Peak concentrations of ground-level ozone during the summer heat waves of 2010 and 2016 in the background region of the Kirov region of the Russian Federation

Evgeniy Stepanov1,*, Sergey Kotelnikov1, Genady Ratushnyk2, and Inna Bogun3

1A.M. Prokhorov General Physics Institute of the Russian Academy of Science, Moscow, 38 Vavilova st., 119991, Russia
2All-Russia Research Institute for Phytopathology, B. Vyazyomy, Moscow Region, 143050, Russia Federation
3Peter the Great Saint Petersburg Polytechnic University, Saint Petersburg, 195251, Russia

Abstract. The analysis of continuous monitoring data on surface ozone concentrations during summer heat waves in July and August 2010 and 2016 in a low-urbanized region of European Russia, Kirov region is presented. The values of the maximum short-term (peak) recorded values, obtained at 20-minute, 1-hour and 8-hour averaging, were analyzed. Under close temperature conditions, the amplitudes and durations of peak ozone concentrations in 2016 significantly exceeded the values observed in 2010. One of the possible reasons for this difference may be associated with an increase in the concentration of ozone precursors in the region’s atmosphere.

1 Introduction

Monitoring the ozone content in the surface atmosphere in different regions of the Russian Federation and the analysis of its spatial and temporal variability and long-term trends are the most urgent tasks [1-4]. Being a small gas component of the atmosphere, ozone plays a key role in the photochemistry of the troposphere, its content determines the balance of many atmospheric gases [5,6]. It is an important greenhouse gas. In addition, ozone is the main component of photochemical smog. In the surface layer of the atmosphere, it is one of the most common and toxic air pollutants. At elevated concentrations, it can cause significant damage to human health and damage natural ecosystems [7,8].

The variability of the ozone content in the surface atmosphere is due to the large variety of the processes of its formation, transport and destruction. The main mechanism of ozone formation in the atmosphere is due to a cascade of photochemical reactions involving nitrogen oxides (NOx), CO, and volatile organic compounds (VOCs) occurring in the presence of sunlight. The rates of ozone formation in these reactions increase with an increase in the intensity of solar radiation and the temperature of atmospheric air [6]. This

* Corresponding author: eugenestepanov@yandex.ru
determines the presence of cyclical daily ozone maxima in the afternoon, which have the greatest amplitudes in the spring and summer months. The local concentration of ozone at a certain point in time depends on a combination of many factors: the meteorological situation, the content of its precursors in the air, both local and remote origin, and especially air temperature [9].

Of particular interest is the dynamics of the ozone content during regularly observed heat waves, since it is during these periods that the highest and most dangerous ozone concentrations for people and the environment can be observed in the surface atmosphere. In meteorology, a heat wave is understood as a temporary significant warming, propagating in a certain direction and associated with the advection of a warm mass [1]. Episodes of heat waves, accompanied by abnormally hot weather, require more attention when, in accordance with meteorological standards for 5 days or more, the average daily air temperature exceeds the climatic norm by 7°C or more [1].

Several parameters have traditionally been used to characterize temporal variability and total level of surface ozone concentrations (SOC). For the analysis of short-time variations, data averaged over 20 minutes, 1 hour and 8 hours are used. To assess the intensity and duration of the maximum short-term (peak) values of SOC, they are correlated with the maximum one-time permissible concentration of ozone, MPCω, which is 160 μg / m³ (average for 20 minutes) [10]. Significant characteristics are also the number of episodes with high SOC, the total time of exceeding the MPCω level, as well as the maximum peak values of SOC observed over the studied time interval [11].

The purpose of this work was a comparative analysis of the peak values of SOCs recorded at the Vyatskiye Polyany monitoring station during summer heat waves in July-August 2010 and 2016, when wavy and abnormally high air temperatures were observed for quite a long time. The choice of these time intervals for comparison was due to the fact that in the summer of 2010 and 2016, heat waves were observed in the south of the Kirov region, which led to abnormally high, record air temperatures, under which conditions were created for the most intensive photochemical ozone formation in the surface atmosphere. The temperature conditions in the summer of 2010 and 2016 were quite close and differed significantly from those usually observed.

