Surface ozone concentration in Moscow environs in 1991-1999

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The basic results of regular 9-year measurements of daytime surface ozone concentration (SOC) from March 1991 at the Dolgoprudnyi station (in a forest-park suburb of Moscow) are presented. A forecast statistical SOC model based on SOC as a regression function of its real value on the previous day and temperature and humidity forecasts for the next day is developed. The model can explain more than 50% of variances of SOC deviations from many-year mean values. Vertical mixing and ozone transport from the free troposphere into the boundary layer are supposed to play the most important part in diurnal SOC variation when maximum diurnal SOC is less than 60–80 ppb. At higher SOC values, the photochemical processes manifest their significant role the more explicitly. Some peculiarities of seasonal and diurnal SOC variation in the central Russia, as compared with analogous SOC characteristics in the West Europe, seem to be connected with the fact that the Russian climate is more continental.

At present, there are more than 1000 stations that regularly measure surface ozone concentration (SOC) in the world (first of all, in the USA, Canada, and West Europe). This is connected with the following factors: surface ozone is a toxic atmospheric pollutant whose concentration often exceeds the maximum permissible concentration and the International Public Health Organization included it in the list of five main pollutants whose content must be monitored in testing the air quality. Rapid development of atmospheric chemistry in the last decades revealed the key role of ozone in chemical and photochemical processes in the troposphere: it causes and controls its oxidizing capacity (and this is the personal merit of P. Krutzen, Nobel laureate on chemistry in 1995); there appeared comparatively inexpensive (about $10,000), high-accuracy tools for ozone measuring, namely, UV photometers that do not demand highly qualified servicing. Measurements of surface ozone at some points have been being performed rather long ago but they seem to be reliable and adequate for calculating trends of SOC measurements only from the mid-1970's.[1] In the West Europe, SOC is measured at a wide network of EMEP stations from the 1980's. Later on, these measurements have been continued at TOR stations. Regular measurements in the former USSR began in Lithuania, at the Baltic Sea coast.[3] In Russia, regular observations of the surface ozone began at the Kislovodsk base of the Institute of Atmospheric Physics since April 1979.[4] Later, observations pioneered by Academician V.E. Zuev began at the Institute of Atmospheric Optics in Tomsk (the station was founded within the TOR subproject of the general European project EUROTRAC).[5] Since 1991, observations are performed in the Central Aerological Observatory (CAO) of the Russian Committee on Hydrometeorology in Dolgoprudnyi, forest-park suburb of Moscow[6]; in the Polar Geophysical Institute (Apatity city) observations began in 1998. In this paper, we describe some results of SOC observations at the Dolgoprudnyi station (56°N, 38°E) from March 1991 to October 1999. Based on these results, salient features of SOC behavior in the central region of Russia have been established.

The measurements of ozone concentration were performed by a device in which a primary instrument transducer of an aerological ozonosonde of electrochemical type was used.[6] Similar devices for SOC measurements were mainly in use at the world ozonometric network up to mid-1980's.[7] First, the observations were performed manually three times a day, at 8, 11, and 14 h (here and below, the local time is being used). Since April of 1997, observations have been automated and the recorded data stored on computers four times a day, at 2, 8, 11, and 14 h, and, hourly when necessary. The mean of observations at 11 and 14 h is taken as the mean estimate of the daytime (below it is called daytime concentration) value. The data on other meteorological quantities of the atmosphere (pressure, temperature and its vertical distribution, etc.) at standard observation time are also obtained at the Central Aerological Observatory.

The temporal behavior of the monthly mean daytime SOC at the Dolgoprudnyi station during the period from March 1991 are presented in Fig. 1. The highest SOC concentrations (more that 60 ppb) are usually observed at about 14 h from September to April; the lowest (0–2 ppb) in autumn, on cloudless nights accompanied by fogs, or on rainy days under the overcast conditions. As the first approximation, the temporal SOC behavior can be well described by a harmonic function having a single significant yearly harmonic; amplitudes of higher harmonics are lower by an order of magnitude thus being statistically insignificant. The observed positive trend of SOC (at the level of 2%) has statistical probability $P = 0.95$ and is connected, first of all, with the SOC increase during the last two years in the last quarter of a year (when the seasonal SOC maximum is observed). The year SOC behavior (ppb) during the last two years at 14 and 2 h (when the day and night maximum and minimum of surface ozone is observed) $O_{3d0}(d)$ and $O_{3n0}(d)$, respectively, are well described by the model functions of the Julian day d:

$$O_{3d0}(d) = 24.1 + 14.2\cos(6.28(d - 149)/365),$$
$$O_{3n0}(d) = 14.5 + 5.4\cos(6.28(d - 81)/365).$$

