SURFACE OZONE IN RUSSIAN AND UKRAINIAN BIG CITIES AND ITS FORECASTING

Zvyagintsev A.M.*, Tarasova O.A.*, I.N. Kuznetsova**, E.A. Lezina†, Ya.O. Romaniuk‡, and M.G. Sosonkin‡
*Central Aerological Observatory, Dolgoprudny, Russia (azvyagintsev@cao-rhms.ru)
**Hydrometeorological Research Center of Russia, Moscow, Russia
†Moscow Service of Ecology Monitoring (Mosecomonitoring), Moscow, Russia
‡Main Astronomical Observatory of the NAS of Ukraine, Kyiv, Ukraine

Abstract

Surface ozone data series for Moscow and Kiev areas are compared. Seasonal and diurnal variability of surface ozone concentrations in Moscow is given in a 3D diagram (ozone over hours and months) together with NO, NO_2 and CO variabilities. Special attention is given to the events with ozone concentrations in excess of maximum permissible values, which occurs under weather conditions unfavorable for the dissipation of minor species. Ozone concentrations correlate well with weather parameters such as air temperature, relative humidity, and wind parameters in the boundary layer. Regression ratios are determined, which permits predicting ozone concentrations based on weather forecast. With these ratios employed, the determination coefficient of the forecast of ozone concentration departure from the norm is up to 60%.

Key words: surface ozone, surface ozone pollution, surface ozone forecasting.

The current importance of monitoring surface ozone concentrations (SOC) in big cities is related with the necessity of monitoring air quality. Its low quality in warm seasons is mostly connected with exceeding maximum permissible concentrations (MPC) of ozone. Regular SOC observations in the green zone of Moscow were initiated in 1991 and are reported in (Zvyagintsev and Kuznetsova, 2002). The time variability of SOC in Moscow area is generally in agreement with that observed in middle latitudes, at continental rural stations of Western Europe. This paper deals with comparing the results of SOC observations in Moscow (56N, 38E, 190 m a.s.l.) and Kiev (51N, 31E, 120 m a.s.l.), where observations have been carried out since August 2006). This lets us judge about the regularities of SOC time variability in CIS big city areas and, in particular, assess the horizontal SOC gradient and the probability of harmful SOC formation in southern Russian cities lacking regular observations.

Observations of SOC and other trace gases in both cities are made with common gas analyzers, and ozone measurement error is not more than ±2 ppb. Additionally, observational data from the world weather network stations in Moscow (No. 27612) and Kiev (No. 33345) are analyzed.

The average SOC dynamics over a year is most comprehensively characterized by the seasonal diurnal variability, which most clearly reveals its main features (Tarasova et al., 2007). Figure 1 shows the variabilities for both city areas. In this figure one can see that throughout the year the mean SOC values in the same periods are much higher in Kiev than in Moscow. The patterns of the seasonal diurnal SOC in both areas very well agree. It can also be seen that, at first approximation, both seasonal and diurnal SOC variabilities correlate well with those of air temperature. However, there are some differences: while both seasonal and diurnal temperature variabilities exhibit only one maximum, the seasonal SOC variability has two local maximums, in spring and in summer, prior to and after the occurrence of temperature maximum. The diurnal SOC variability has a usual maximum whose occurrence nearly coincides with the time of temperature maximum (2 – 3 hours after the local noon) and a pseudo-maximum at night. Such a nighttime SOC pseudo-maximum can be observed in every European city, with none at rural and remote stations (NEGTAP 2001), and is associated with the slowing down of ozone destruction due to man-made NO emission at night. According to Fig.1, the nighttime maximum in Kiev is less pronounced than in Moscow, which seems to result from the lower anthropogenic pollution concentration.

According to the classification given in (Tarasova et al., 2007) the seasonal SOC variabilities in both city areas can considered as characteristic of flat-terrain stations with moderate pollution by ozone precursors. In this classification, the level of pollution is estimated by the ratio of maximum mean-hour SOC values at spring and summer maximums. Such summer-to-spring ratios in both Moscow and Kiev are smaller than at rural stations in the north of Germany, Poland, etc., but larger than in the north of Italy, south of Germany, Hungary, etc. The summer ozone maximum is likely to be associated with photochemical ozone forming processes, which proceed in the presence of sufficient enough solar UV radiation and concentrations of ozone precursors, including anthropogenic pollutants. The spring SOC maximum is due to the seasonal features of atmospheric transport rather than photochemical processes. The nighttime SOC pseudo-maximum is observed over relatively small territories (typically several tens of kilometers) around big cities. The territory having similar SOC values at the time of summer ozone increases is typically of an order of several hundred kilometers (Logan, 1989; Zvyagintsev and Kruchenitsky, 1997; Zvyagintsev, 2004), which indicates the influence on SOC of the overall regional amount of ozone precursors.

