

## ON THE INTERNATIONAL AND RUSSIAN HYGIENIC REGULATIONS FOR OZONE CONTENT IN THE SURFACE LAYER

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**Abstract.** The Russian and international standards for ozone content in the surface layer are presented. It is shown that the standard for maximal mean daily ozone concentration in the surface layer currently in force in the Russian Federation is unjustified. This standard is lower than the background values in most of years even in the rural sites, where ozone sources in the surface layer are natural, while the maximal one-time ozone concentrations do not approach the one-time maximum concentration limit at all. It is necessary to abrogate or re-estimate its value.

### 1. Introduction

Ozone is the most important photochemical oxidant in the troposphere. According to the common view, ozone sources in the surface layer are turbulent diffusion from the upper troposphere layers and photochemical generation in the surface layer. The hemispheric background concentrations of tropospheric ozone vary in time and space but can reach average levels of around  $80\mu\text{g}/\text{m}^3$ . The highest and most dangerous ozone concentrations in the surface layer are formed by photochemical reactions in presence of precursor pollutants such as  $\text{NO}_x$  and volatile organic compounds. Ozone concentrations can reach unhealthy levels when the weather is hot and sunny with relatively light winds.

Even at relatively low levels, ozone may cause inflammation and irritation of the respiratory tract, particularly during physical activity. The resulting symptoms can include breathing difficulty, coughing, and throat irritation. Breathing ozone can affect lung function and worsen asthma attacks. Ozone can increase the susceptibility of lungs to infections, allergens, and other air pollutants. Medical studies have shown that ozone damages lung tissue and complete recovery may take several days after exposure has ended. The repeated exposure to ozone pollution for several months may cause permanent lung damage. Anyone who spends time outdoors in summer is at risk, particularly children and other people who are active outdoors.

Ozone damages the leaves of trees and other plants, ruining the appearance of cities, national parks, and recreation areas. Ozone reduces crop and forest yields and increases plant vulnerability to disease, pests, and harsh weather.

The World Health Organization (WHO) includes the ground-level ozone in the list of five most important components of atmospheric air which is recommended for the constant control. It is recommended that the air quality guideline for ozone is set at the level of  $100\mu\text{g}/\text{m}^3$  for daily maximum 8-hour mean (WHO Air Quality Guidelines - Global Update 2005 (Report on a Working Group meeting, Bonn, Germany, 18-20 October 2005).

The concentration up to  $100\mu\text{g}/\text{m}^3$  will provide adequate protection of public health, though some health effects may occur below this level (an estimated 1-2% increase in daily mortality; likelihood that ambient ozone is a marker for related oxidants).

The 8-hour interim target-1 level has been set at  $160\mu\text{g}/\text{m}^3$ . Based on time-series evidence, the number of attributable deaths brought forward can be estimated at 3-5% for daily exposures above the estimated background.

At concentrations exceeding  $240\mu\text{g}/\text{m}^3$ , important health effects are likely. This is based on findings from a large number of clinical inhalation and field studies. Both healthy adults and asthmatics would experience significant reductions in lung function as well as airway inflammation that would cause symptoms and alter performance. There are additional concerns about increased respiratory morbidity in children. Based on time-series evidence, the number of attributable deaths brought forward can be estimated at 5-9% for daily exposures above the estimated background.

\*Deaths attributable to ozone concentrations above the estimated baseline of  $70\mu\text{g}/\text{m}^3$ . Based on the range of 0.3 to 0.5% increase in daily mortality for  $10\mu\text{g}/\text{m}^3$  8-hour ozone

### 2. Overview of standards

In order to protect people and nature, the EU has adopted standards for the concentrations of substances in the outside air (i.e. air quality). Table 1 provides an overview of the main standards for ozone content in the surface layer.

