Methods for estimation of surface ozone concentration trends at Kislovodsk High Mountain Station

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Methods for estimation of surface ozone concentration trends are analyzed based on measurements of the surface ozone concentration at Kislovodsk High Mountain Station since 1989 until now. Statistical methods, filtering on the basis of different parameters, and modeling of the meteorologically adjusted trend are considered. It is shown, that the first mentioned group of methods confirms the presence of statistically significant negative trends in the surface ozone concentration at the measurement site. The filtering methods allow one to study the mechanisms of long-term changes. The integrated contribution of meteorological factors to the long-term changes of the surface ozone concentration is about 30%.

Introduction

Investigations into the long-term variability of the surface ozone concentration are very important. They were first stimulated by the cases of serious plant damage at smog situations in Los Angeles. Recent Moscow fires of 2002 that gave rise to smog formation over vast areas attracted attention of various specialists in our country to the surface ozone problems.

For studying factors determining variations of the surface ozone in Europe, the EUROTRAC Program was unfolded in the late 1980s. This Program was aimed at studying the variation of atmospheric chemical composition. In September 8–12 of 2002 the Physical Department of Moscow State University held the Workshop on tropospheric ozone within the framework of the TOR-2 (Tropospheric Ozone Research) Subprogram of the EUROTRAC-2 Program. At this Workshop, it was mentioned that along with a significant progress in understanding of ozone climatology the contribution of various processes to formation of surface ozone trends is not absolutely clear yet. Besides, different papers devoted to analysis of such trends in Europe use different techniques for their estimation, what often complicates not only comparison between stations, but even internal interpretation of the mechanisms of variations.

The main objective of this paper is to harmonize the methods and approaches to investigation of surface ozone trends using, as an example, the measurements at Kislovodsk High Mountain Research Station and to evaluate their internal consistency and the possibility of using for separating the contributions of different mechanisms to formation of the trend.

Measurements

The Kislovodsk High Mountain Research Station (KHMRS) situated in Northern Caucasia (43.7°N, 42.7°E, 2070 m above the sea level) occupies a unique place in the surface ozone monitoring system.[10] It is far from both European and local emission sources of ozone precursors and can be considered as a background one.

The surface ozone concentration has been measured at KHMRS since March 1989 until now (Fig. 1). The measurements of meteorological parameters were started in 1991.

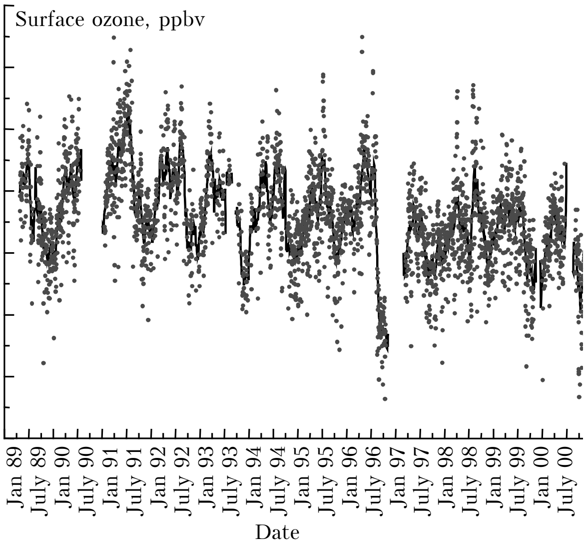

Fig. 1. Diurnally mean (dots) surface ozone concentration at the Kislovodsk High Mountain Research Station and 30-day sliding average (solid line) for the period of 1989–2000.

The tentative analysis showed[2] that the surface ozone conditions at KHMRS differ markedly from the regularities observed in surface ozone variations in Alps. The main feature of surface ozone variations is the presence of negative trend in the observation series. The thirteen-year observation series allows us to apply various methods for estimation of surface ozone concentration trends.

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2. Statistical methods

The group of statistical methods for trend estimation incorporates the methods based on transformations of the initial observation series. The detailed description of widely used statistical methods can be found in Ref. 4. These methods include the graphical method, linear regression schemes, autoregressive process scheme, and statistical tests. Some of these methods were used for estimating the surface ozone trends at KHMRS.

2.1. Linear time regression

Drawing the time plot of the concentration and estimating the slope of the straight line of the linear regression model give the estimate of the linear trend in a measurement series. The reliability of a linear trend can be checked by using the *t*-test. Application of this method reveals a significant negative trend in the surface ozone concentration at KHMRS (–1.75 ± 0.4)% a year for the period of 1989–2000). Similar estimates were obtained for some samples determined by the observation conditions. For example, the trends were obtained for different months (Table 1) and different concentration levels (percentiles) and for nighttime conditions [(–1.4 ± 0.35)% a year] corresponding to the time of formation of the diurnal peak at KHMRS.

