Surface ozone variations at Novosibirsk city

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Measurements of surface ozone in Novosibirsk in 2003–2005 are analyzed; its diurnal and seasonal variations are estimated. The models are built connecting surface ozone levels with meteorological parameters in different seasons. Among the parameters mostly affecting daily maximum surface ozone level are the maximum ozone concentration in the previous day, the daily (first of all, maximum) temperature, the wind velocity at a level of 925 GPa, the minimal relative humidity, and O_3 levels in the morning hours (about 7 a.m.; because the closer to the noon, the stronger their effect). The meteorological conditions, under which surface ozone concentrations in Novosibirsk exceed the maximum permissible values, are determined.

According to the recommendations of the World Health Organization, the surface ozone is one of the five matters, concentrations of which are to be measured to control the atmospheric air quality. Systematic measurements of the surface ozone have been started since 2002 by Federal Service for Hydrometeorology and Environmental Monitoring (RosHydroMet) in seven Russian regions, including Novosibirsk.[1] Earlier the results of long-term surface ozone measurements in big Russian cities and their suburbs were reported in Refs. 2–7. The peculiarities of surface ozone variations in Novosibirsk are described in these works based on the measurements carried out by the web department of the Western Siberian RosHydroMet Service in 2003–2005.

Surface ozone concentration (SOC) was measured with the ozone gas analyzer of chemiluminescence type, the 3-02 P-A model produced by the instrument-making enterprise "OPTEK" (St. Petersburg). The instrumental measurement error is 6 $\mu g \cdot m^{-3}$ within the concentration range 0–30 $\mu g \cdot m^{-3}$ and 20% for larger concentrations. The observation point was located at the urban settlement territory beyond the zone of direct influence of industrial enterprises and highways. The 20-minute averaged ozone concentrations were used for the analysis, as well as standard meteorological parameters (temperature, humidity, wind, etc.) measured by the RosHydroMet web department.

Time variations of SOC in Novosibirsk are characterized by a significant diurnal and day-to-day variability. Seasonal SOC variability is illustrated in Fig. 1 by its discrete (20-min averaged) maxima in 2003–2005. Seasonal variability of daily-averaged SOC is of similar character: the coefficient of correlation between maximum and daily-averaged SOC value for a long period (more than 3 months) virtually always exceeds 0.90, like in other observation points.[8] Maximal SOC values are usually observed in the warm period (from May to August), minimal ones – in the cold period from October to February and at drizzly precipitations. Average seasonal variations of daily maximum discrete SOC $C_0(\mathrm{d})$, $\mu g \cdot m^{-3}$, where d is the Julian day, can be satisfactorily described as a sum of first three harmonics of the annual variations (curve *2* in Fig. 1) by the method from Ref. 9:

$$C_0(\mathrm{d}) = 49.6 + 27.3\sin(2\pi \mathrm{d}/365) - 25.2\cos(2\pi \mathrm{d}/365) - 4.3\sin(4\pi \mathrm{d}/365) + 4.1\cos(4\pi \mathrm{d}/365). \quad (1)$$

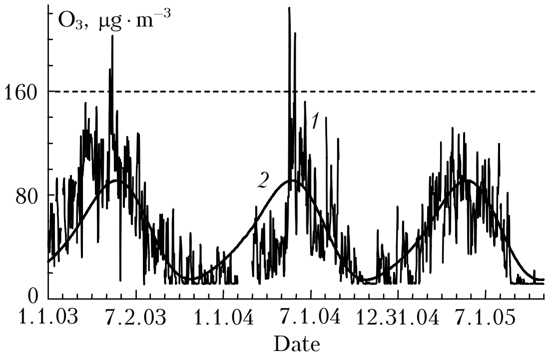

Fig. 1. Behavior of the daily maximum ozone concentration in 2003–2005 (*1*) and model estimation of its seasonal variations (*2*). Dashed line shows the maximum permissible ozone concentration.

The diurnal variability of SOC in Novosibirsk is illustrated in Fig. 2 for the periods of daily maxima and minima. Peak SOC values in the warm (May–August) season are usually observed at 2–4 hours after the local noon; small peak is also pronounced at the nighttime. The value of the night peak in the cold season is slightly higher than the daytime one while in the warm season the latter is much higher than the night peak. Such diurnal behavior of SOC is characteristic for big cities,[7,10,11] while rural areas of the northern hemisphere are characterized by only one maximum at the afternoon and the minimum at the nighttime just before sunrise.

