ISSN 1068-3356, Bulletin of the Lebedev Physics Institute, 2018, Vol. 45, No. 1, pp. 24–28. © Allerton Press, Inc., 2018.
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# Positive Trend of Surface Ozone in the North of the Privolzhskii Federal Region of the Russian Federation

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Received May 11, 2017

**Abstract**—The results of long-term continuous measurements of surface ozone concentrations, performed in 2010–2016 in the relatively low-urbanized region in the north of the Privolzhskii Federal Region of the Russian Federation (Vyatskie Polyany, Kirov oblast) are presented. A regular increase in the amplitude of diurnal variations of yearly average surface ozone concentrations is detected. The possible causes of this phenomenon can be both an increase in the atmospheric concentration of pollutants, i.e., precursors of tropospheric ozone, and climatic changes.

**DOI:** 10.3103/S1068335618010062

**Keywords**: tropospheric ozone, surface ozone, low-urbanized region, diurnal variations, ozone precursors, Vyatskie Polyany.

*Introduction.* Ozone is among the most hazardous atmospheric pollutants; therefore, its concentration in the air medium, i.e., the human environment, requires close attention. In the atmospheric boundary layer, ozone appears due to photochemical reactions involving precursor molecules such as volatile hydrocarbons, nitrogen oxides, carbon oxides, and due to horizontal transport and transport from upper atmospheric layers [1–4]. Currently, ozone precursors of anthropogenic origin (industry, transport, municipal service) play a major role in photochemical processes. In the pre-industrial epoch, the ozone concentration in the near-surface atmosphere was at the level of 20 $\mu$g/m$^3$; currently, a significant increase in both background (to $\sim$40 $\mu$g/m$^3$) and peak (higher by an order of magnitude) surface ozone concentrations (SOC) is observed [3]. Due to the high oxidation activity, such $O_3$ concentrations are hazardous and can cause significant harm to the public and ecosystem health, lead to considerable economic losses in agriculture and forestry [2, 4–6]. The SOC increase is also caused by occurring climatic changes, e.g., an increase in the heat wave frequency and amplitude or a number of hot sunny days in regions. The variations associated with climatic changes become most urgent in the last years for the central Russia.

An ozone concentration decrease in the atmospheric boundary layer, desirable for reducing population health risks, is possible due to a decrease in emissions of its precursors to the atmosphere. It is a complex technological and administrative problem requiring active administrative regulation from the side of the state, the development and use of new ecologically clean technologies. The first step to its solution is to provide accurate data on the ozone concentration in the atmospheric boundary layers in the territory of the entire country, which would allow revealing existing long-term trends in the changes in an observed quantity. For such purposes, in a number of European countries and in the USA where the problem of near-ground atmosphere contamination by ozone arose as early as in the mid-nineteenth century, rather dense networks of stations of its continuous monitoring were developed [2, 4]. Information collected by these stations over the past 20 years makes it possible to trace the time series of SOC vertical distribution and long-term trends in ozone concentration variations in the atmosphere, to determine the efficiency of technical, economic, and organizational measures directed to reducing the level of pollutant concentrations in the atmosphere, to estimate and predict possible risks for population health, environment, and agriculture.

In Russia, systematic long-term and continuous measurements allowing tracing of trends in SOC variations are still unique. There are only a few stations arranged in regions significantly differing in geography and weather conditions, where such observations are performed [2, 7–10]. This explains