2 Instruments and Methods

In order to study the various mechanisms of formation of SOC, in 2010 we created an automated station for monitoring atmospheric air [3]. It is located in the low-urbanized region of the Volga Federal District of the Russian Federation in the city of Vyatskiye Polyany, located in the south of the Kirov region (latitude: 56°13′N, longitude: 51°4′E). The choice of this location for research complies with the recommendations of the Guidelines for Atmospheric Pollution Control [12] and is determined by the location of this district city at a sufficient distance from the nearest industrial centers - Naberezhnye Chelny (105 km), Kazan (120 km), Izhevsk (140 km), Yoshkar-Ola (200 km), Kirov (260 km). The population of the city of Vyatskiye Polyany, together with the surrounding area, is about 50,000 people; there are no enterprises with toxic gas emissions in the city and the region. Regional air background of pollutants in the city is formed mainly due to local transport and regional transport. Thus, this station can be attributed to the group of lowland stations in rural areas, and the data collected on it can characterize the state of atmospheric pollution at the regional level.

A serial chemiluminescent gas analyzer of the model 3.02 P-A produced by OPTEC Ltd, St. Petersburg, Russia, with international certification of the US Environmental Protection Agency (U.S. Environmental Protection Agency) [13] was used to measure the SOC. The main metrological characteristics of the analyzer are: the dynamic range is 0-500
μg/m³, the sensitivity is 1 μg/m³, the margin of error is 15%, the integration time is 1 minute, the recording frequency is 1 time per minute. When operating in continuous long-term monitoring mode, the instrument is automatically calibrated every 10 minutes using a calibration gas mixture and “zero gas”. Once a year, the manufacturer performs calibration and calibration of the device using the working standard of the 1st grade of a unit of the ozone molar fraction in ozone-air mixtures RE 154-1-33-2008, stored in the OPTEC Ltd. The gas analyzer operates as part of an automated measuring system that provides for the collection, storage, preliminary processing and transmission of data, as well as remote control and data visualization. The measuring complex also includes the carbon monoxide (CO) analyzer K-100, also produced by the OPTEC Ltd.

The associated meteorological parameters at the station are measured by the Davis Instruments (USA) Weather Station II Automatic Meteorological Station. The values of meteorological parameters recorded with averaging of 1 minute during digital processing are averaged over 20 minutes, 1 hour, 24 hours. The measuring complex is installed in the park area of the village, the sampling of the analyzed atmospheric air was carried out at an altitude of ~12 meters.

The analysis of ozone monitoring data was carried out on a number of indicators. To assess the intensity and duration of the SOC peaks, the averaging of the current data for 20 minutes and 1 hour was carried out, the total duration of time intervals was also determined, during which the average values exceeded the MPC, 160 μg/m³ [2].

In order to compare the obtained results with foreign data the analysis was also carried out using the method widely used abroad [8]. In this case, for the maximum SOC values obtained by averaging over 8 hours, the number of episodes of exceeding the threshold recommended by the World Health Organization (WHO) set at 50 ppb was calculated. In this case, the averaging was carried out in the time interval from 10:00 to 18:00.

In addition, the data obtained by averaging over 1 hour were used to calculate the average daily SOCs for the analyzed month.

Time series of 1-hour SOCs were examined for normality using the Shapiro-Wilk test at a significance level of p <0.05. Since the data obtained did not comply with the normal distribution, the statistical indicators were calculated using nonparametric methods. Statistical processing of measurement results was performed using the STATISTICA licensed software package.