Table 1. Surface ozone trends at KHMRS for the period of 1989–2000 as estimated by the method of linear time regression for different months

Month	Trend, % a year
January	0.06 ± 0.96
February	–1.21 ± 0.53
March	–1.71 ± 0.65
April	–1.27 ± 0.43
May	–1.63 ± 0.53
June	–2.2 ± 0.67
July	–1.86 ± 1.1
August	–2.45 ± 1.4
September	–2.1 ± 1.3
October	–2.01 ± 1.1
November	–0.50 ± 0.62
December	–1.12 ± 0.81

As can be seen from Table 1, a significant negative trend is observed for most months. The slightly negative and even positive trend, which is not statistically sound, is observed only in November–January.

Application of the linear regression method for trend estimation in the samples at different concentration levels – percentiles – may be an effective way to reveal some mechanisms of the trend formation. Analysis of different percentile levels at KHMRS showed that a significant negative trend is observed for all samples. Its value is maximum for low concentrations [(–2.1 ± 0.3)%/year] and minimum for high concentrations [(–1.5 ± 0.3)%/year]. It is noticeable that at European Alpine high mountain stations the distribution of the trends is just the opposite, namely, as the concentration increases, the trend alternates from slightly positive (for the ozone concentration levels from 1 to 50 percentiles) to negative (concentration values higher than the median level).[5] For most of the European stations, the negative trend of the maximum surface ozone concentrations is usually associated with introduction of restrictions on emissions of ozone precursors or, in other words, with moderation of the photochemical mechanism of ozone generation.

Such differences are indirect indicators of different mechanisms of the ozone trend formation at European high mountain stations and KHMRS. If we assume that long-term variations of the surface ozone concentration at the European high mountain ozonometric stations and at KHMRS are largely determined by the relation between the dynamic (governed by transport) and photochemical (governed by local pollution) factors, then it can be concluded that since the level of ozone precursors decreases both in Europe and Russia, the photochemical trends should have the same sign (negative), and only the transport conditions may determine significant differences between the mean values of observed surface ozone trends.[11]

2.2. Mann-Kendall test

The nonparametric Mann-Kendall test was used to estimate the surface ozone trends at KHMRS. Application of this test is convenient, since the procedure is insensitive to the presence of values missing in the series; besides, data can have any distribution. The analysis can account for data lying below the instrumental detection limits through assigning them the values smaller than the minimum measured ones. This assumption is justified by the fact that analysis does not employ the measurement data themselves, but their relative values: 1 – if $x_i < x_{i+1}$, 0 – if $x_i = x_{i+1}$, and –1 – if $x_i > x_{i+1}$. The idea of the test is to check the null hypothesis about the absence of a trend by calculating normalized statistical sums and comparing them with the tables of the normal distribution. The seasonal Kendall test was implemented on a computer as the MULTIMK Visual Basic macro for Excel (Linkoeping University (LIU), Linkoeping, Sweden).[12] The calculated results for KHMRS are presented in Table 2, from which it can be seen that the negative trend is present in the data array with high probability for almost all seasons.

The only exception is winter months (the corresponding confidence probability: D^{***} – higher than 0.99, D^{**} – higher than 0.95, D – higher than 0.75). These probability values are in a good qualitative agreement with the estimates by the method of linear time regression.

Table 2. Results of seasonal Kendall test for the period of 1989–1999 at KHMRS

Month	IV	V	VI	VII	VIII	IX	X	XI	XII	I	II	III
Normal statistical	−1.88	−2.41	−2.72	−1.70	−1.67	−2.50	−2.06	−0.99	−0.49	−0.83	−1.73	−2.77
Probability to discard the null hypothesis	D**	D***	D***	D**	D**	D***	D**	D		D	D**	D***

3. Filtering methods

To evaluate qualitatively the influence of mechanisms determining the long-term variations of the surface ozone concentration, trends are analyzed in samples collected according to a certain parameter. The filtering parameters may be both meteorological conditions (for example, the level of relative humidity, wind velocity, transport direction, back trajectory income sector) and the concentrations of some gas components – ozone precursors. The choice of the CO or NO_x concentration level as a physical filter allows analyzing trends in more or less polluted air masses.