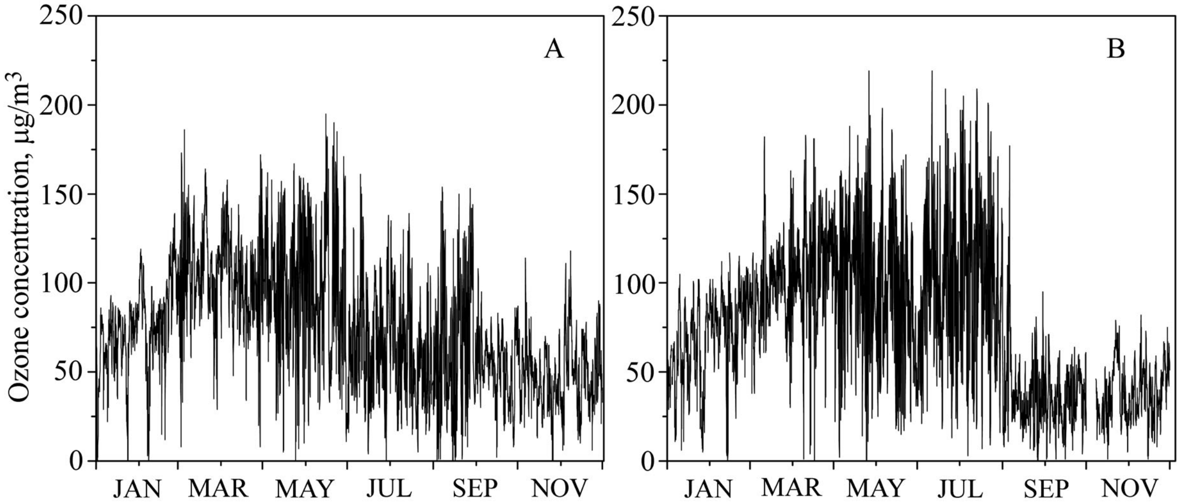


**Fig. 1.** Annual behaviors of hourly average SOCs at the Vyatskie Polyany station in (A) 2015 and (B) 2016 years.

the absence of an accurate and system picture of processes occurring in the country territory and an objective evaluation of the importance of the surface ozone problem for Russia. To reveal the above mentioned long-term trends, in 2009 we developed and implemented an automated station of SOC monitoring in the relatively low-urbanized region in the north of the Privolzhskii Federal Region of the Russian Federation in Vyatskie Polyany town of the Kirov oblast south (56°13′ N latitude and 51°4′E longitude). The choice of this region for studies was caused, in particular, by the arrangement of this town with a population of ∼50 thousands including the region far enough from the nearest industrial centers: Naberezhnye Chelny (105 km), Kazan (120 km), Izhevsk (140 km), Ioshkar Ola (200 km), Kirov (260 km), and the absence of any enterprises with harmful gas pollutions. The regional air background of pollutants in the town is formed due to local motor transport and long-range transfer. Thus, this station can be attributed to "slightly polluted flat" stations.

*Devices and methods*. SOCs were measured using a 3.02 P-A commercial chemiluminescent gas analyzer (OPTEC Company, St. Petersburg) having international certification of the (U. S. Environmental Protection Agency). The ozone concentrations is determined in this analyzer using the heterogeneous chemiluminescence method. The basic metrological characteristics of the analyzer are as follows: the dynamic range is 0–500 $\mu$g/m$^3$, the sensitivity is 1 $\mu$g/m$^3$, the error limit is 15%, measurements are performed every second, the recording frequency is once per minute, the integration time is 1 minute. When operating in the mode of continuous long-term monitoring, to decrease the measurement error, the device is automatically calibrated every 10 minutes using a calibration gas mixture and "zero gas". The manufacturer yearly tests and calibrates the device using the "Working standard of the first rank of the ozone molar fraction unit in ozone–air mixtures RE 154-1-33-2008" kept at the OPTEC instrument-making enterprise. The analyzer operates as a part of the automated measurement system providing data collection, storage, preprocessing, and transmission, as well as remote control and data visualization. The measurement system is installed in the park region of the town; analyzed atmospheric air is sampled at a height of ∼12 meters.

*Experimental results*. In the present study, SOC monitoring was performed continuously for 7 years, from 2010 to 2016, with a data recording frequency of once per minute. Figure 1 shows the annual behaviors of the ozone concentration in the near-surface atmosphere for 2015 and 2016. To facilitate the graphical representation of long series of measured data, their hourly averaging was performed.

Let us indicate several characteristic features of these time series. We can see significant SOC variability over a year. The behavior features are reproduced from year to year only in the most general terms. We can distinguish both slow increases and decreases with characteristic times from a month to several months, and rapid variations which look as specific "noise" when the data are represented on the chosen time scale. In fact, these sharp jumps reflect the diurnal SOC dynamics whose behavior is clearly seen in Fig. 2 where variations of the measured value over several days are presented on a larger scale.

