Anomalously high concentration of near-ground ozone in winter near Tomsk

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We discuss the cases of extremely high concentration of ozone (480 μg/m^3) observed at nighttime in winter near Tomsk. Analysis of such episodes, in relation to other air components, usually of the anthropogenic origin, leads to a conclusion that the episodes of such an anomalous behavior of the near-ground ozone concentration are due to the industrial emissions.

Ozone in the near-ground air is one of the most toxic admixtures, because it is harmful for both biological objects and elements of the technogenic medium. Therefore, according to the Resolution of the World Meteorological Organization, it is included into the list of six principal compounds, which should be continuously controlled in the inhabited areas.

Such a control is being done at the TOR station of IAO SB RAS near Tomsk. Full description of the TOR station is given in Ref. 1. The 3-02P ozonometer developed and constructed by the OPTEK enterprise (St. Petersburg) was used for measurements. It was regularly calibrated by means of the GS-2 ozone generator designed by the same enterprise. The ozonometer and generator are certified at D.I. Mendeleev Scientific Research Institute of Metrology when needed. The relative error of measurements with this ozonometer does not exceed 15% in the range from 5 to 1000 μg/m^3.

Monitoring of the near-ground ozone concentration (NGOC) started in September 1989 and continues up to date. The measurements are carried out near Akademgorodok every hour round-the-clock in an automated mode. The results of measurements during 10 years are summarized in Ref. 2. It was shown that the increase in the NGOC since 1990 until 1992, and the tendency of its decrease was observed since 1993 until 1999. Usually NGOC at the measurement site does not exceed 240 μg/m^3 in spring and summer, when vegetation surrounding the city has emitted great amount of gaseous organic substance leading to the appearance of natural smog.[3]

Secondary maxima exceeding the daytime ones are sometimes observed at night during the fall and winter when no ozone generation occurs.[2] Since maximum of the ozone generation is elevated over the ground surface,[4] it is reasonable to suppose that their appearance is caused by the descent of air mass from the upper layers of the atmosphere. Vertical profiles of the ozone concentration measured at different time of a day have confirmed this conclusion.[2,4]

Second possible reason for the appearance of the nighttime maxima can be transfer of air enriched with ozone from the territory of the city of Tomsk, where ozone could be generated in photochemical processes from the anthropogenic gas emissions. This hypothesis was examined by means of synoptic maps and actual wind direction (measured at the TOR station) but has not met its confirmation. However, the results of recent measurements since October 2000 forced us to return to this hypothesis. It occurred that on some nights the ozone concentration significantly exceeded the daytime maxima, and sometimes the maximum once-only MPC. Since the ozone generation essentially depends on the concentration of the ozone forming substances and the intensity of solar radiation, it is significantly weaker in cold time.[5] So, one can suppose that the increase of NGOC at night is caused by the ozone transfer from the places where conditions are more favorable for its generation. Obviously, the air over a city is such a place, because of the emissions from motor transport and from boiler houses and stove heating.

The episode of one of the most intense increases of NGOC was observed on February 10–11, 2001. As is seen in Fig. 1*a*, the increase of NGOC began at noon of local time. It was accompanied by the change of wind direction from the north to southwest one. If consider the map (Fig. 2), in which the arrangement of the city and the observation site in Akademgorodok is shown, it is well seen that at the observed wind direction the air comes to the observation site from the southern part of the city. It is also seen in Fig. 1*a* that the daytime maximum of NGOC was 3 times less intense than the nighttime one, when the ozone concentration reached 480 μg/m^3. The decrease of NGOC coincided with the change of the wind direction from southwest to the south and southeast. It is seen from the map that in this case the air is transferred across the areas outside the city territory.

According to the ideas accepted,[6] photochemical processes, in which ozone, aldehydes, and other chemical compounds are formed from methane, carbon oxide or gaseous hydrocarbons in the presence of nitrogen oxides and hydroxyl under the effect of solar light, play the key role in the NGOC change.

