# VARIATIONS OF THE OZONE CONCENTRATION IN THE GROUND AIR LAYER

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*The dynamics of the ozone concentration in the ground air layer over the region of Tomsk is examined based on the measurements performed over the period of several years. Both its general physical and purely regional behaviors are elucidated. The diurnal variations of the ozone and other gas concentrations are compared.*

The measurements of the ozone concentration in the ground air layer have been performed at the Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences since 1989. These measurements were used in 1991 as part of the SATOR program as the reference data for comparison of the results of individual measurement cycles. The present paper is concerned with the dynamics of the ozone concentration in the ground air layer between 1989 and 1991 and with their relationship to the other parameters of the air measured in the course of the SATOR experiments.

The observations were performed at the High–Altitude Lidar Sounding Station located to the north–east of Tomsk Akademgorodok. A 3–02 P portable chemiluminescent gas analyzer developed and produced at the LEK (Leningrad) on the order of the Institute of Atmospheric Optics was used as a measuring device. The gas analyzer has the following specifications:

| | |
|---|---|
| range of variation of measurable concentrations | 1 ... 1000 μg/m$^3$ |
| measurement error | 15% |
| time response not longer than | 1 s |
| parameters of the examined medium (upon entering an air–intake tube 5 m long): | |
| temperature | – 40 ... + 50°C |
| pressure | 700...820 mm Hg |
| relative humidity | 30 ... 98% |

The instrument was equipped with a built–in ozone calibrator (at an adjustment level of 18.5 μg/m$^3$) which provided its periodic test with analog and digital outputs for being connected to recording systems. The air was intaken through a teflon tube at an altitude of 6 m. The measurements were carried out continuously. The counts were taken in 10 min and were subsequently hourly averaged.

Shown in Fig. 1 is the annual behavior of the ozone concentration in the ground layer between 1989 and the beginning of 1992. The vertical bars denote standard deviations.

As can be seen from Fig. 1, the ozone concentration over the region of Tomsk sharply increased from February to March (by a factor of three) and then smoothly decreased. Minimum ozone concentrations near the ground were observed in October and November. Then the concentration has insignificantly increased by February.

The annual behavior of the ozone concentration in the ground layer shown in Fig. 1 could be considered representative[1–3] but that its early and sharp maximum in March. At least such an early maximum has not been found elsewhere before.[1–3] This maximum is probably due to geographic location of Tomsk surrounded by forests. The forests are powerful sources of terpenes and isoprenes which under natural conditions produce ozone.[3]

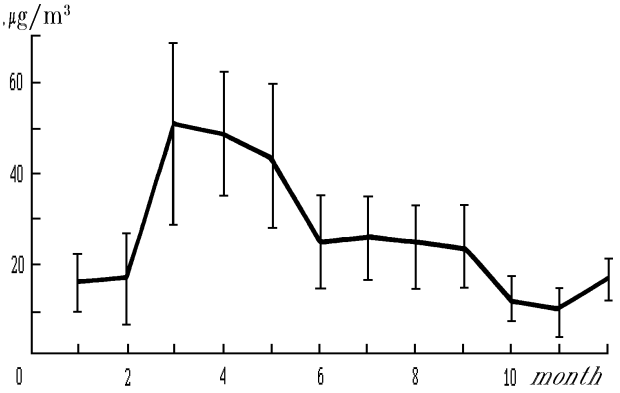


*FIG. 1. The annual behavior of the ozone concentration.*

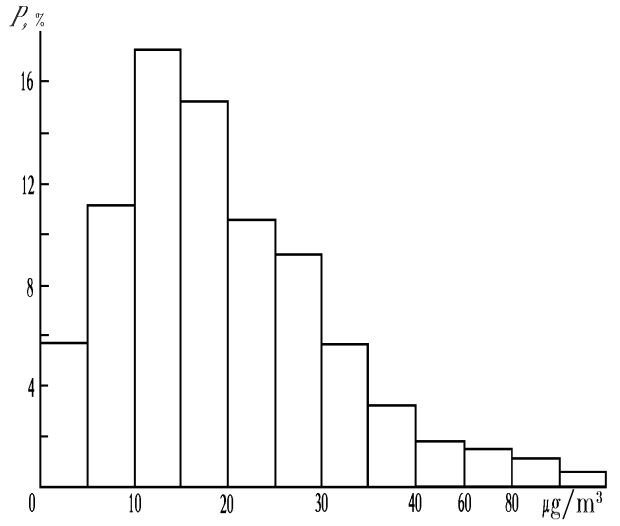


*FIG. 2. Recurrence of different values of ozone concentration in the ground air layer.*

