the change of the balance of the initial ozone-forming substances, those, which provide that substantial trend of the ozone concentration nearby Tomsk, occurred due to hydrocarbons, which were not measured in our experiments.

The main sources of hydrocarbons are methane emitted from soil and vegetation that produces all other organic gases.[25] Data obtained by global network[24] show that, during the period we are interested in, the concentration of methane increased in all places.

But the data presented in Ref. 12 show that the trend in concentration of some hydrocarbons of phytogenous origin was similar to the behavior of the ozone observed nearby Tomsk for the same period. The latter allows us to suppose that the vegetation emitted less ozone-forming gases during the period of ozone depletion.

A detailed investigation of the emission of organic gases was carried out by V.A. Isidorov.[26] There were specified the composition of emissions of most types of plants, the rate and yield of emissions, and the dependence of the emission rate on air temperature. Factors revealed indicate that emission of organics can change under the influence of external disturbance. It can be, besides the climatic factors, the solar UV radiation.[27,28]

Since we have no long-term measurements of RH as well as there are no those for other regions, except the data presented in Ref. 12, the question arises as to whether the emission of organic compounds changed at the measurement site during the period from 1990 to 2001 and how can we verify it.

At present, the so-called Normalized Difference Vegetation Index (NDVI) is used for the complex characterization of vegetation conditions. To measure its magnitude, there are used 1st and 2nd channels of AVHRR radiometer of NOAA satellites. First channel (0.58 to 0.68 μm) provides information on the absorption of solar radiation by chlorophyll. The second one collects reflected radiation in the 0.78 to 0.90 μm wavelength range. Then NDVI is calculated by use of the following equation:

$$\mathrm{NDVI} = \frac{J_{\lambda_1} - J_{\lambda_2}}{J_{\lambda_1} + J_{\lambda_2}},$$

where J_{λ_1} and J_{λ_2} are signals from 1st and 2nd channels of the radiometer, respectively. The NDVI data can be found in the Internet.[29]

In accordance with data presented in Ref. 30, NDVI strongly correlates with the vegetation parameters such as biomass and area of the green surface. Shishkin noted[31] that the magnitude of the NDVI depends on the growth and evolution of the leaf surface of trees and it well reflects their dynamics. At the same time, he has drawn a conclusion that, since real intensity of the photosynthesis and productivity depends not only on the solar energy, but on some other factors too, real intensity of the photosynthesis will be always lower than NDVI measured from satellites. Investigations carried out at the All-Russian Scientific Research Institute of Agricultural Meteorology (ARSRIAM) showed[32] that in 90% of cases the difference between NDVI and ground-based measurements did not exceed 10 percent. Therefore, it is possible to assume that NDVI, reflecting vegetation condition, thereby will reflect indirectly the emission of organic gases to the atmosphere.

Figure 5 presents the comparison of annual mean NDVI calculated for Tomsk region within the square of 55–57°N and 85–87°E and annual mean concentration of the surface ozone measured at TOR station nearby Tomsk. It is seen that the behavior of the SOC is close to that of NDVI with negligible deviations. In our opinion, this indicates that the volume of hydrocarbons incoming to the atmosphere as well as the volume of the ozone formed from RH depend on the intensity of plant vegetation.

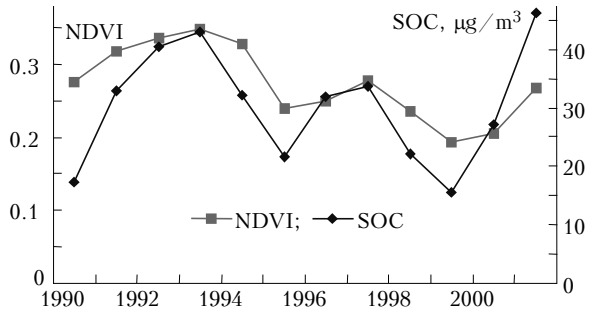

Fig. 5. Annual mean values of NDVI and SOC (μg/m^3) nearby Tomsk.

Figure 6 demonstrates that this correlation occurs not only in the long-term behavior. Also it becomes well apparent in a seasonal behavior for individual years. In particular, it is seen from Fig. 6 that secondary maximum of the SOC occurred periodically in spring season is the result of vegetative peak of plant activity.