As a meteorological filtering parameter, we took the 60% level of relative humidity similar to the parameter taken for data filtering at European high mountain stations. It was assumed that samples with the humidity level lower than 60% correspond, on the average, to prevalent downward motions at the site of observation of drier air masses and vice versa. Therefore, the dynamics of trends in humidity samples reflects the effect of the vertical exchange processes on the surface ozone variations. The regression analysis of trends in humidity showed that for the group with high relative humidity exceeding 60% the trend is (–2.2 ± 0.6)% a year, while for the group with low humidity the surface ozone trend is (–2.0±0.6)% a year. Although the difference between the trends lies within the standard deviation, it can be concluded that for air of the free troposphere, which falls in the group with low humidity, the ozone concentration trend is, on the average, somewhat smaller than that for the group with the high humidity.

In contrast to the humidity samples, which characterize the effect of dynamic processes on the surface ozone conditions, analysis of precursors along the back trajectories of air mass motion allows estimating the effect of photochemical factor on the surface ozone trends.

To separate unpolluted and moderately polluted air masses, samples with NO_x accumulation levels of 0.9 and 1.1 of the average level along the back trajectories were collected. The surface ozone trend differed markedly for different pollution samples. For high NO_x concentrations the trend was (–1.82 ± 0.16)% a year, while for the low NO_x concentrations it was (–1.66 ± 0.12)% a year. Such values confirm that the local photochemical source of surface ozone reduces due to diminishing emissions of ozone precursors.

The effect of long-range transport on the surface ozone trends at KHMRS was earlier thoroughly discussed elsewhere.[9] It is important to note that the distribution of transport sectors changes from year to year. The average effect of each sector was separated out, and it was shown that repetition of transport from the sectors with an increased ozone content decreases for the observation period. This fact allows us to assume the partly dynamic origin of the negative trend of the surface ozone concentration at KHMRS.

4. Simulation of meteorologically corrected trend

The first attempts to separate out the time scales of surface ozone variations were undertaken in Ref. 3, where the regression scheme of separation the seasonal component based on temperature and dew point was described.

To take into account the effect of long-term variations of local meteorological conditions on the surface ozone trends, the multiparameter regression scheme was developed at KHMRS. This scheme includes temperature, relative humidity, pressure, and wind velocity. Meteorological variables were chosen as those usually used in schemes accounting for the effect of meteorological conditions on the surface ozone.[1,8] The model was constructed in three stages.

At the first stage, time variations with different scales were separated: seasonal variations with periods longer than three months and the series of remainders. The former includes both seasonal variations and the trend component. For separation of time variations, the Kolmogorov–Zubenko (KZ) filtering was used. The apparatus function of the filter can be found in Ref. 7. The KZ filtering consists essentially in multiple application of the moving average to a series. This provides for a good noise suppression and separation out of signal with preset periods.

Another advantage of this method is its resistance to the missing values.[6]

Thus, the initial surface ozone concentration series can be written as

$$O_3 = KZ_{29,3}(O_3) + RE,$$

where $KZ_{29,3}(O_3)$ is 29-day filter applied to the measurement series; RE is the series of remainders after subtraction of the filtered series from the initial one. The results of separation are shown in Figs. 2 and 3. The long-period components in local meteorological parameters are separated in a similar way.

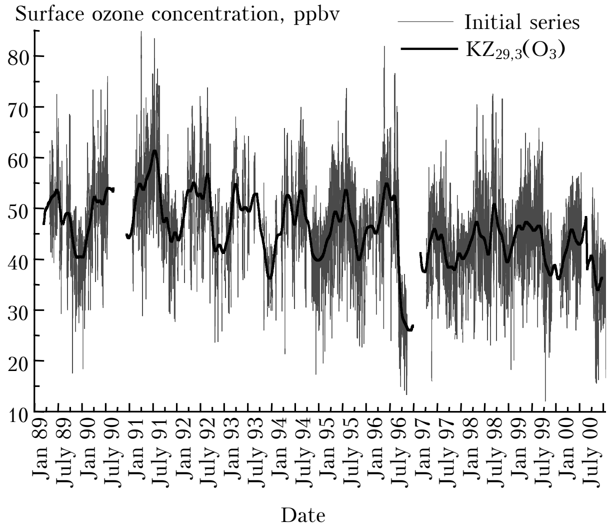

Fig. 2. Three-hour values of the surface ozone concentration at KHMRS and the separated long-period component ($KZ_{29,3}(O_3)$).