Figure 2 shows the histogram of recurrence of the ozone concentration over the aforementioned period. More than 18 000 hourly averaged counts were used for its plotting. It can be seen from Fig. 2 that 67% of all the ozone concentration values are smaller than 30 μg/m$^3$ (a daily mean maximum permissible concentration for a

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residental area). If ozone in the ground air layer had not undergone diurnal variations, then the remaining 33% could have been a very dangerous index. Therefore it is expedient to examine the particular features of diurnal variation of ozone.

The diurnal variation of the ozone concentration calculated from the entire data array is shown in Fig. 3. The standard deviations are denoted by vertical bars. The minimum concentration can be seen between 6:00 and 10:00 a.m. (LT) and the somewhat smoothed maximum can be seen between 15:00 and 18:00 p.m. The same diurnal behavior of the ozone concentration was reported in Refs. 2 and 3. These papers pointed out that the amplitude of diurnal variation depended on season.

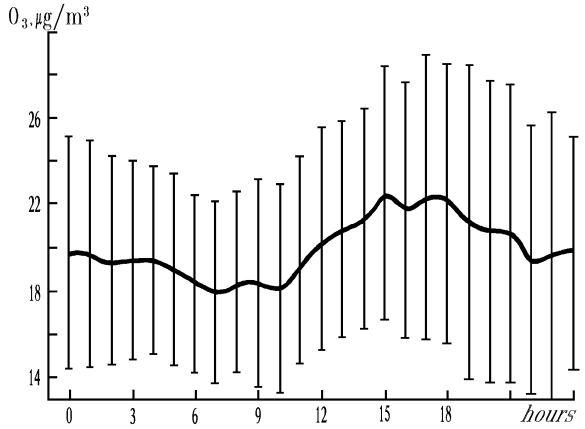


*FIG. 3. The diurnal behavior of ozone averaged over the period of many years.*

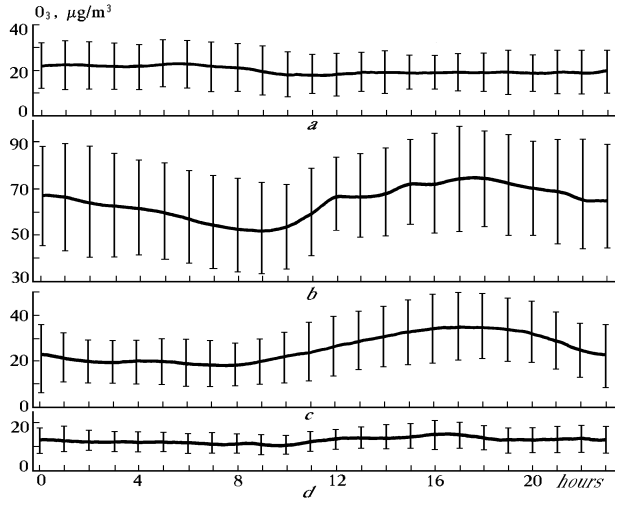


*FIG. 4. The diurnal behavior of ozone: for January (a), for April (b), for June (c), and for October (d).*

The last statement is well illustrated by Fig. 4. Thus, while in January the diurnal behavior is almost neutral and even, to some extent, reverse (a small maximum can be seen before sunrise), in April and June, when ozone is produced in the ground layer, the behavior of the ozone concentration becomes classic: it is minimum in the morning and maximum at afternoon. The behavior observed in October was close to the neutral and classic diurnal behavior. As for the diurnal variation of the amplitude over a year period, we can notice that it rises with increase in the ozone concentration. It should be noted, however, that in April over Tomsk it exceeds a daily mean maximum permissible concentration.