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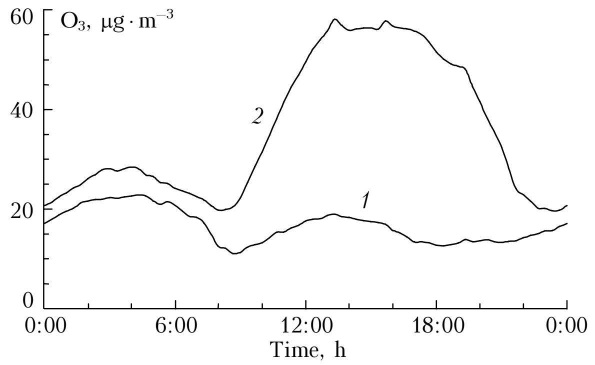

Fig. 2. Average variations of diurnal ozone concentration in cold (*1*; November–February) and warm (*2*; May–August) seasons.

The SOC maximum at the afternoon is caused by the ozone-rich air inflow from higher layers of the boundary layer or free troposphere due to vertical mixing intensifying at daytime, and photochemical ozone formation under the action of solar radiation.[5,6,12]

The decrease of SOC in the warm period in the absence of solar radiation is connected with the attenuation of ozone downward transfer due to vertical mixing and its depletion in the surface layer in chemical reactions on the ground surface (so called "dry deposition") as well as homophase (e.g., when interacting with NO emitted by motor transport) and heterophase (on surfaces of air aerosols) reactions in air.

Of special note is the shape of diurnal SOC curve in the cold period, when the main ozone peak occurs at nighttime (curve *1*, Fig. 2). Inasmuch as the only reaction of ozone molecule formation is the interaction between molecule and atom of oxygen; since the oxygen atom is formed only photochemically,[4,5] the night ozone peak is seemingly related to ozone advection from the outside, i.e., from the suburbs with a cleaner air.

From early morning to deep night, the ozone depletion due to the nitric oxide emission by motor transport and industrial enterprises is more intensive than its inflow due to advection, vertical mixing, and photochemical formation. The fact that two diurnal ozone minima are close in time to diurnal maxima of nitric oxide and dioxide in Moscow[7,11] confirms this hypothesis.

Like in other observation points,[6,9,13–16] the day-to-day and diurnal SOC variability in Novosibirsk is strongly related to the variability of meteorological parameters. This allows the development of empirical SOC model suitable for forecasting, e.g., maximal SOC. This work studies quantitative characteristics of the relations of the maximal SOC with the temperature, relative humidity, 925-GPa wind (bearing more information content in comparison with near-ground wind parameters[9]), the ozone concentration in previous days and morning hours.

The procedure and technique of finding such relation were described in Ref. 9. At the first step, the assessments of "standards" of annual variations for the predictand (maximal SOC) and each predictor are calculated in the form of sum of the constant and three first harmonics of the annual variations (such equation for SOC has been given above). Then, the "remainders" are calculated, i.e., differences between observation data and the "standards". At the next step the coefficients of regression of the "remainders" of daily maximum SOC are calculated from the "remainders" of meteorological parameters and SOC in previous dates. Model SOC is the sum of "standard" and "remainder", calculated by the regression equation.

The dependence of the model daily maximum SOCs $C_1(\mathrm{d})$ and $C_1'(\mathrm{d})$ on meteoparameters and daily maximum SOC in the previous day $C(\mathrm{d}-1)$ can be described by the equations

$$\begin{aligned} C_1(\mathrm{d}) = C_0(\mathrm{d}) + 0.02 + [0.636 + 0.07\sin(2\pi\mathrm{d}/365) + \\ + 0.091\cos(2\pi\mathrm{d}/365)]\Delta C(\mathrm{d}-1) + \\ + [0.92 + 0.39\sin(2\pi\mathrm{d}/365) - \\ - 0.63\cos(2\pi\mathrm{d}/365)]\Delta T - \\ - 0.135\cos(2\pi\mathrm{d}/365)\Delta H, \end{aligned} \quad (2)$$

provided the meteorological predictors are only the temperature and relative humidity and by

$$\begin{aligned} C_1'(\mathrm{d}) = C_0(\mathrm{d}) + 0.19 + [0.659 + \\ + 0.102\cos(2\pi\mathrm{d}/365)]\Delta C(\mathrm{d}-1) + \\ + [0.94 + 0.42\sin(2\pi\mathrm{d}/365) - \\ - 0.82\cos(2\pi\mathrm{d}/365)]\Delta T + 0.66\cos(2\pi\mathrm{d}/365)\Delta v_{925}, \end{aligned} \quad (2a)$$

if 925 GPa wind parameters adds to the two above predictors. In Eqs. (2) and (2a) $\Delta C(\mathrm{d}-1)$, ΔT, ΔH, and Δv_{925} are "remainders" of $C(\mathrm{d}-1)$, daily maximal temperature (°C), minimal relative humidity, and 925-GPa wind speed ($\mathrm{m \cdot s^{-1}}$), respectively.