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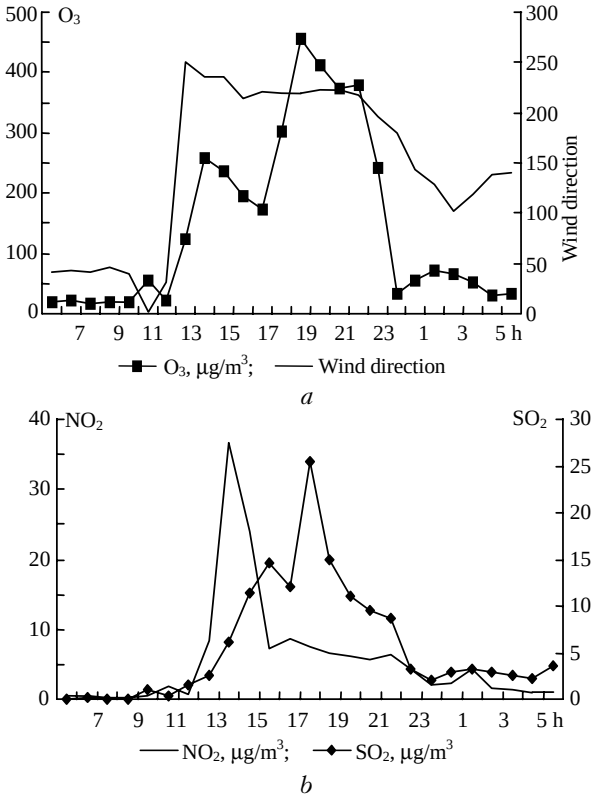

Fig. 1. Temporal behavior of the wind direction, ozone concentration, nitrogen and sulfur dioxides on February 10–11, 2001 in Tomsk Akademgorodok.

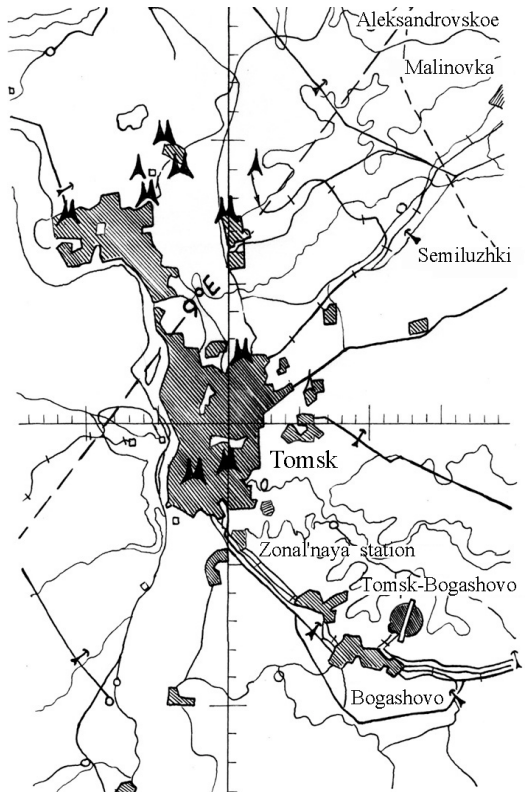

Fig. 2. Arrangement of the measurement site relatively to Tomsk.

In our case the anomalous increase of NGOC is most likely caused by the anthropogenic emission, as is seen in Fig. 1*b*, the nitrogen dioxide concentration at the very beginning of the ozone generation process increased up to 38 μg/m^3. It corresponds to the initial phase of smog formation, when the nitrogen oxide emitted from anthropogenic sources is transformed to the dioxide.[4] Then, the balance of the cycle $NO–O_3–NO_2$ is broken, because hydrocarbons are added, and the concentration of NO_2 decreases. Sulfur dioxide usually does not make great contribution to the ozone generation.[4,6] The change of the SO_2 concentration shown in Fig. 1*b* indicates that this admixture has no natural sources in the region of Tomsk. Therefore, one can conclude from the SO_2 concentration growth that the sudden change of NGOC is provoked by the anthropogenic emission, the indicator of which is sulfur dioxide.