At the second stage, the multiparameter regression scheme of the long-period component of surface ozone variations is constructed based on meteorological parameters. Thus, the model concentration series can be presented as

$$MO = aKZ_{29,3}(T) + bKZ_{29,3}(h) + cKZ_{29,3}(w\_s) + dKZ_{29,3}(p),$$

where MO are the model values of the surface ozone concentration; T is the local temperature; h is the relative humidity; w_s is the wind speed; p is the atmospheric pressure; a, b, c, and d are the regression coefficients.

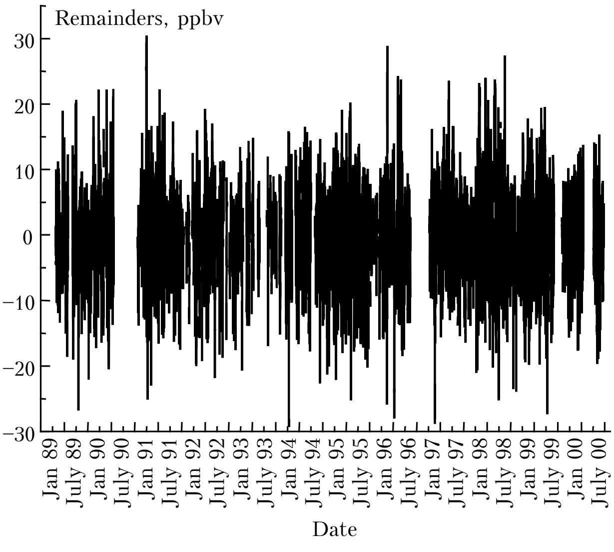

Fig. 3. Series of remainders of the surface ozone concentration after subtraction of the long-period component from the initial measurement series at KHMRS.

At the third stage, the model value of the surface ozone concentration is subtracted from the initial measurement series and the change in the slope of the regression line is estimated by the method of linear time regression. Comparison of the obtained regression curves (Fig. 4) showed that subtraction of the model series leads to a decrease in the negative trend. If in the initial measurement series this trend for the period since November 1991 until June 1999 was −0.85 ppbv/year, then once the long-time variations of local meteorological parameters were taken into account the trend took the value of −0.62 ppbv/year.

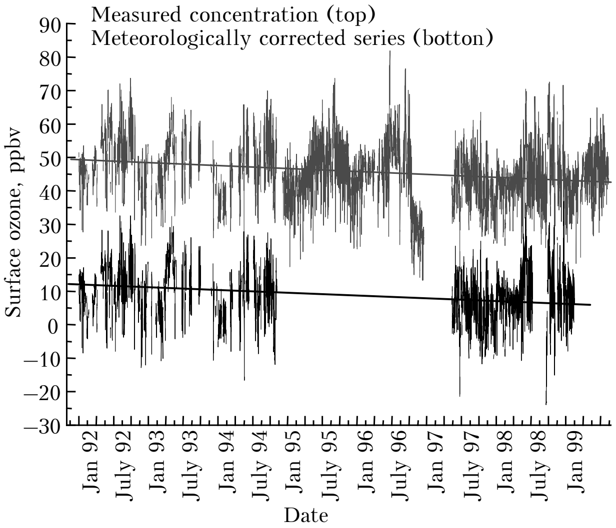

Fig. 4. Comparison of linear regressions for the initial measurement series of the surface ozone concentration at KHMRS for the period since November 1991 until June 1999 with linear regression of the meteorologically corrected series.

Thus, long-term variations of such meteorological parameters, as temperature, relative humidity, wind velocity, and atmospheric pressure are responsible for 27% of the negative trend of the surface ozone concentration at KHMRS. Estimating this value, we should keep in mind its parametric significance. The further development of this scheme, inclusion of physical-chemical mechanisms in it, account for direct relations and feedbacks with meteorological parameters will allow us to assess both qualitatively and quantitatively the contributions of various mechanisms determining surface ozone trends and to answer the question on the role of the anthropogenic factor in the trend formation.

Conclusion

This paper has analyzed the methods for estimation of the surface ozone trends based on measurements at Kislovodsk High Mountain Research Station since 1989 until now. Application of different statistical methods and approaches yields consistent results. Statistical tests and estimates by the methods of linear regression have revealed a significant negative trend for all months of a year except for the period since November until January. It was shown that filtering by physical parameters could be used as an efficient method for estimation of the contributions of different mechanisms to formation of surface ozone trends. Analysis of the results obtained allows the conclusion on the significant effect of dynamic processes on the formation of the surface ozone trends to be drawn. Simulation of the meteorologically corrected series suggested that the integrated contribution of meteorological factors to variations of the surface ozone concentration is about 27%.

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