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### **Results of many years monitoring of surface ozone nearby Tomsk**

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#### ABSTRACT

The surface ozone concentration is analyzed based on the results of 10-year hourly monitoring. Many-year trends, change in the character of the seasonal behavior in some years, and peculiarities of the diurnal dynamics are revealed. The probabilities of excess over diurnally mean and one-time maximum permissible concentrations are calculated.

Keywords: ozone, surface concentration

#### 1. INTRODUCTION

In the stratosphere, ozone serves a protective function preventing arrival of hard UV radiation to the Earth's surface. In contrast, the tropospheric ozone that forms *in situ* in the atmospheric boundary layer is a substance belonging to the first class of danger. In high concentrations, it strongly inhibits vital activity of plants and diversely affects the human body. Biological and medical investigations<sup>1</sup> have shown that ozone in the troposphere is a virulent poison, which is generally toxic, mutagenic, carcinogenic, and radiomimetic (its action on blood is similar to that of ionizing radiation). In the degree of toxicity, ozone exceeds such well-known poison as prussic acid. As well as acting on a human body and vegetation, ozone also is very strong oxidizer, which attacks rubber and Indian rubber and oxidizes many metals, including even metals of the platinum group.<sup>2</sup>

Having a long lifetime in the atmosphere (from several days to several months) and intense absorption lines, the tropospheric ozone can play a significant part in the greenhouse effect. According to the estimates given in Ref. 3, its contribution exceeds 8% in total air heating due to the solar radiation absorption by greenhouse gases. Recent estimates<sup>4</sup> show that this contribution may exceed 20%.

Ozone can act on a human body in two ways: directly and indirectly. The direct effect of ozone is caused by its toxic properties. At low concentrations, its action manifests itself in irritation of mucous membrane and nasopharynx, cough, and disturbed breathing. An increase of its concentration leads to respiratory affection and disturbs the  $\alpha$ -rhythm. <sup>5,6</sup> In high concentrations, ozone causes a spasm of bronchi and pulmonary edema. Lesion of lungs has a character of respiratory stress and numerous hemorrhages are developed; affections are localized in bronchioles and at places where the conductive respiratory tract goes into respiratory sections.

Because of particular toxicity of ozone (it belongs to the first class of danger), its hygienic regulations are rather stringent in Russia:

 $MPC_{w.z}$  in working zone100 µg/m<sup>3</sup>;  $MPC_{d.m}$  in atmospheric air30 µg/m<sup>3</sup>;  $MPC_{o.t}$  in atmospheric air

(with probability of 0.01%)160  $\mu$ g/m<sup>3</sup>.

 $(MPC_{d,m})$  is the diurnally mean maximum permissible concentration of a chemical substance in air of populated areas;  $MPC_{o,t}$  is the one-time maximum permissible concentration of a substance).

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In the U.S.A., the following regulations are accepted: the threshold ozone level for atmospheric air  $-120 \ \mu g/m^3$ , the one-time maximum permissible concentration  $-240 \ \mu g/m^3$ .

In Sweden, the maximum permissible concentration for living and non-industrial quarters is 100  $\mu$ g/m<sup>3</sup>, for atmospheric air the one-time permissible concentration is 120  $\mu$ g/m<sup>3</sup>, and the one-time maximum concentration is 200  $\mu$ g/m<sup>3</sup>.

Since ozone does not smell strong, a problem arises how to identify a cause of intoxication. The symptoms of the ozone intoxication are summarized in Table 1.

The ozone concentration threshold, causing a fatal outcome, is yet to be determined. A short stay (0.5 hour) of a man at the ozone concentration as high as 50 mg/m<sup>3</sup> was mentioned. At the same time, a lot of cases of appearance of the eye mucosa irritation, headache, giddiness, poor eyesight, difficulty in breathing, retrosternal pain, and significant decrease of the partial oxygen pressure in arterial blood just at the ozone concentration of only 200  $\mu$ g/m<sup>3</sup> were observed repeatedly.

Such a wide variety of possible negative consequences of increase of the tropospheric ozone concentration for both human health and the environment calls for special attention to the tendencies of ozone change in the surface air. Strangely enough, the spatiotemporal dynamics of the tropospheric ozone is far less studied than that of the stratospheric one. This fact has several explanations.

Concentration, µg/m3	Duration of inhalation, h	Effect
4-15	-	Threshold of smell perception in pure air
≥ 120	8	Degradation of working efficiency at high load
≥ 160	24	Degradation of pulmonary function
≥ 200	8	Cough, hoarseness, tickle in a throat
≥ 240	3	Loss of sensitivity to other toxicants and allergens
≥ 400	8	Inflammation of lower respiratory tracts, possible pulmonary edema

Table 1: Symptoms of ozone intoxication (Ref.7)

First, it has been believed for a long time that the level of the ozone concentration in the troposphere is low. Therefore, only few stations conducted the ozone monitoring. And only in the last three decades, when the danger of the increasing tropospheric ozone concentration became obvious, the network of observational sites began to grow extensively.