Returning to the anomalous diurnal variation in January, we may assume that it is due to sedimentation of ozone from the overlying layers in which its concentration is higher while its destruction on snow is minimum.[2,3] We came to this conclusion based on the results of airborne sounding of ozone and its simultaneous ground–based measurements made in the Far East[4] where we determined definitely the sedimentation of ozone at night during a cold season.

The SATOR program was accomplished in two stages and included summer and fall experiments. In the course of the summer experiment the observations were being continuously performed from June 14 to July 6. We carried out 24 complete diurnal cycles of measurements. The fall experiment was implemented by 24–hour cycles with week's intervals and day/night shifts. In the course of the fall experiment we obtained 8 complete 24–hour cycles.

In the course of the SATOR experiments, in addition to ozone concentration, the total aerosol number density was measured using an AZ–5 counter. Carbon oxide and dioxide concentrations were also measured using a GIAM–15 home–made gas analyzer. The AZ–5 photoelectric counter was used for measuring the number of particles with radius $\geq 0.2$ μm per unit volume in the range 0–300 $cm^{-3}$ with a 20% error. The GIAM–15 gas analyzers depending on their adjustment had the following specifications. When adjusting according to carbon oxide, the measurement range was 0–100 ppm with a ± 5% error, when adjusting according to carbon dioxide, it was between 0 and 1000 ppm with a ± 10% error. The AZ–5 counter was equipped with a built–in calibrator, the GIAM–15 gas analyzers were supplied with reference gas mixtures which allowed us to control the performance of the instrument in the course of a 24–hour measurement. The air was intaken in the same way as it was described for ozone.

An average daily variation of the above–mentioned components and ozone in the ground air layer for summer and fall stages of the SATOR experiment are shown in Figs. 5 and 6, respectively.

As can be seen from Fig. 5, ozone and carbon dioxide possessed reverse dependences in summer. Ozone behavior followed a conventional scheme with minimum before sunrise and in the morning and sharply pronounced maximum at afternoon. The maximum concentration of carbon dioxide was observed before sunrise and its minimum was detected at afternoon. Such a diurnal behavior of carbon dioxide is accounted for by vital activity of plants which, as is well known,[5] produce carbon dioxide at night and oxygen in the daytime. Carbon oxide concentration varied in a more complicated manner. Two small maxima can be seen in the morning and at night which are probably associated with exhausts of the motor transport. Near the observation site there was an automobile enterprise and these maxima appeared when the automobiles left and arrived at its territory. Two not very deep minima can be seen in the diurnal behavior of carbon oxide at around midnight and noon. Their appearance could also be related to the traffic when it became less heavy. The aerosol number density reveals the most obscure behavior. This could be the superposition of several processes such as aerosol formation from gases, ozone sinks through an aerosol, turbulent ascent, and transport of dust. According to the data obtained earlier[4] such a superposition of different processes took place under urban conditions.

