ON VARIABILITY OF THE SURFACE OZONE CONCENTRATION IN MOSCOW ENVIRONS AND ITS RELATIONSHIPS WITH THE METEOROLOGICAL PARAMETERS

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Results of five-year regular measurements of the daytime surface ozone concentration (SOC), started in 1991*, are presented. In the first approximation, the normal annual behavior of the SOC is well described by the first harmonic of its annual oscillation. The residues (the differences between the true behavior and the model one) of the SOC are described by regression on residues of temporal series of the meteorological parameters, among which the temperature and the relative humidity at noon are most important. The second residues are described by autoregression of the third order. The total efficiency of the model approximation is about* 0.8*, with the efficiency of expansion in two key meteorological parameters being about* 0.30 *and the autoregression efficiency being about* 0.36*. These data agree well with the results obtained at the European Ozone Network.*

The surface ozone concentration (SOC) varies strongly with space and time[1–8] under the effect of dynamic, radiative, and chemical processes. The SOC variations are largest above continental regions where the sources of anthropogenic air pollution are concentrated and various dynamic processes are more pronounced than above the oceans. Now the SOC is considered to be increased by 1–3% per year[4,5,8] due to the increase of the atmospheric pollution. In spite of a large array of experimental data that has already been accumulated, many long-term trends in the SOC behavior have not yet been elucidated[4–8]; in particular, numerical estimates of the SOC trends show insufficient statistics[7] and relationships of the SOC with local (associated with industrial emissions and exhausts of engines into the atmosphere), regional (whose scales are typical of the meteorological fields), and global[9] factors have not yet been established.

Some measurements of the SOC, performed during the first 2.5 years at the Central Aerological Observatory (CAO) located in Dolgoprudnyi at a distance of 25 km to the north of the Moscow center in its environs, were reported in Ref. 10. An empirical model of numerical relationships of the SOC with the meteorological parameters (the surface temperature, the pressure, the relative humidity, the diurnal temperature gradient, the cloud amount, the temperature lapse rate, and the wind velocity at a pressure of 850 mbar), measured by aerological radar sensing methods, was constructed in Ref. 11 on the basis of the obtained experimental data. The present paper is based on the results of regular measurements of the SOC in Dolgoprudnyi from March 1991 to the end of 1995 and is devoted to elucidating the trends in its temporal behavior and its relationships with the meteorological parameters.

The ozone concentration was measured with a device analogous to that reported in Ref. 1 in which the measuring transducer of an aerological ozonesonde was used as a sensitive element. Measuring procedure was described in Ref. 10. The minimum detectable concentration was 1 $\mu g/m^3$. The systematic error of an individual measurement did not exceed 10 $\mu g/m^3$ and the random error was 6 $\mu g/m^3$. Results of measuring the SOC at 11:00 and 14:00, LT were used in the paper and their average was taken as an estimate of the average daytime value (below it is referred to as the daytime concentration). These data are sufficiently representative considering that the average daily, average daytime, and maximum hourly average values of the ozone concentration are well correlated. The other meteorological parameters (the pressure, the temperature, etc.) were measured at regular intervals at the aerological station.

The temporal behavior of the SOC is illustrated by Fig. 1, in which the average monthly SOC in Dolgoprudnyi is shown (curve *1*) for the period of observation. Some experimental data averaged over shorter intervals were reported in Refs. 2 and 3. The temporal behavior of the SOC in Dolgoprudnyi exhibits well pronounced seasonal variability, like everywhere at mid-latitudes of the northern hemisphere.[4,5,8] The normal annual behavior of the average monthly daytime concentration $C_0(m)$, in $\mu g/m^3$, in Dolgoprudnyi can be approximately described by the formula

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$$C_0(m) = 39.3 + 26.3\cos(\pi m/6 - 3.077) + 1.7\cos(\pi m/3 + 1.69) + 2.3\cos(\pi m/2 - 0.54), \quad (1)$$

where m is the serial number of month (for January, $m = 1$, etc.).