![Fig. 1. SOC monitoring data at the Vyatskiye Polyany station in July and August 2010 (A) and 2016 (B), averaged over 60 min.](image)

### 3 Results and Discussion

Fig. 1 shows the monitoring data of the SOC in July and August 2010 and 2016, averaged over 60 minutes. Despite the strong temporal variability of the observed ozone
concentrations, a higher ozone level is clearly visible in 2016 compared to 2010. Table 1 presents the average monthly and maximum air temperature at the measurement point, the maximum SOC for 20 minutes, the total for a month, the time of exceeding MPC, the number of episodes exceeding the threshold of 50 ppb for 8-hour SOC in July and August 2010 and 2016. Fig. 2 shows the monthly average daily variation of average hourly SOCs in July and August 2010 and 2016.

Table 1. The average monthly (according to the data of FGBU “VNIIGMI-WDC) and the maximum air temperature, the maximum SOC for 20 minutes, the total for a month time of exceeding the maximum permissible concentration, the number of exceeding the threshold of 50 ppb for 8-hour FFP in July and August 2010 and 2016 Vyatskiye Polyany.

|          | T_{\text{mon,av}}, C | T_{\text{max}}, C | SOC_{\text{max}} [\mu g/m^3] | Total exceeding time, min | Epizodes’ number |
|----------|-----------------------|-------------------|-----------------------------|---------------------------|------------------|
|          | 2010                  | 2016              | 2010                        | 2016                      | 2010             | 2016             | 2010             | 2016             |
| July     | 23.9                  | 21.2              | 39.0                        | 33.2                      | 143              | 222              | 0               | 2960             | 5                | 27               |
| August   | 21.0                  | 22.8              | 39.1                        | 36.0                      | 208              | 215              | 80              | 5280             | 9                | 29               |

Fig. 2. The average monthly daily variation of the average hourly FFP in July (□) and August (■) of 2010, as well as in July (□) and August (■) of 2016.

In the summer of 2010 and 2016, abnormally hot weather was observed over a large territory of Russia. According to the VNIIGMI-MCD [14], "July 2010 was the hottest in Russia during the observation period. In most of the European territory of Russia "more than a month, daily air temperatures of more than 30 °C were kept, and at once in all federal districts of the European territory of Russia the average monthly air temperature reached an absolute maximum… The summer of 2016 was very warm, the anomaly of seasonal air temperature was 1.79°C, which was a record value over the observation period since 1939...""

Correlation analysis of average daily values of ambient air temperature and average daily SOC showed a positive statistically significant relationship between these variables in July-August 2010 and August 2016, and in July 2016 this relationship was absent.

The maximum average hourly SOC values in the summer of 2010 and 2016 reached their values in the afternoon between 16-17 hours. As shown in Table 1, the maximum hourly average SOC in July 2010 was 123 μg/m³, and in July 2016 it was 219 μg/m³. Similarly, for August 2010 - 186 μg/m³ and August 2016 - 209 μg/m³. From Fig. 2, where
the daily variations averaged over the month are presented, it can be seen that the maximum average hourly SOCs were slightly more in August than in July and in 2010 and in 2016. At the same time, there is a significant, up to 2 times, difference in the maximum average hourly SOC in July-August 2010 and 2016.

Note that according to our data, the maximum averaged for a year daily-1-hour value of SOC in 2010 was 55 μg/m$^3$, and in 2016 it increased to 92 μg/m$^3$ [4]. As shown in [4], the monotonous growth of the average annual 1-hour SOC values was observed by us at the Vyatskiye Polyany station from 2010 to 2016.

As can be seen from Table 1, the total time of exceeding MPC ot also significantly increased in July and August 2016 compared with the summer months of 2010. There were no exceeding MPC ot in July 2010, and in July 2016 the time of excess was 2960 minutes, this indicator for August 2016 also increased many times compared to 2010. The WHO-recommended [15] threshold value of 50 ppb was exceeded by the maximum 8-hour SOC values in July 2010 5 times, and in July 2016 27 times. Similarly, 9 and 29 times in August 2010 and 2016, respectively.