As seen from these functions, the night-time seasonal SOC maximum is observed at the time close to that of the yearly maximum of the total ozone, and the day-time maximum two months later (but almost a month earlier than the yearly maximum of temperature). According to formal criteria of world practice, Dolgoprudnyi station can be considered as "suburban" (it is situated at about 25 km to the north of the center of a big city); however, the temporal

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SOC behavior (both diurnal and seasonal) is more typical for a "rural" station.[8] Quantitatively, the behavior strongly differs from that at the center of Moscow[9] but it is quite similar to the behavior observed at the Zvenigorod station of the Institute of Atmosphere Physics[10] (the station is about 80 km far from Moscow). Figure 2 (curve *1*) presents the averaged diurnal SOC behavior at the Dolgoprudnyi station during the period from 6 to 11 of June 1999, when a slowly moving area of high pressure with the characteristic higher temperature, low cloudiness, and weak wind existed. In this period, the drop of maximum and minimum diurnal temperatures was about 15° and more; in the absence of cloudiness before the sunrise, SOC dropped to 5 ppb and lower. For a comparison, the same figure presents the SOC diurnal behavior recorded in summer 1988 at the Fedchenko glacier (38°N, 72°E) at the height of 3800 m above sea-level in sunny weather,[11] i.e., in a region where one cannot expect considerable anthropogenic air pollution. It should be noted that the last observation point can be considered as a "surface" one in spite of its large height above sea-level because it does not towers over the soil level (at European stations that are at about 2000 m above sea-level, diurnal variation is in fact absent[12]). Figure 2 demonstrates similarity of diurnal SOC variations at the Dolgoprudnyi station and Fedchenko glacier. So the supposition about common nature of the SOC diurnal variation in both of these cases seems to be most substantiated. Namely, the variation is determined by vertical air mixing significantly weakened at night while becoming most intense by the moment when maximum daytime temperatures establish on the surface what must be accompanied by a considerable increase in SOC up to the levels of 50–80 ppb which are characteristic of the free troposphere. On the contrary, existence of considerable and almost similar diurnal photochemical ozone productivity in both of these cases, under conditions of significantly different concentrations of atmospheric pollutants (nitrogen oxides, carbon oxide, and hydrocarbons), seems to be improbable.

The time series of SOC remainders (deviations of real SOC from model ones or from many-year data) are described by the linear regression by time series of meteorological parameters' remainders. The most important parameters are temperature (or diurnal temperature drop) and relative humidity at 14 h; the second remainders are described by the autoregression model of the third order in which the first order term dominates.[13] The total efficiency of the regression model for the remainders' series is more than 0.5, including efficiency of expansion over the most important meteorological parameters and efficiency of autoregression expansion (0.30 and 0.36, respectively). This agrees well with the results obtained at European ozonometric stations.[14,15]

According to the SOC model described earlier in Ref. 13, the forecast for the daytime SOC (ppb) for the next day $O_{3d}(d + 1)$ can be expressed by its "norm" $O_{3d0}(d + 1)$ and deviations from the many-year mean Hydrometeorological Center forecasts for the next day by temperature $\Delta T(d + 1)$ (°C) and relative humidity $\Delta U(d + 1)$ (%):

$$O_{3d}(d + 1) = O_{3d0}(d + 1) +$$
$$+ A(d + 1)\,\Delta T(d + 1) + B(d + 1)\,\Delta U(d + 1) +$$
$$+ 0.6[O_{3d}(d) - O_{3d0}(d)],$$

where

$$A(d) = 0.54 + 0.55 \cos(6.28(d - 187)/365);$$
$$B(d) = -0.14 - 0.03 \cos(6.28(d - 160)/365).$$

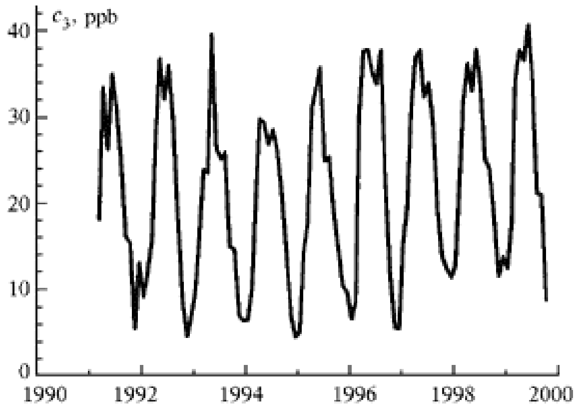

Fig. 1. Time variation of the monthly mean daytime surface ozone concentration c_3 (ppb) in 1991–1999 at the Dolgoprudnyi station.