To clarify the question on whether or not the southwest direction is the key one for the formation of smog, other cases of the ozone concentration were considered, for example, that on January 2001 (Fig. 3).

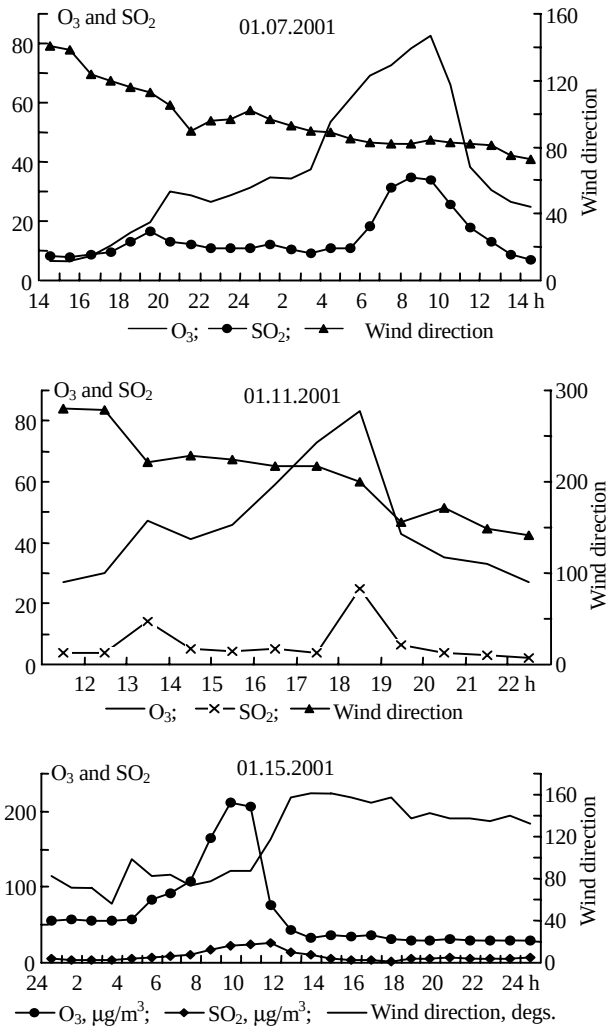

Fig. 3. Time behavior of the wind direction, ozone concentration, and sulfur dioxide on some days of January 2001.

It is seen from Fig. 3 that the increase of NGOC on January 7 occurred at east wind in the morning. No industrial objects which can emit anthropogenic ozone forming substances are situated in this direction (see the map, Fig. 2). The same situation repeated on January 15. In the third case, on January 11, the wind direction again was southwest. The increase of O_3 concentration in all cases was accompanied by the increase of SO_2, that is an obvious evidence of its anthropogenic origin in the episodes considered. It is important to emphasize that the increase of NGOC was not observed at a pronounced transfer of air from the west.

If one pays attention to the time of appearance of the maxima in O_3 concentration, it is seen that they appear in the evening at southwest transfer and in the morning at the transfer from the east. In the second case the transfer occurs along a longer trajectory if one assumes that the source of emission is the same and it is quite powerful. Otherwise it is impossible to explain the differences in the delay of occurring the NGOC maxima. This conclusion is theoretically stated in Ref. 7. The pattern of circulation in the region of Tomsk, which shows the presence of local flows in the region of Akademgorodok at the generally westward transfer, is also presented there.

Let us emphasize for the conclusion that the appearance of high ozone concentrations in the region of Tomsk is an evidence of the fact that the sources capable of forming smog of Los Angeles type have appeared in the city. So it is necessary to clarify composition and the source of emissions in making the nature protection decisions.

Acknowledgments

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