It was of interest to compare the averaged seasonal diurnal SOC variabilities and those of ozone precursor concentrations (Fig.2). Apparently, such seasonal diurnal variabilities of these most important atmospheric pollutants are also common to other big cities the world over, with only the concentrations differing. This difference is equally determined by both the emission source intensity and local weather conditions, and first of all, by the features of vertical mixing in the boundary layer. Comparison between seasonal diurnal variabilities of

SOC and concentrations of the major atmospheric pollutants seems to demonstrate that the most important process governing SOC diurnal variability in Moscow and Kiev is the vertical mixing. Still it may be possible that under adverse weather conditions, infrequent in warm seasons, the process of photochemical ozone formation becomes dominant.

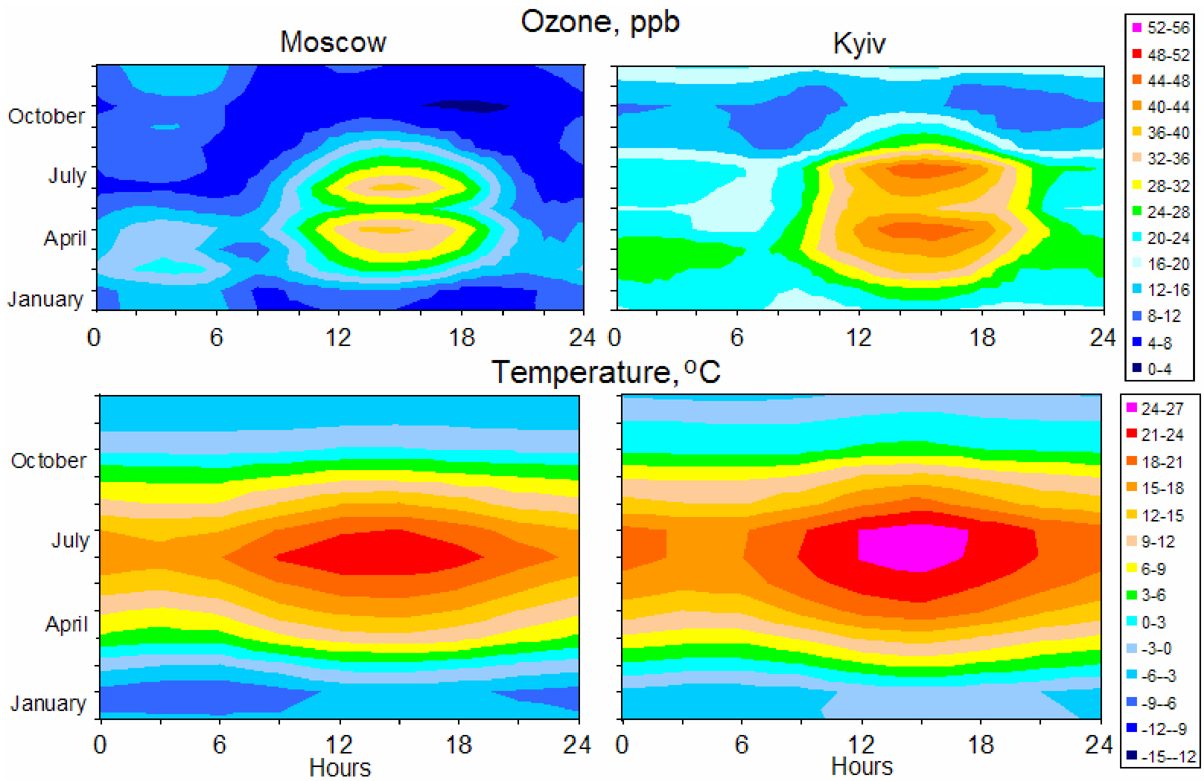

Fig.1 Mean seasonal diurnal variability of ozone concentration (top, ppb) and temperature (bottom, ºC) in Moscow, 2002-2008 (left), and Kiev, 2006-2008 (right).