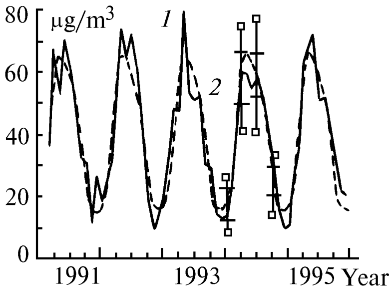

FIG. 1. Observed behavior (1) of the average monthly values of the daytime surface ozone concentration C(m) in Dolgoprudnyi in 1991–1995 *and its model normal behavior in accordance with EC. (1) considering only the first harmonic (2). In* 1994, *vertical bars denote monthly variability (*±1 *standard deviation) for the SOC. The horizontal bars denote the estimated year–to–year variability of the average monthly SOC (*±1 SD*).*

It is seen from Eq. (1) that the amplitude of the first harmonic exceeds approximately by an order of magnitude the amplitudes of higher harmonics (for the confidence level $P = 0.8$, the second and third harmonics appear significant, but for $P = 0.95$ they are also insignificant).

Obviously the observed annual behavior $C(d)$ of concentration vs. the day of the Julian calendar d can be related with the normal annual behavior $C_0(d)$ by the expression

$$C(d) = C_0(d) + R_{C1}(d), \quad (2)$$

where $R_{C1}(d)$ is a temporal series of the SOC residues. Its mathematical expectation is equal to zero and its variance takes the minimum possible value.

As known,[3,12,13] the SOC depends on predictors, among which the standard meteorological parameters (the temperature, the atmospheric pressure, and the relative humidity) and the solar radiation intensity, etc. are most important. Their qualitative effects depend on geographic location of the observation station. Each of these predictors exhibits its own normal annual behavior. We have already pointed out[10,11] that the surface temperature T and the relative humidity u at noon are the most informative predictors for the SOC in Dolgoprudnyi. The series of the SOC residues $R_{C1}(d)$ can be represented in the form of regression on the series of residues of these predictors

$$R_{C1}(d) = A_T R_T(d) + A_u R_u(d) + R_{C2}(d), \quad (3)$$

where A_T and A_u are the coefficients and the subscripts T and u indicate the temperature and the relative humidity, respectively. We obtained the following values of the coefficients: $A_T = 0.78(\pm 0.54)$ μg·m^{-3}·°C^{-1} and $A_u = -0.48(\pm 0.20)$ μg·m^{-3}·%$^{-1}$ (the errors in the estimates for the confidence level $P = 0.95$ are given in the parenthesis).

To illustrate the validity of Eq. (3), the temporal behavior of the first average monthly residues of the SOC, the temperature, and the relative humidity are shown in Fig. 2 for short observational period. It is well seen from the figure that, for example, the enhanced SOC in May 1993 was correlated with the elevated temperature and the reduced relative humidity. The reduced SOC in June and July was correlated with the increased humidity. The reduced values of the SOC in May–July 1994 were correlated with decreased temperature and increased humidity.

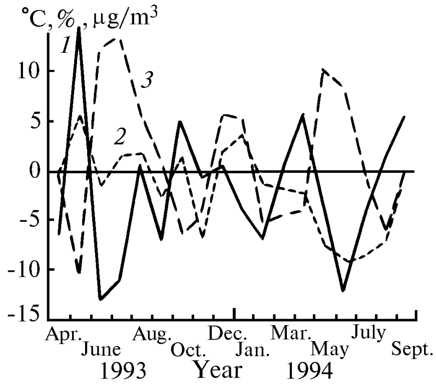

FIG. 2. Temporal behavior of the first residues of the average monthly SOC (1), the daytime temperature (2), and the relative humidity (3) in April 1993–*September* 1994.

We note that significant correlation between the temporal series of the SOC residues and the total ozone content (TOC) is observed; however, the correlation coefficient is small (about − 0.15) and the degree of mutual coherence does not exceed 0.5 for all frequencies (analogous results were obtained in Hohenpeisenberg, Germany). Therefore, the quantitative relationships between the SOC and the TOC are weak and are likely caused by their dependence on the other weather factors.