Second, the satellite monitoring system is ill-adapted to monitoring of tropospheric ozone, since it is aimed to monitoring of total column ozone, in which the share of tropospheric ozone is insignificant.

Third, for a long time the scientists held to the idea that the major portion of tropospheric ozone is produced in the stratosphere and then transported into the surface layer. Consequently, the subject of study should be the ozone transport through tropopause.

Fourth, it was believed that the spatial and temporal variability of ozone in the troposphere is caused mostly by dynamic processes, while photochemical ones play a minor part.

Nevertheless, the analysis of few available long-term measurement series on the surface ozone concentration (SOC) shows that there is an unambiguous tendency to its increase in the last decades. According to the data of chemical measurements in Paris for the period from 1876 to 1986 (110 years), the mean ozone concentration has doubled – from 10 to 20 ppbv (Ref. 8). Megie et al. <sup>9</sup> determined the fivefold increase of the ozone concentration in the background regions of Europe for 100 years. The detailed review of this problem can be found in Ref. 10. The beginning of the ozone increase in the troposphere is dated back to 1895. Based on numerous measurements, the EUROTRAC commission concluded that the current growth of ozone in the troposphere is about 1-3% a year, and it varies depending on the geography. In the commission's opinion, the tropospheric ozone will continue to grow with the rate of 0.25% a year. This prognosis, like many others, forces us to analyze more carefully the regularities of the ozone formation and destruction in the troposphere.

According to the current ideas, <sup>11</sup> the key role in the ozone change, caused by photochemical processes, is played by methane, carbon oxide, nitrogen oxides, and hydrocarbons. The increase of their concentration in the troposphere, especially, due to human activity, and their reactions with hydroxyl radicals are most significant factors determining the ozone formation and destruction in the lower atmosphere and the tendency to ozone increase in the last decades.

#### 2. RESULTS OF TEN-YEAR MONITORING OF SURFACE OZONE NEAR TOMSK

Measurements of the ozone concentration in the surface air near Tomsk (Akademgorodok) were started by the Laboratory of Optical Weather of the Institute of Atmospheric Optics SB RAS in September 1989 as a part of the TOR (Tropospheric Ozone Research) Project of the EUROTRAC Program. It was thought that Tomsk is a background station relative to Europe, where smog situations often occur in the urban air, producing high ozone concentrations.

The measurements were conducted with the use of 3-02P ozonometers designed and made at the OPTEK enterprise (St. Petersburg). These ozonometers were calibrated with the help of a GS-2 oscillator made at the same enterprise. As needed, the ozonometers and oscillator were checked at the D.I. Mendeleev Institute. Continuous round-the-clock measurements of the ozone concentration were performed in the regime of hourly readings.

Ozone observations are now continued within the TOR-2 Project (EUROTRAC-2 Program). The Laboratory of Optical Weather became the member of this program after two-year many-stage competitive selection.

In this paper, we present the results of ten-year ozone observations and analysis of the surface ozone concentration variability.

First we consider the many-year behavior of the ozone concentration in the region of Tomsk for the entire period of observations. Figure 1 presents the annually mean ozone concentration in the surface air for the period from 1990 to 1999. This figure also shows linear trends of the ozone concentration for this period. It should be emphasized that since each reading has the same weight in monitoring, the data were not pre-averaged or filtered.

It is seen from Fig. 1 that in the period from 1990 to 1992 the ozone concentration increased with the rate up to  $10 \ \mu g/m^3$  a year. Since 1993, the ozone content in the surface air began to decrease with the rate of 3–4  $\mu g/m^3$  a year and reached its minimum in 1999. It also follows from the figure that in the periods 1991–1994 and 1996–1997 the annually mean ozone concentrations exceeded the diurnally mean maximum permissible concentrations. Since ozone is an effective indicator of photochemical processes,<sup>1</sup> this fact demonstrates their high activity in the atmosphere of Tomsk.



Figure. 1: Many-year behavior of ozone concentration in the region of Tomsk.

The intra-annual variability of the ozone concentration also turned to be quite unstable. It is believed that the peak of the ozone concentration must be observed in spring. However, the data obtained in Tomsk and in other regions show that this rule is sometimes violated. What's more, the mechanism of the spring ozone peak appearance in the surface atmospheric layer is still unclear.

The intra-annual variability of surface ozone as derived from the monthly mean data is shown in Fig. 2 for the entire period of observations. It is seen that in most cases the peak of the ozone concentration is observed in spring, although in some years purely summer peaks occur as, for example, in 1995, 1996, and 1998.