Due to its relatively low chemical activity and hence long lifetime (about a month) CO is taken as an efficient marker of the basic anthropogenic emissions. The seasonal diurnal concentration variabilities of CO and NO_x (NO and NO_2) in Moscow are each year qualitatively close to the mean ones shown in Fig. 2, while differing in the time of occurrence of the extremes, first of all, maximums in late autumn and early spring. Within a year, two minimums of mean diurnal NO_x and CO concentrations are observed, from May till July in warm seasons and from October till January in cold seasons. Within a day in the period from February till October two concentration minimums also occur, at night (0:00 to 06:00) and in the daytime (12:00 to 18:00), the interval between the morning and evening maximums being proportional to the length of the light period of the day. In autumn, the interval between the maximums is reduced to zero, with only one maximum in the diurnal NO_x and CO variabilities in the daytime and one minimum at night until January-February. At rural stations in Western Europe (the Netherlands, Czechia, etc.) diurnal variabilities of NO_x and CO concentrations are either low or practically nil, the only seasonal maximum is considerably lower than in Moscow and is observed in the cold season, with the minimum occurring in the warm season (according to the World Data Centre for Greenhouse Gases, WDCGG). Due to the variability over a year of the underlying surface radiation balance, which causes steady stratification in cold seasons and unstable in warm ones, assuming also approximately constant pollution levels throughout a year, a single maximum of mean diurnal NO_x and CO concentration in a cold season and minimum in a warm one are likely to occur. It is this seasonal variability that NO_x and CO concentrations observed at Payerne station (Switzerland) correspond to. Therefore, the small winter NO_x and CO concentration minimum in Moscow seems to be due to the reduced motor traffic in winter.

For both cities efficient enough statistical models are constructed, which present observed SOC as a regression function of temperature, relative humidity, Mean wind speed and its direction in boundary layer (Zvyagintsev and Kruchenitsky, 1996). For maximum hour's mean SOC $C_{mx}(d)$, ppb, in Moscow and Kiev (subscripts M and K for Moscow and Kiev, respectively) the model allowing for temperature and relative humidity (wind parameters proved to be statistically of little significance) is as follows:

$$C_{mxM}(d)=C_{mx0M}(d) + 0.1+ 0.34*\Delta C_{mx}(d-1) + (0.80 - 0.70*\cos(2\pi\ d/365))*\ \Delta T(d) + (-0.172 - 0.134*\ \cos(2\pi\ (d-47)/365))*\Delta RH(d) \quad (1a)$$

$$C_{mxK}(d)=C_{mx0K}(d) - 0.2 + 0.41*\Delta C_{mx}(d-1)+ (0.76 - 0.66*\cos((d-8)*2\pi/365))*\Delta T(d) + (-0.111 - 0.275*\cos(d*2\pi/365))*\Delta RH(d)\ , \quad (1b)$$

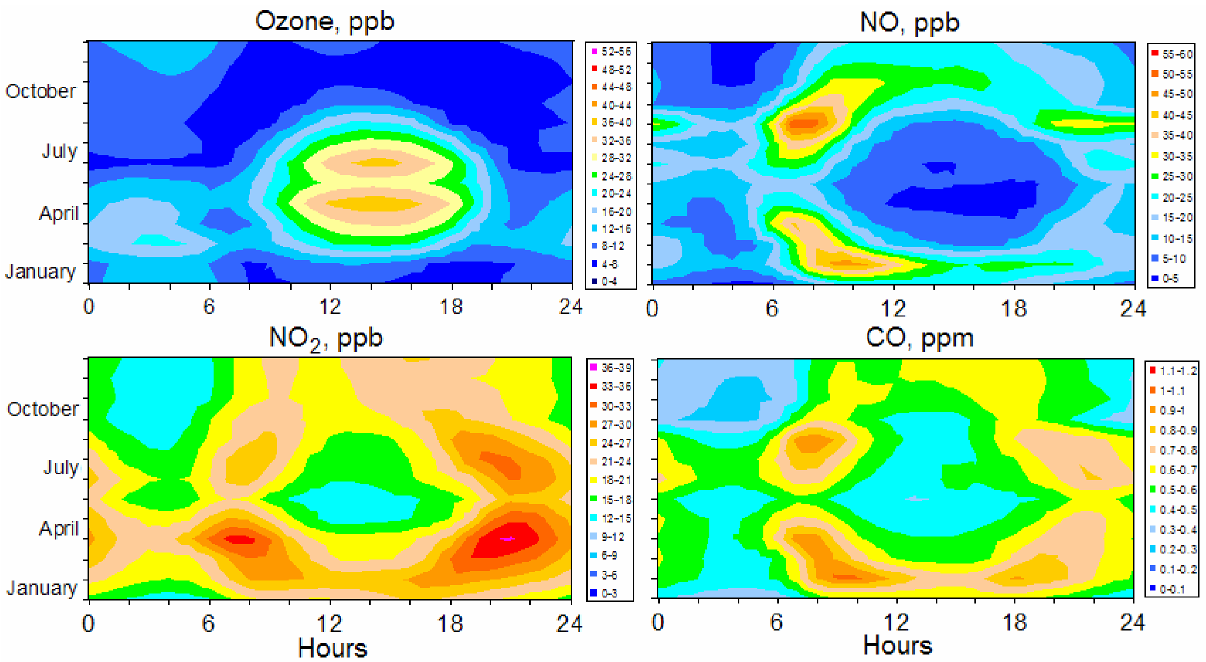

Fig.2. Mean seasonal diurnal variability of ozone concentration (left top; ppb), NO (right top; ppb), NO_2 (left bottom; ppb) and CO (right bottom; ppm) in Moscow 2002-2005.