Such a significant increase in the amplitude of peak SOCs and the duration of exceeding the threshold values in July-August 2016 compared with the same indicators in 2010 may be due to various factors. As is known, the values of the maximum values of the average hourly and 8-hour SOCs are most sensitive to the content of ozone precursors in the air of local (regional) origin and air temperature [6,16-19]. Thus, a decrease or increase in peak concentrations of SOCs recorded at a rural-type monitoring station may indicate, respectively, a decrease or increase in the concentrations of ozone precursors in the region’s atmosphere, which may have different origins. In particular, in the period from 2010 to 2016, at this weather station, we recorded a monotonous increase in the average daily hourly CO concentrations in the summer months. So, in July 2012 this value was 139 μg/m$^3$, and in July 2016 - 400 μg/m$^3$, in August 2012 - 267 μg/m$^3$, and in August 2016 - 323 μg/m$^3$. As is known [11], CO is a reliable marker of general air pollution by impurities, including those that are not controlled, but are involved in the generation of ozone (for example, VOC). The increase in CO content we recorded in the summer months from 2012 to 2016 indicates an increase in total air pollution in the city of Vyatskiye Polyany, including gas impurities involved in the generation of ozone. In countries where regulation of ozone predictors occurs, it is noted that it is in July and August that the values of peak SOC reflect the degree and efficiency of regulation of ozone precursors.

4 Conclusions

Analysis of monitoring data on surface ozone concentrations in the city of Vyatskiye Polyany in July and August 2010 and 2016, during the heat waves that led to a record increase in ambient temperature, showed the following.

The temperature conditions for the formation of ozone in the summer of 2010 and 2016 in the city of Vyatskiye Polyany differed slightly. In July and August 2016, there was a significant increase in SOC values obtained by averaging over 20 minutes, 1 hour, and 8 hours. The total time of exceeding MPC ot also significantly increased in July and August 2016 compared to the summer months of 2010. The number of exceeding the threshold values of 50 ppb for 8-hour SOC in 2016 significantly, exceeded the number of exceedances in 2010.

A significant increase in the amplitude of peak SOCs and the duration of exceeding the threshold values in July-August 2016 compared with the same indicators in 2010 may be due to an increase in the concentrations of ozone precursors in the region’s atmosphere, in particular CO. Such an increase in SOC during hot weather indicates the relevance of a more detailed study of the reasons for the growth of SOC due to climate change. Our data
show that in low-urbanized areas of central Russia, summer abnormal heat waves can lead to episodes of a significant (significantly higher than MPC\textsubscript{50}) increase in the ozone content in the surface atmosphere, which can pose a danger to public health, agriculture and ecological systems. The new scientific results obtained as a result of our studies are in good agreement with the data of various scientific studies that have been obtained by other scientists [20-29].

This work was performed at the Prokhorov General Physics Institute of the Russian Academy of Sciences and supported in part by research project "Physical methods in agriculture and ecology" (No. 0024-2019-0004).