According to current ideas, the maximum concentration of surface ozone is connected with the spring income of phytoncides due to plant florescence. In the years mentioned above, spring was long, and plants came to life very late. Probably, this is the cause of the late concentration peaks.



Figure 2: Seasonal behavior of ozone concentration near Tomsk in different years.



Figure 3: Diurnal behavior of ozone concentration (1) and total solar radiation (2) in Tomsk for central months of seasons, 1996.

The data on the diurnal behavior of ozone are important for understanding of its dynamics. These data are shown in Fig. 3. Here we have chosen 1996 year as the most characteristic one.

It is seen from Fig. 3 that the diurnal behavior of ozone, in view of its photochemical nature, generally represents the income of total solar radiation to the Earth's surface. This is also confirmed by the fact that the concentration peak lags behind the peak of the incoming radiation. As follows from the figure, the diurnal behavior is pronounced in all seasons. However, in October it has one more feature, namely, a secondary peak at night time.

The appearance of the night secondary peak contradicts the photochemical theory of its formation. Therefore, we have analyzed the entire array of measurements. It turns out that this peak is a characteristic not only of October, but of the fall season as a whole (Fig. 4).



Figure 4: Diurnal behavior of ozone concentration (curve 1) and total solar radiation (2) in Tomsk for the period from August 1997 to January 1998.

It follows from Fig. 4 that the process of night peak formation begins in September and terminates in January. In our opinion, this is caused by the following reasons. The active period of vegetation comes to end in September. As a result, hydrocarbons, giving rise to ozone in the surface layer, cease to enter the atmosphere. The level of ozone generation lifts up to 200–400 m. This fact was confirmed by the data of airborne sensing in the previous years near Tomsk and in the 90's near Novosibirsk. At night, when the turbulent exchange weakens, ozone deposits from the altitude of 200–400 m to the surface.

To confirm the existence of the secondary peak of the ozone concentration in the ground atmospheric layer, we present Fig. 5, which shows the vertical profiles of the ozone distribution averaged for the warm and cold seasons in the atmospheric boundary layer.



Figure 5: Vertical (relative to the surface value) distribution of ozone concentration in summer and fall-winter periods above Tomsk.

As is seen from the figure, in summer the maximum of ozone generation is in the top of the boundary layer, while in the winter-fall season it is located much lower. Therefore, in summer at usual sedimentation rate of 1-2 cm/s and short night periods, the layers with the increased ozone concentration simply have no time to reach the Earth's surface. In the winter-fall period, when the altitude of the ozone concentration maximum is low, several hours of the decreased air turbulence are sufficient for the layers with high ozone concentration to descent to the surface layer.

For some applications the data on the diurnal amplitude of the ozone concentration variations are needed. They can be used for probability forecasting, estimating the danger of the ozone effect on biota, etc. (Table 2).

Month	Year									
	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
January	4.4		3.6	3.6	5.2	4.9	2.4	2.3	4.8	4.8
February	6.1	5.9	7.6	12.4	7.5	8.9	10.9	8.3	5.8	17.8
March	9.5	34.5	11.1	21.5	14.3	19.2	25.5	14.7	13.5	10.9
April	13.4	25.1	10.8	22.5	16.6	14.7	15.7	20.2	9.5	7.8
May	16.7	27.5	68.1	17.4	31.2	18.4	22.8	26.3	17.6	21.3
June	12.2	20.8	37.3	39.2	44.5	23.9	35.2	39.8	24.9	17.1
July	-	18.0	44.3	54.9	44.8	40.9	52.4	38.8	26.3	32.8
August	-		47.0	50.8	29.8	28.0	39.6	20.9	25.9	20.0
September		15.7	30.6	12.0	12.9	16.2	12.8	16.5	10.1	7.9
October	4.4	4.0	22.9	7.3	5.6	7.4	9.5	11.4	4.4	7.2
November	7.3	3.6	11.0	7.1	4.2	4.6	4.9	5.5	5.1	4.9
December		2.8	4.0	8.0	2.9	3.2	3.4	5.3	2.7	2.1

Table 2: Monthly mean diurnal amplitudes of variation of the ozone concentration (in  $\mu g/m^3/day$ )

The data of Table 2 represent two tendencies in the behavior of the surface ozone concentration: inter- and intra-annual variability. Thus, the highest monthly average diurnal amplitudes are observed in summer months in the years with the highest ozone concentration. The minimum amplitudes are observed in winter months of the years with the low annually mean ozone concentration.

Let us estimate the dynamics of the ozone concentration from the ecological point of view (Table 3).

It is seen from the data presented in Table 3 that in the Tomsk region the diurnally mean MPC was exceeded up to five times and the one-time MPC was exceeded in 0.2% of cases.