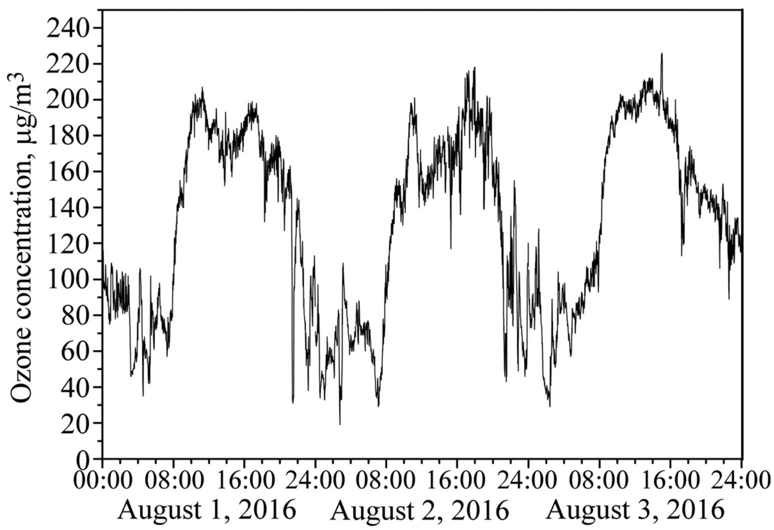


**Fig. 2.** SOC variations at the Vyatskie Polyany station from August 1 to August 3, 2016.

We can see in Fig. 1 that the ozone concentration slowly increases at the beginning of every year. This increase is caused by both an increase in the daylight (and, hence, a daily dose of ultraviolet radiation) and a gradual increase of the atmospheric air temperature. In the summer period, maximum ozone concentrations are as a rule observed in the atmospheric boundary layers. The features of the summer dynamics are controlled by the specific summer, i.e., it was droughty, with a large number of clear and hot days, or it was cloudy and rainy. In autumn, the SOC decreases due to a gradual daylight reduction, a decrease in the air temperature, and an increase in the number of cloudy days with rainfall. We can see in Fig. 1 that peak SOC values reaching more than 200 $\mu$g/m$^3$ are observed in summer. We intentionally note that SOC values close to zero are observed from time to time, under corresponding weather conditions, throughout the observation period, which indicates the correctness of the basic zero level of the used analytical system. This factor is essential for further interpretation of the results obtained.

From Fig. 2, we can gain insight into the typical daily behavior of the SOC. As an illustration, Fig. 2 presents the data obtained from August 1 to August 3, 2016; the plot was constructed using the data with one-minute averaging.

We can see that minimum ozone concentrations are observed at night in pre-dawn hours. In this case, despite the fact that a night decrease in the concentration of ozone produced for a day is most intense, complete atmosphere purification from ozone may not be observed. This can be explained by both low rates of ozone outflow at night in countryside (the absence of intense sources of anthropogenic pollutions) and the phenomena of night ozone transport to the region where the analysis is performed from the nearby regions or upper atmosphere layers. With sunrise, an intense increase in the ozone concentration is observed, which is caused by photochemical processes of its formation involving ozone precursors, i.e., nitrogen oxides, carbon oxides, and hydrocarbons. Throughout the light day, ozone is produced and a daily maximum is observed. Its particular shape and amplitude are determined by the presence of ozone precursors in air and variations of illumination, temperature, and humidity during the day.

To study long-term trends in SOC variations, the variation unrelated to seasonal and meteorological variations and diurnal rhythms should be separated in the obtained annual behaviors. It follows from the general view of curves in Figs. 1 and 2 that a direct comparison of annual behaviors or calculation of average values for a year does not allow us to make reliable conclusions about long-term trends due to the significant variability of the quantity under study. To this end, it is convenient to use a special technique for processing annual behaviors of ozone concentrations, which makes it possible to minimize the effect of the above-listed variations of the measured value [2, 3, 9]. In the first processing step, all data recorded for a hour are averaged. Then, daily variations are averaged over the entire year under study, and the annual average of the ozone concentration is calculated for every hour. Thus, annual average daily SOC variations are calculated.

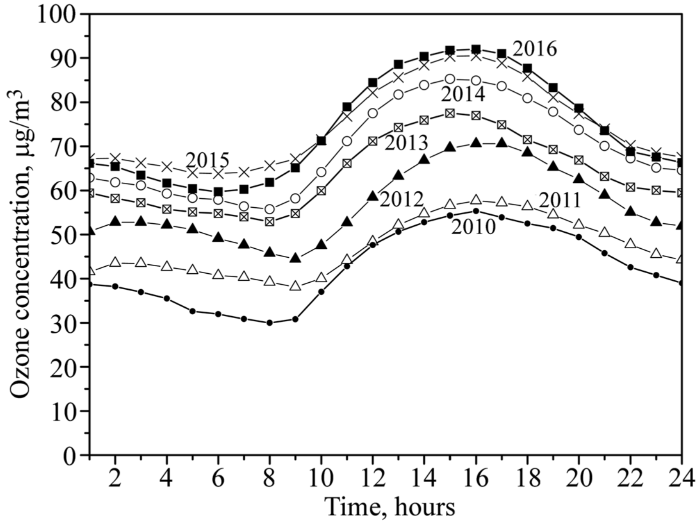


**Fig. 3.** Annual average daily SOC variations at the Vyatskie Polyany station from 2010 to 2016.

To use such a technique, the processed data series should satisfy several conditions. Their quality and completeness should be provided, i.e., it is necessary to have a continuous data series throughout the year and for all studied years. This is achieved by providing continuous and long-term monitoring. In this case, the measurement frequency of ozone concentrations in air should be sufficiently high, of the order of one measurements per minute, and the sensitivity should be at the level of 1 $\mu g/m^3$; the long-term zero drift should not exceed 5 $\mu g/m^3$ for a year, and the analysis selectivity should be no worse than 95%.