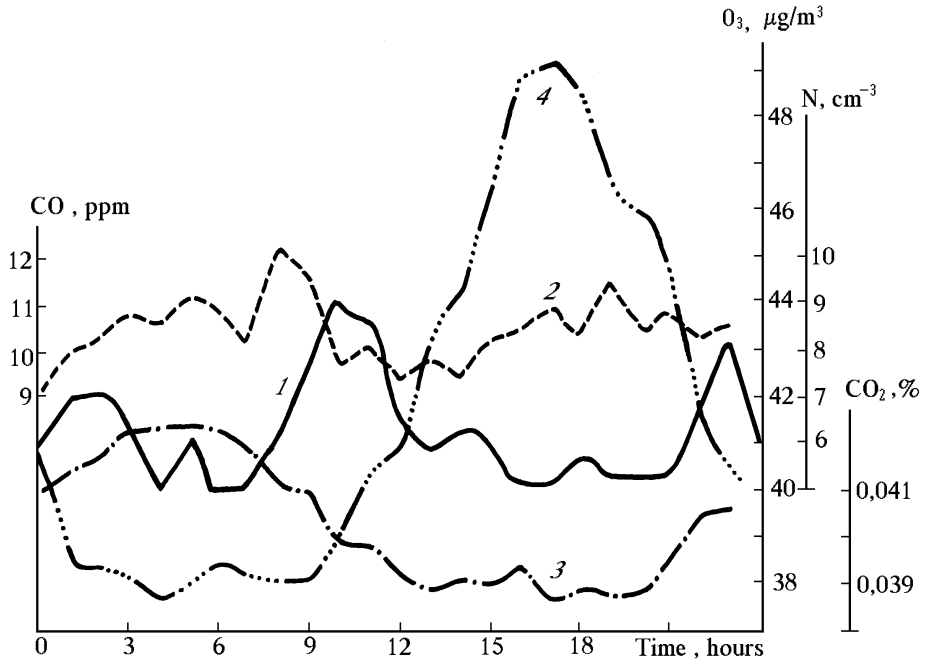


*FIG. 5. The diurnal behavior of the number densities: 1) aerosol. 2) carbon oxide, 3) carbon dioxide, and 4) ozone in summer.*

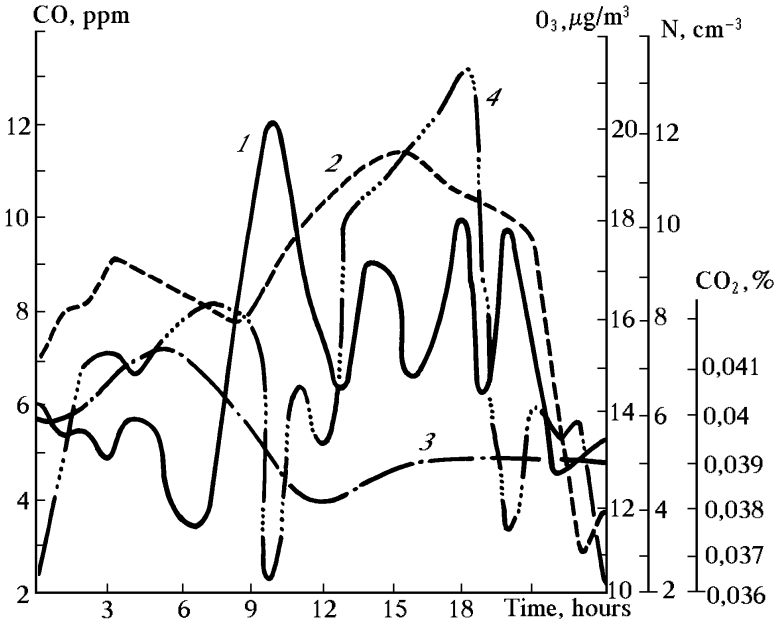


*FIG. 6. The diurnal behavior of aerosol, carbon oxide, carbon dioxide, and ozone in fall. Designations are the same as in Fig. 5.*

In the course of the fall cycle of measurements the diurnal behavior of the air components under study except for carbon dioxide, sharply changes. As can be seen from Fig. 6, there appears a secondary night maximum for ozone. The only explanation for this maximum is that the ozone sedimentates from the overlying layers of the air. The aerosol number density in its diurnal behavior reveals minima and maxima that can be explained only by duration of the measurement period when different air masses flew into the region of measurements and the aerosol was incapable of recovering in contrast to gas composition, which was recovered in one or two days.[4] The diurnal behavior of carbon oxide also changed strongly. However, this fact has not yet been explained.

To summarize, we note that the dynamics of the near–ground ozone concentration over the region of Tomsk following the general physical behavior has its own regional features, e.g., as the early onset of spring maximum and the existence of secondary night maximum in diurnal behavior. A qualitative comparison of diurnal behavior of ozone with those of the other gases and aerosol does not reveal close relationships, with the exception of carbon dioxide in summer. The industrial enterprises of Tomsk located at a

distance of several kilometers from the measurement site may have a significant impact in this case.

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