Year	MPC <sub>d.m</sub>	2 MPC <sub>d.m</sub>	3 MPC <sub>d.m</sub>	4 MPC <sub>d.m</sub>	5 MPC <sub>d.m</sub>	MPC <sub>o.t</sub>
1990	17.8	0.7	_			-
1991	46.6	27.6	9.2	0.6	_	_
1992	51.6	18.7	9.0	3.5	2.1	1.77
1993	67.8	22.3	4.2	-	-	0.13
1994	48.6	13.7	1.1	0.3	-	0.04
1995	28.8	0.6		-	-	0.01
1996	45.1	11.6	2.0	0.3	-	0.05
1997	47.2	7.1	0.6	-	-	0.12
1998	22.3	0.8	_	-	-	-
1999	10.8	-	-	-	_	-
On the average	38.6	11.4	2.6	0.5	0.2	0.21

Table 3: Repetition (%) of excess over the diurnally mean and one-time MPC's in Tomsk

For the last two years the situation became much better: the one-time MPC was not exceeded at all, and the diurnally mean MPC was exceeded only slightly (no more than one MPC). It is now hard to tell whether this is a result of natural processes or nature-protective activity.

The excesses over the MPC are distributed nonuniformly in time, as can be judged from Fig. 6. It is seen that there are periods, when the diurnally mean MPC is always exceeded and, conversely, when it is not exceeded for a long time. This is connected with seasonal character of ozone generation in the atmosphere. In the fall–winter period, much less ozone-forming substances come to the atmosphere and the income of solar radiation, under exposure to which ozone is formed, is much less too. Therefore, the ozone concentration in the surface layer in this period lowers markedly.



Figure 6: Monthly mean ozone concentration in Tomsk in 1990–1999.

As the snow cover melts and the intensity of solar radiation increases, the underlying surface and vegetation begin steady generation of the ozone-forming substances. Just in these periods, the MPC is exceeded, as a rule.

Thus, in the considered period the surface ozone concentration in the region of Tomsk widely varied. In the period from 1990 to 1992 it increased. Between 1993 and 1999 it significantly decreased. Over the course of a year, the concentration peak moved from spring to summer.

The annual behavior of the ozone concentration also has some features, namely, the secondary night peak in the ozone concentration in the fall–winter period. This peak is caused by air deposition from the upper layer (400–500 m), where the major portion of ozone is generated.

#### 3. ANOMALOUSLY HIGH CONCENTRATION OF SURFACE OZONE IN WINTER NEAR TOMSK

Secondary maxima exceeding the daytime ones are sometimes observed at night during the fall and winter when no ozone generation occurs.<sup>12</sup> Since maximum of the ozone generation is elevated over the ground surface,<sup>13</sup> 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.<sup>12,4</sup>

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.<sup>14</sup> So, one can suppose that the increase of SOC 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.



Figure 7: Temporal behavior of the wind direction, ozone concentration, nitrogen and sulfur dioxides on February 10–11, 2001 in Tomsk Akademgorodok.

The episode of one of the most intense increases of SOC was observed on February 10–11, 2001. As is seen in Fig. 7*a*, the increase of SOC 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. 8), 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. 7*a* that the daytime maximum of SOC was 3 times less intense than the nighttime one, when the ozone concentration reached 480  $\mu$ g/m<sup>3</sup>. The decrease of SOC 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.



Figure 8: Arrangement of the measurement site relatively to Tomsk.

According to the ideas accepted,<sup>15</sup> 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 SOC change.

In our case the anomalous increase of SOC is most likely caused by the anthropogenic emission, as is seen in Fig. 7*b*, the nitrogen dioxide concentration at the very beginning of the ozone generation process increased up to 38  $\mu$ g/m<sup>3</sup>. It corresponds to the initial phase of smog formation, when the nitrogen oxide emitted from anthropogenic sources is transformed to the dioxide.<sup>13</sup> Then, the balance of the cycle NO–O<sub>3</sub>–NO<sub>2</sub> is broken, because hydrocarbons are added, and the concentration of NO<sub>2</sub> decreases. Sulfur dioxide usually does not make great contribution to the ozone generation.<sup>13.6</sup> The change of the SO<sub>2</sub> concentration shown in Fig. 7*b* indicates that this admixture has no natural sources in the region of Tomsk. Therefore, one can conclude from the SO<sub>2</sub> concentration growth that the sudden change of SOC 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. 9).

It is seen from Fig. 9 that the increase of SOC 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. 8). 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<sub>2</sub>, that is an obvious evidence of its anthropogenic origin in the episodes considered. It is important to emphasize that the increase of SOC was not observed at a pronounced transfer of air from the west.



Figure 9. Time behavior of the wind direction, ozone concentration, and sulfur dioxide on some days of January 2001.

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 SOC maxima. This conclusion is theoretically stated in Ref. 16. 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.

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