where $C_{mx0}(d)$ is the norm for maximum hour's mean SOC (ppb) depending on the Julian day, d;
$\Delta C_{mx}(d-1)$ is the deviation from the norm of the value of SOC on the previous day (d -1);
$\Delta T(d)$ and $\Delta RH(d)$ are the deviation from the norm of maximum hour's mean temperature (^oC) and minimum hour's mean relative humidity (%) per day d.

The presence in the $\Delta T(d)$ and $\Delta RH(d)$ coefficients of a periodic component is indicative of the varying influence upon SOC of weather parameters in different seasons. Thus the influence of anomalous temperatures is the strongest in summer and insignificant in winter and that of relative humidity is the strongest in winter, while being insignificant in summer.

The normal maximum hour's mean SOCs in Moscow (Zvyagintsev, 2008) and Kiev, depending on the Julian day, are written as follows:

$$C_{mx0M}(d)=28.3+13.98*\cos((d-154)*2\pi/365)+1.93*\cos((d-46)*4\pi/365)+4.77*\cos((d+21)*6\pi/365)\ ;. \quad (2a)$$
$$C_{mx0K}(d)=38.7+15.48*\cos((d-162)*2\pi/365)+3.78*\cos((d-70)*4\pi/365)+2.66*\cos((d+12)*6\pi/365)\ . \quad (2b)$$

The relationships for the normal maximum temperature and minimal relative humidity have a similar form. The main difference between the normal maximum means for Moscow and Kiev, according to the above relationships, is due to the first terms in the right-hand part of (2a) and (2b): in Kiev this term is by 10 ppb larger than in Moscow, which can be seen in Fig.1. The difference between normal SOC for Kiev and Moscow is nearly invariable over a year.

In both city areas, under adverse (for air pollution dissipation) weather conditions in the period from May till early October, there may be episodes with ozone concentrations exceeding maximum permissible level and thus harmful to human health. In both Russia and Ukraine this level is a one-time (20-min. mean) ozone concentration of 160 μg m^{-3} (or 80 ppb). In Western Europe the critical ozone concentration of which, according to the law, the citizens ought to be informed, is taken to be 180 μg m^{-3}. This approximately corresponds to the Russian maximum permissible level of pollution. The background SOC values there are by about 20 μg m^{-3} higher than in Moscow area. In Moscow the highest SOC was observed 2002, with reaching 259 and 183 μg m^{-3}, respectively. The frequency of such episodes is generally the highest in July – August, being evidently higher in Kiev than in Moscow. Over the last 12 years, such events have been observed In Moscow area once in two years (with none in 2008). In Kiev, such episodes were observed in 2007 and 2008. In 2008, in particular, there were 4 such events, all of them in August, the hour's and 8-hour's SOC means reaching 182 and 159 μg m^{-3}, respectively.

The models incorporating relationships (1) and (2) yield fairly good results in a quantitative description of SOC in different periods of the day, primarily, as concerns maximum daily values (Zvyagintsev, 2008). The determination coefficients for SOC in models described by relationships (1) and (2) are within the range 0.4-0.6 for both cities. One of the deficiencies of the SOC model described by relationship (1) is underestimation for both cities when an observed value exceeds maximum permissible level.

Conclusion

1. As a results of comparing time variability of SOC in Moscow and Kiev, a similarity of their seasonal diurnal variabilities is revealed. Both SOC and temperature in Kiev are generally higher than in Moscow during the corresponding periods. The seasonal variability of SOC in both cities exhibits two maximums, in spring and summer. Throughout the day, a usual ozone concentration maximum, approximately 2 or 3 hours after the local noon, and a nighttime one, typical of big cities, are observed in both city areas. The seasonal SOC variability in both cities is typical of moderately polluted plain-terrain European stations.
2. The summer maximum seems to be associated with the photochemical processes of ozone formation, and the spring one with the dynamic processes of atmospheric transport. The frequency of events with SOC in excess of the maximum permissible level and harmful for human health is the highest in July – August. In Kiev such episodes within the observation period were more frequent than in Moscow. Therefore, it is likely that in big city areas in the south of Russia (Volgograd, Rostov-on-Don, etc.) episodes with SOC higher than maximum permissible occur more often than in Moscow.
3. For both city area the time SOC variability can be efficiently enough described by a statistical model presenting ozone concentrations observed in the form of a regression function of temperature, relative humidity, mean wind speed and its direction.

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