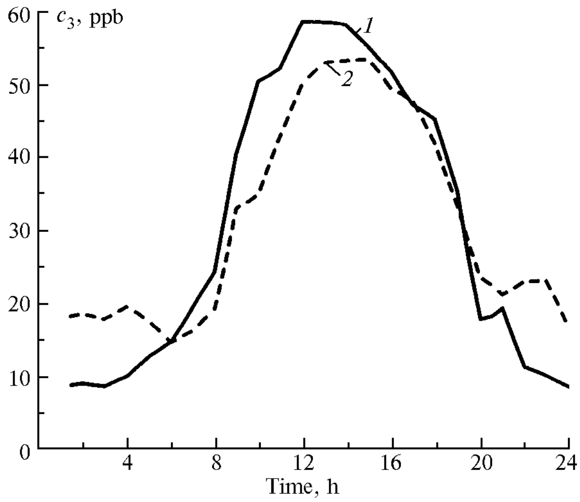

Fig. 2. Average diurnal variation of the surface ozone concentration during the period from 6 to 11 of June 1999 at the Dolgoprudnyi station (solid line) and in summer 1998 at the Fedchenko glacier (dashed line).

The daytime SOC, both predicted by this formula (the coefficients in it are calculated using data of 1991–1995) and really observed in July 1999 are presented in Fig. 3. The figure demonstrates that the prediction formula correctly reflects the trend of SOC variation in the overwhelming majority of cases. On the other hand, as seen from Fig. 3, the formula based on statistical regularities does not permit one to predict sharp SOC variation connected, first of all, with the photochemical process of the surface ozone formation. Such a case for the period presented in Fig. 3 took place on July 14 and it is demonstrated in detail in Fig. 4.

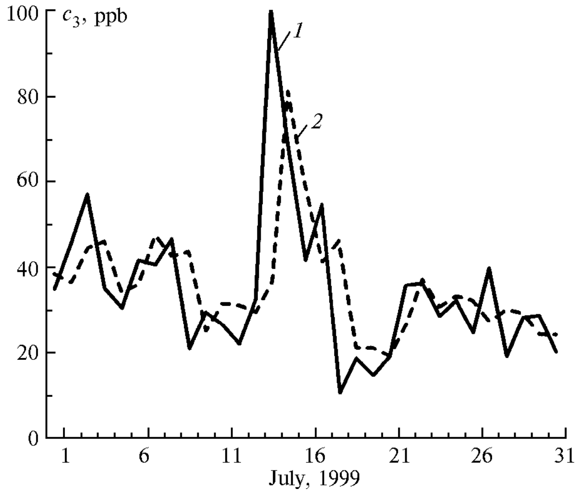

Fig. 3. Time variation of daytime surface ozone concentration (solid line) and forecast (dashed line) in July, 1999.

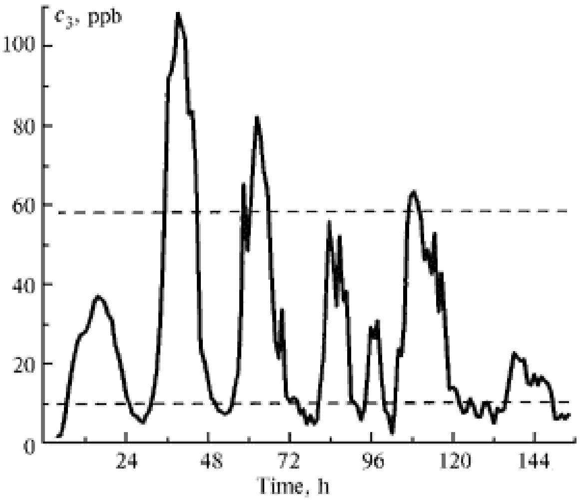

Fig. 4. Hourly variation of the surface ozone concentration beginning with 0 h (local time) on the July 13, 1999. Dashed lines denote the variation limits of surface ozone concentration for this season (for the 95% confidence level).