The dependence of the model daily maximal SOC $C(\mathrm{d})$ on all the above-listed meteoparameters, daily maximal SOC in the previous day $C(\mathrm{d}-1)$, and the discrete SOC at 11 a.m. can be described by the equation

$$\begin{aligned} C_2(\mathrm{d}) = C_0(\mathrm{d}) + 0.31 + 0.453\Delta C(\mathrm{d}-1) + \\ + 0.512\Delta C_{11}(\mathrm{d}) + [0.84 - 0.40\cos(2\pi\mathrm{d}/365)]\Delta T + \\ + 4.1\cos(2\pi\mathrm{d}/365)\Delta\cos(2\pi\mathrm{D}/180) + \\ + 0.67\cos(2\pi\mathrm{d}/365)\Delta v_{925}, \end{aligned} \quad (3)$$

where $\Delta C_{11}(\mathrm{d})$ and $\Delta\cos(2\pi\mathrm{D}/180)$ are the "remainders" of discrete SOC at 11 a.m. and cosine of 925-GPa wind direction D (in degrees), respectively.

Coefficients of correlation of the time series $C(\mathrm{d})$ with model ones $C_1(\mathrm{d})$, $C_1'(\mathrm{d})$, and $C_2(\mathrm{d})$ for 2003–2005 are 0.88; 0.89; and 0.91, respectively. RMS errors (differences between observed and model values) of model series $C_1(\mathrm{d})$, $C_1'(\mathrm{d})$, and $C_2(\mathrm{d})$ for all observation period are 19.5, 19.6, and 16.9 $\mu\mathrm{g \cdot m^{-3}}$, respectively, at 37.2 $\mu\mathrm{g \cdot m^{-3}}$ RMS deviation of the initial series $C(\mathrm{d})$. Figure 3 illustrates the quality of compliance of the model series to observation data. Equations (2) and (2a) can be used for forecasting the maximal SOC for tomorrow, provided the today's maximum ozone concentration and meteoparameters, forecasted for tomorrow, are used as predictors.

Equation (3) can be used for morning updating of the forecasted maximal SOC for today, if the predictors are the observed morning ozone concentration and morning-updated forecasts of meteoparameters for today. An equation similar to Eq. (3) and noticeably updating ozone forecast for today can be calculated provided the observation data from about 7 a.m. are available.

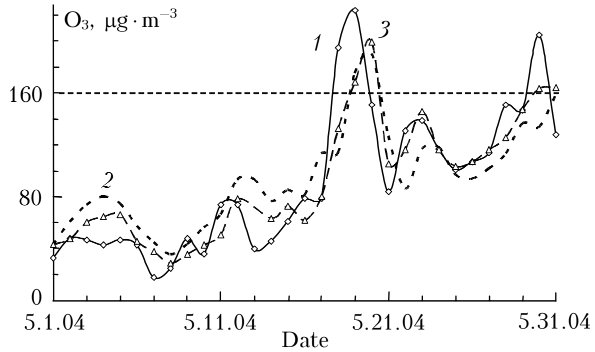

Fig. 3. Variations of the daily maximum ozone concentration in May, 2004 (*1*) and its forecast made in previous (*2*) and current (*3*, 11 a.m.) days. Dashed line corresponds to the maximum permissible ozone concentration.

As is evident from Figs. 1 and 3, events when discrete SOCs exceed the maximum permissible values (160 μg · m^{-3}) sometimes occur in Novosibirsk. Three such events were recorded in 2003 and 2004, no such events occurred in 2005. The event in May, 2004, was also recorded in Tomsk (May, 15–19) at the TOR-station of the IAO SB RAS (http://meteo.iao.ru/), 200 km north-eastward from Novosibirsk. The events were accompanied by a high temperature (up to 28°C in 2003 and 36°C in 2004) and weak wind; in 2004, the air came to the region from regions of grass and forest fires. Such conditions resulted in accumulating ozone precursors, sufficient for intensive photogeneration, first of all, nonmethane hydrocarbons of both natural and anthropogenic origin. Just such weather is characteristic for the events of dangerous ozone concentrations in middle and high latitudes of the northern hemisphere.[17]

Conclusions

1. Assessments of diurnal and seasonal surface ozone variability have been worked out on the base of data for 2003–2005 measured at the automated weather station No. 26 in Novosibirsk.

2. The models have been built correlating SOC with meteoparameters in different seasons. Daily maximal SOCs are mostly affected by its magnitude in the previous day, temperature (most of all, daily maximum), 925-GPa wind speed, daily minimal relative humidity, and SOC measured at morning hours (about 7 a.m., because the closer to noon, the stronger the effect).

3. It has been noted, that SOCs exceeding the maximum permissible values were recorded in Novosibirsk during two years from three years of continuous observations. Seemingly, this is the evidence of the problem of air ozone pollution in Novosibirsk, which is urgent today and can be aggravated with the increase of motor transport in the region.

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