Using the above-described technique, data series on ozone concentrations in the near-surface atmosphere, we obtained for 7 recent years, from 2010 to 2016, at the Vyatskie Polyany monitoring station, were processed. The obtained annual average daily SOC variations are shown in Fig. 3.

*Discussion of the results.* The shape of the envelope of SOC daily variations is well enough reproduced, reflecting main features in the ozone production and decomposition in the atmospheric boundary layer for a day. As can be seen, minimum values of hourly ozone concentrations are observed early in the morning, and they do not reach a zero level. That is, on average, ozone is continuously

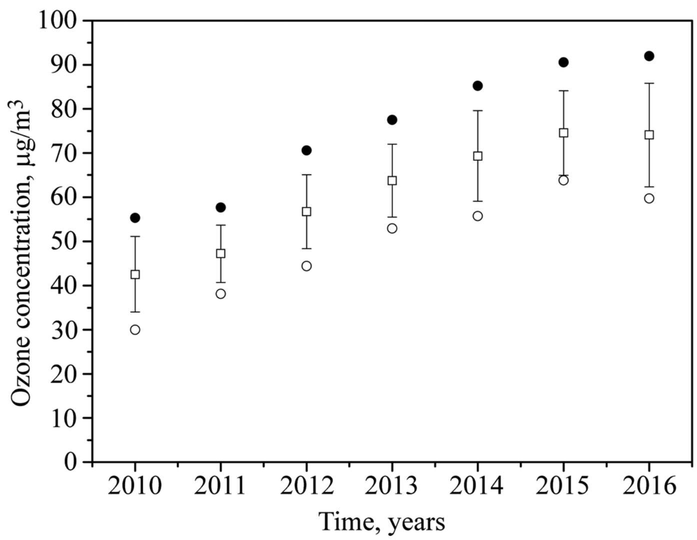


**Fig. 4.** Maximum (closed circles) and minimum (open circles) annual average daily SOC variations and annual averages SOCs (squares) at the Vyatskie Polyany station in 2010–2016.

present in atmospheric air over a year, and the annual average is comparable to the established maximum permissible concentration MPC (30 $\mu$g/m$^3$), and even exceeds this value by a factor of two and larger in the last few years. After 8 a.m., the ozone concentration in the atmosphere gradually increases, which is caused by the photochemical mechanism of its formation and an increase in both the solar radiation level and air temperature. Maximum values are reached in the afternoon (15–16 o'clock). In the evening, a gradual decrease of the ozone concentration is observed due to decreases in the temperature and illumination, which also continues at night. In the evening and at night, gradual destruction of ozone produced in the morning and day time is observed.

The most significant result we detected is the monotonic increase from year to year (see Fig. 3) of almost all hourly SOC values. Thus, the maximum daily ozone concentrations increased for the observation time from $\sim$50 to $\sim$91 $\mu$g/m$^3$, and the minimum morning values increased from $\sim$30 to $\sim$65 $\mu$g/m$^3$. The dynamics of these values is shown in Fig. 4.

We note that the reliability of the observed slow increase (trend) is provided by using the regular (every 10 minutes) calibration of the used ozone analyzer (using a special ozone generator and "zero gas"), incorporated into the protocol of performed automated measurements, the regular metrological verification of the used UV sensor and the analyzer as a whole, and a regular control of the zero level shift. These technical measures almost exclude both a systematic monotonic increase in the analyzer sensitivity, which could lead to a gradual increase in obtained values, and a systematic shift of the analyzer baseline, which could result in a parallel shift of curves in Fig. 4 throughout the seven-year measurement cycle. It also should be emphasized that, according to the used data processing procedure, each point in the plot is in fact averaging over 21900 measurements (60 measurements per minute for 365 days). This provides a very low standard error in calculated average values, lower than 1 $\mu$g/m$^3$, even with rather strong systematic (seasonal) and random variations of the observed quantity (the standard error in the average in Figs. 3 and 4 is lower than the size of the symbols used for data representation).

*Conclusions.* Thus, long-term continuous measurements of ozone concentrations in the atmospheric boundary layer, performed in 2010–2016 in the relatively low-urbanized region of the Russian Federation, i.e., Vyatskie Polyany town, Kirov oblast, allowed the detection of the monotonic increase in the total content of this gaseous substance and the determination of the rate of its increase. The use of the special technique for data averaging made it possible to minimize the effect of seasonal and meteorological variations on results and to take into account the presence of diurnal rhythms. It was found that maximum daily ozone concentrations observed in the afternoon increased for the observation time from 2010 to 2016 from $\sim$50 to $\sim$91 $\mu$g/m$^3$, and the minimum morning values increased from $\sim$30 to $\sim$65 $\mu$g/m$^3$. The possible causes of this phenomenon can result from the increase in the total content of pollutants in the atmosphere, i.e., precursors of tropospheric ozone, caused by the development of transport and industry, as well as climatic changes.

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