A large deviation of the Darbin–Watson statistics for a series of the second residues $R_{C2}(d)$ from 2 (its theoretical value under assumption that all terms of the series are independent) and integrated spectrum periodogram indicate that the second residue $R_{C2}(d)$ can be represented in the form of autoregression

$$R_{C2}(d) = \sum_{i=1}^{n} AR(i)\, R_{C2}(d - i) + R_{C3}(d), \quad (4)$$

where n is the autoregression order and the third residue is the white noise, as evidenced by the residue spectrum (or by integrated periodogram) and the Darbin–Watson statistics (close to 2). The third–order autoregression shows the best correlation. The values of the coefficients are $AR(1) = 0.41$, $AR(2) = 0.12$, and

$AR(3) = 0.11$. The error in determining these coefficients for the confidence level $P = 0.95$ is 0.05. We note that the same order of autoregression (from 2 to 5) is typical for the meteorological parameters in Dolgoprudnyi and for the SOC measured at the European and American Ozone Networks.[6,13,14]

The standard deviations of the series $C(d)$, $R_{C1}(d)$, $R_{C2}(d)$, and $R_{C3}(d)$ are 24.6, 15.3, 12.8, and 10.7 $\mu g \cdot m^{-3}$, respectively. This means that the total efficiency of the model described by Eqs. (2)–(4) is (see, for example, Ref. 13)

$$Q = 1 - (10.7/24.6)^2 = 0.8.$$

Efficiency of the autoregression (0.36) and that of the combination of the regression on two meteorological parameters (the temperature and the relative humidity) and autoregression (0.50) agree well with the estimates[13] obtained at the German Ozone Network (located in the territory of the former German Democratic Republic). It seems likely that the effects of the atmospheric processes in Germany and in the Moscow environs on the SOC are similar and that the measurement errors have nearly the same effects in both cases.

As known,[6,11] the SOC fields have a typical scale of about 1000 km (the distance at which the temporal series of observational data obtained at two stations are highly cross-correlated). For this reason, we investigated the cross-correlation function for the series of the first residues of the SOC in Dolgoprudnyi and at the station Preila[15] of the World Ozone Network located in Lietuva on the coast of the Baltic Sea at a distance of about 1050 km to the west of Dolgoprudnyi. A small but significant correlation was established between these series, whose value and temporal lag were close to those observed for the pairs of stations Sibton (Great Britain)–Neuglobsov (Germany) and Neuglobsov–Preila of the Ozone Network located at the same parallel and closely spaced (Fig. 3).

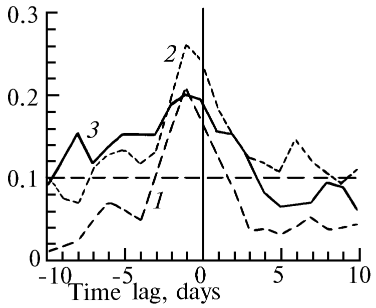

FIG. 3. Cross-correlation functions for the temporal series of the SOC residues for the pairs of stations: 1) Sibton–Neuglobsov (separation L = 666 km*; data of* 1987–1990*), 2) Neuglobsov–Preila (L =* 840 km; 1988–1990*), and 3) Preila–Dolgoprudnyi (L =* 1035 km; 1991–1995*). Dashed straight line indicates the confidence level P =* 0.95.

The above correlation is indicative of the satisfactory quality of measurements at these stations and of the fact that the SOC in the Moscow environs is determined to a marked extent by synoptic processes common to all stations. This also testifies that the surface ozone fields drift predominantly from the west to the east with a velocity of 5–10° per day.

Thus, the normal annual behavior, described by the first harmonic of the annual oscillation, was revealed in the temporal behavior of the SOC in Dolgoprudnyi within the span of five years. The residues (the differences between the true behavior and the normal annual one) of the SOC are well described by regression on residues of temporal series of the meteorological parameters, among which the temperature and the relative humidity at noon are most important. The second residues are described by the autoregression model of the third order. The total efficiency of the model approach is about 0.8, with the efficiency of expansion in two key meteorological parameters being about 0.30 and the autoregression efficiency being about 0.36. These data agree well with the results obtained at the European Ozone Network.[13]

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