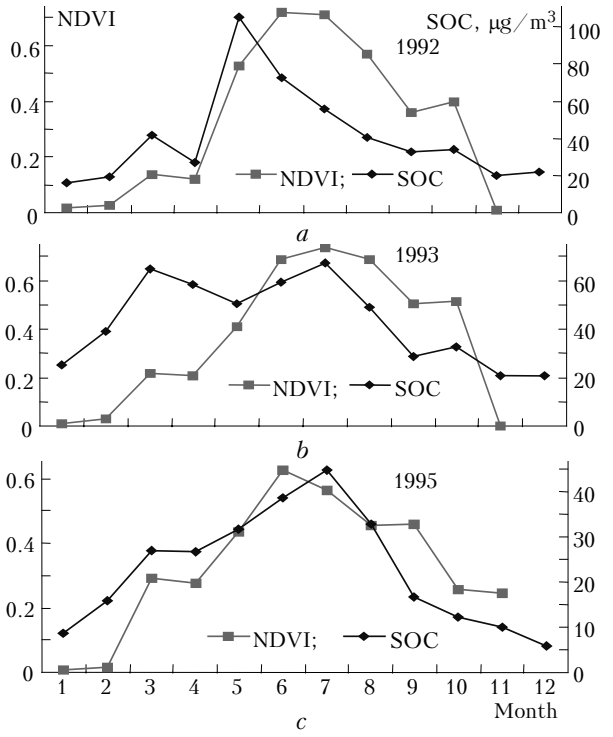

Fig. 6. Monthly mean values of NDVI and SOC in 1992, 1993, and 1995.

4. Results an discussion

Let us focus attention on a different problem. Since the temporal behavior of NDVI and SOC are in a good correlation, this means that former is also lagged with respect to the long-term behavior of the solar UV radiation shown in Fig. 2. There are two possible explanations of this process.

The first one consists in the fact that the growth of the UV radiation, being the initial source of the intensification of photochemical processes, leads to the formation of additional ozone. And ozone starts depressing the vegetation[2] that leads to weakening of the vegetative activity.

The second one is a less studied process of a possible ambiguous response of the vegetation to strengthening of the UV radiation. The reaction of vegetation to the changes in the UV irradiance was discussed by several authors.[33–37] Principal results of these studies can be explained in the following ways.

The radiation at 330-nm wavelength can be considered as a short-wavelength limit of the photosynthesis of green plants. Harder ultraviolet radiation ($\lambda \le 330$ nm) extremely suppresses the process of photosynthesis. Namely in this spectral region the variation of the intensity occurs when varying the solar activity. Features of the UV-B radiation ($295 \text{ nm} < \lambda < 320$ nm) effect on plants depend on its doses. At small doses stimulation occurs and *vice versa* a depression is observed at heavy doses. Moreover, protein, chlorophyll, and other compounds intensively absorb UV-B radiation. Therefore its strengthening adversely affects the vital functions.

Turning back to Figs. 5 and 6, we can draw a conclusion that in nature the second mechanism is realized. Otherwise, the behavior of the SOC will be in advance of the NDVI variations.

It is realized in the following way. Since the increasing influx of the hard UV radiation depressively affects the plants, the vegetation needs for adaptation period of 2 or 3 years in order to adjust to the new UV irradiance. It is appropriate to present results of Ref. 38, in which authors showed that Earth's biota reacts according to Le Chatelier principle. Namely, at the appearance of some external disturbances in the environment, biosphere triggers the process that compensates for these disturbances. Plants adapted to the enhanced UV background start emitting additional volatile organic compounds. To judge from the gross-equation, in the presence of a high UV background this should provide maximum of the ozone generation in the troposphere.

The results presented in Refs. 39–41 evidence in favor of this mechanism. It was revealed the so-called "long-duration cumulative effect" of UV-B radiation on the vital functions of plants. The authors showed that photosynthesis is renewed 2 or 3 years after a prolonged (4 years) exposure of plants to UV-B radiation.

It can be taken into account that the yield of organic compounds produced by vegetation will depend, except the UV radiation, on air temperature and relative humidity as well as on the soil conditions. However, it is worth mentioning here that these factors are in good correlation with solar activity.[42–44] Moreover, Chizhevsky found the 2 and 3-year lag of maximum in temperature with respect to the solar activity maximum.[45]

Conclusions

Many-year monitoring of the aerosol number density and ozone revealed a cyclicity in its variations with the period close to 11 years that has a 2(3)-year phase lag with respect to solar activity. Analysis of possible causes of the lag allows one to assume that it can be caused by long-term cumulative effect of the UV-B radiation influence on vegetation that leads to the reduction of photosynthesis processes and, as a result, the concentration of organic compounds decreases and the process of the ozone formation becomes weaker.

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