References
1. G. Korshin, Ch. Li, M. Benjamin, Water Res., 31 1787 (1997)
2. B.D. Belan, Ozone in the Troposphere (Tomsk: Institute of Atmospheric Optics of SB RAS, 2010)
3. S.N. Kotelnikov, E.V. Stepanov, V.P. Chelibanov, Atmospheric and Oceanic Optics, 29 1086 (2016)
4. S.N. Kotelnikov, E.V. Stepanov, Bulletin of the Lebedev Physics Institute, 45 24 (2018)
5. P.J. Crutzen, P.H. Zimmermann, Tellus, 43 136 (1991)
6. P.S. Monks, A.T. Archibald, A. Colette, Atmos. Chem. Phys. 15 8889 (2015)
7. N.S. Myazin, V.V. Davydkov, V.V. Yushkova, T.I. Davydkova, V.Yu. Rud, Journal of Physics: Conference Series, 917\textbf{4} 042017 (2017)
8. Kh. Il'ina, N. Gavrilova, E. Bondarenko, M. Andrianova, A. Chusov, Magazine of Civil Engineering, 76 241 (2017)
9. M. Daniel, A. Monteneblo et al. Water, Air, and Soil Pollution, 136 189 (2002)
10. D. de Sousa, A. Mozeto, R. Carneiro, P. Fadini, Sci. Total Environ., 484 19 (2014)
11. I. Nemirovskaya. Water Resources, 39 533 (2012)
12. N.S. Myazin, S.E. Logunov, V.V. Davydkov, V.Yu. Rud’, N.M. Grebenikova, V.V. Yushkova, Journal of Physics: Conference Series 929 (1) 012064 (2017)
13. V.P. Chelibanov, S.N. Kotelnikov, N.V. Smirnov, E.A. Yasenko, Biosphere, 7 119 (2015)
14. V.V. Davydkov, S.V. Kruzhalov, N.M. Grebenikova, K.J. Smirnov, Measurement Techniques, 61\textbf{4} 365-372 (2018)
15. N.M. Grebenikova, K.J. Smirnov, V.V. Davydkov, V.Yu. Rud, V.V. Artemiev, Journal of Physics: Conference Series, 1135\textbf{1} 012055 (2018)
16. S.V. Gudkov, S.N. Andreev, E.V. Barmina, N.F. Bunkin, B.B. Kartabaeva, A.P. Nesvat, E.V. Stepanov, N.I. Taranda, R.N. Khramov, A.P. Glinushkin, Physics of Wave Phenomena, 25 207–213 (2017)
17. V.V. Davydkov, N.S. Myazin, Measurement Techniques, 60\textbf{5} 491-496 (2017)
18. N. Otero, J. Sillmann, J.L. Schnell, H.W. Rust, T. Butler, Environ. Res. Lett. 11 024005 (2016)
19. S. Solberg, Ø. Hov, A. Savde, I.S.A. Isaksen, P. Coddeville, H. De Backer, C. Forster Y. Orsolini K. Ulse. J. Geophys. Res. Atmos. 113 L1(2008)
20. A.V. Moroz, V.V. Davydkov, V.Yu. Rud, Yu.V. Rud, V.C. Shpunt, A.P. Glinushkin, Journal of Physics: Conference Series, 1135\textbf{1} 012060 (2018)
21. V.B. Fadeenko, V Davydkov, ‘V Yu Rud’, A P Glinushkin, Yu V Rud’, V Ch Shpunt, Journal of Physics: Conference Series, 1197\textbf{9} 092015 (2017)
22. I.A. Zharikov, R.V. Davydov, V.A. Lyapishev, V.Yu. Rud, Yu.V. Rud, A.P. Glinushkin, Journal of Physics: Conference Series, 917(5) 052011 (2017)
23. I.S. Kudryashova, V.Yu. Rud, Yu.V. Rud, V.Ch. Shpunt, A.P. Glinushkin, N.N. Bykova, Journal of Physics: Conference Series, 929(1) 012021 (2017)
24. N. Grebenikova, A. Korshunov, V. Rud, I. Savchenko, M. Marques, MATEC Web of Conference, 245 11006 (2018)
25. R. Davydov, M. Sokolov, W. Hogland, A. Glimushkin, A. Markaryan, MATEC Web of Conference, 245 11003 (2018)
26. J. Stenis, W. Hogland, M. Sokolov, V. Rud, R. Davydov, IOP Conference Series: Materials Science and Engineering, 497(1) 012061 (2019)
27. I.S. Kudryashova, V.Yu. Rud, V.Ch. Shpunt, Yu.V. Rud, A.P. Glinushkin, Journal of Physics: Conference Series, 741(1) 012106 (2016)
28. N.M. Grebenikova, K.J. Smirnov, V.V. Davydov, V.Y. Rud, Journal of Physics: Conference Series, 1124(4) 041011 (2018)
29. I.A. Zharikov, V.Yu. Rud, Yu.V. Rud, E.I. Terukov, V.V. Davydov, N.N. Bykova, Journal of Physics: Conference Series, 1038(1) 012100 (2018)