This figure presents the hourly SOC variation starting from July 12. On July 14, at 14 h, the maximum hourly average SOC was observed during the whole observation time at the Dolgoprudnyi station since 1991: 108 ppb (the previous SOC maximum, 94 ppb, was observed on September 1, 1996 when, just as in the described case, the surface temperature exceeded the norm more than by 10°C). In following days, maximum diurnal SOC decreased, especially after July 17 due to cloudiness that led to raining and a decrease in UV irradiation. There is no doubt that considerably increased SOC in Moscow region on July 14 was caused by a strong air pollution by products formed due to intensive fires in forests and peat bogs in the neighboring territories (this was caused by dry and hot weather and, in its turn, it was a consequence of a low-mobile blocking anticyclone over the central region of Russia). The increase of concentration indicated formation of a photochemical smog of the Los Angeles type in Moscow region. Forecasting of atypically high SOC seems to be possible only in combination with monitoring of other low-concentration gaseous components of the atmosphere (first of all, nitrogen oxides and hydrocarbons) and on the base of a model forecasting of air mass motion and taking into account photochemical transformations in the surface layer.

There are some features in the SOC temporal variation at the Dolgoprudnyi station as compared with "rural" stations of the West Europe. They are as follows: 1) larger ratio of maximum and minimum SOC during a year; 2) larger ratio of maximum and minimum SOC during 24 hours; 3) lower absolute SOC values. No doubt that these features are connected with climatic differences between Russia and West Europe. First of all, these are temperature differences caused by more continental position of the central region of Russia and its plant cover (it seems so that it promotes higher ozone destruction near the Earth's surface in Russia). The level of surface layer pollution also seems to be an important factor. The cases when surface ozone was accumulated in amounts exceeding the level of 60–80 ppb, which can indicate formation of photochemical smog, are observed very rarely in Russia. On the other hand, most of SOC characteristics in the central Russia demonstrate clear connections with similar characteristics observed in the Western Europe. In particular, dependences of the surface temperature and SOC deviations on the "norms" recorded days before (and, probably, on solar irradiation) are similar. There is a correlation between SOC at the Dolgoprudnyi station and that recorded at a station situated at a distance of 1000 km to the west of it on the Baltic sea coast. At this station, in its turn, one can observe similar connections with stations in Germany and Sweden.

References

1. D. Kley, A. Volz, and F. Miilheims, in: *Tropospheric Ozone - Regional and Global Scale Interactions*. NATO ASI Series C **227**, 63–72 (1988).

2. EMEP/CCC Report 3/89. *Ozone measurements January 1985 – December 1985*. Report No. 1 (by U. Feister and U. Pedersen), GDR–Norway (1989).

3. R. Girgzdiene, in: *Proc. of XVIII Quadrennial Ozone Symposium*, L'Aquilla, Italy, (1996), pp. 371–374.

4. N.F. Elanskii and I.A. Senik, Izv. Ros. Akad. Nauk, Ser. Fiz. Atmos. Okeana **31**, No. 2, 251–259 (1995).

5. M.Yu. Arshinov, B.D. Belan, V.V. Zuev, et al., Atmos. Oceanic Opt. **7**, No. 8, 580–584 (1994).

6. A.M. Zvyagintsev and G.M. Kruchenitskii, Atmos. Oceanic Opt. **9,** No. 9, 809–811 (1996).

7. S.J. Oltmans and W.D. Komhyr, J. Geophys. Res. **91**, No. D4, 5229–5236 (1986).

8. EMEP/CCC Report 4/95. *Ozone measurements 1990–1992* (by A.-G. Hjelbrekke), Kjeller, Norway: NILU (1995).

9. N.F. Elanskii and O.I. Smirnova, Izv. Ros. Akad. Nauk, Ser. Fiz. Atmos. Okeana **33**, No. 5, 597–611 (1997).

10. E.A. Kadyshevich and N.F. Elanskii, Izv. Ros. Akad. Nauk, Ser. Fiz. Atmos. Okeana **29**, No. 3, 346–352 (1993).

11. L.S. Ivlev, V.P. Chelibanov, and I.K. Shurgalina, in: *Atmospheric Ozone* (Gidrometeoizdat, Moscow, 1990), pp. 105–108.

12. H.E. Scheel, R. Sladkovic, E.G. Brunke, et al., in: *Proc. of Quadr. Ozone Symp*. (1992), pp. 11–14.

13. A.M. Zvyagintsev and G.M. Kruchenitskii, Izv. Ros. Akad. Nauk, Ser. Fiz. Atmos. Okeana **32**, No. 1, 96–100 (1996).

14. U. Feister and K. Balzer, Atmos. Environ. **25A**, No. 9, 1781–1790 (1991).

15. A.M. Zvyagintsev and G.M. Kruchenitskii, Atmos. Oceanic Opt. **12,** No. 1, 6–9 (1999).