**EU standard for public health**

The new European standard for exposure of the population to high ozone concentrations provides for a target value of  $120\mu\text{g}/\text{m}^3$  for the highest 8-hour average ozone concentration a day. From 2010 onwards, this target value must not be exceeded by more than 25 days a calendar year on average over three years. The average is based on the year in question and the two previous years.

**Table 1.** European air quality standards for ozone content in the surface layer (Directive 2002/3/EC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient)

Substance	Targeting	Standard	Level	Status
Ozone (O <sub>3</sub> )	humans	highest 8-hour average	110 $\mu\text{g}/\text{m}^3$	threshold value; applies until 09-09-2003
	humans	highest progressive 8-hour average a day; exceedance not permitted on more than 25 days a year.	120 $\mu\text{g}/\text{m}^3$	desired quality standard; with effect from 09-09-2003
	humans	hourly average	180 $\mu\text{g}/\text{m}^3$	information threshold; with effect from 01-03-2001
	humans	hourly average observed during three successive hours in an area of at least 100 km <sup>2</sup> .	240 $\mu\text{g}/\text{m}^3$	alarm threshold; with effect from 01-03-2001
	nature	24-hour average	65 $\mu\text{g}/\text{m}^3$	threshold value; applies until 09-09-2003
	nature	AOT40	18 000 $\mu\text{g}/\text{m}^3\cdot\text{hour}$	desired quality standard; with effect from 09-09-2003

The highest 8-hour average for the ozone concentration on one day is determined on the basis of the progressive averages for periods of eight hours, with these periods being calculated using hourly values and updated every hour. Each average for eight hours calculated in this way applies for the day on which the period of eight hours ends, in other words the first calculation period for a given day starts at 17.00 hours on the previous day and ends at 01.00 hours on that day, and the last calculation period is from 16.00 hours to 24.00 hours.

**EU standard for nature**

The AOT40 (Accumulated Ozone exposure over a Threshold of 40 ppb) is a unit that is relevant for nature for expressing ozone concentrations. The AOT40 takes into account both the level of excess of the threshold value of  $80\mu\text{g}/\text{m}^3$  (= 40 ppb) and the duration of the excess. This standard is calculated only during the three summer months May - July, from 08.00 to 20:00 (Central European Time). The target value set for the protection of vegetation is 18000 ( $\mu\text{g}/\text{m}^3\cdot\text{hour}$ ), averaged out over 5 years. The calculation of the average is based on the year in question and the four previous years. A long-term objective of 6,000 ( $\mu\text{g}/\text{m}^3\cdot\text{hour}$ ) has been adopted.

The EU standards health protection threshold of  $110\mu\text{g}/\text{m}^3 \approx 55$  ppb as fixed 8 hour mean (0:00-8:00, 8:00-16:00, 16:00-24:00, and 12:00-20:00). The mean eight-hour value of concentration in the countries of the Western Europe and North America is the main characteristic of the ground-level ozone. This standard is intended to be more protective of the health of children and adults who play and work outdoors in summer.

<sup>\*</sup> 1 part per billion (ppb) is one part, by volume, in one thousand million, or 1 in 10<sup>9</sup>. 1 ppb of ozone is equivalent to  $2.00\mu\text{g}/\text{m}^3$  at 20°C and 1,013 millibars.

The Air Quality Standard for ozone in the United Kingdom of 50 ppb as a running 8-hour average. The UK standard is similar to the EU standard, although as the UK uses a moving average and a lower threshold value they are not directly comparable.

The current and proposed air US and Canada standards for ozone are presented in tables 2 and 3.

**Table 2.** Summary of US Current and Proposed Standards for PM and Ozone (Source: EPA - Final Revisions to the Ozone and PM Air Quality Standards, August, 1999).

Pollutant	Current Primary Standards		Proposed Standards (revised)	
Ozone	1-Hour 120 ppb	To attain this standard, the daily maximum 1-hour average concentration measured by a continuous ambient air monitor must not exceed 120 ppb more than once per year, averaged over 3 consecutive years.	8-Hour 80 ppb	To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average of continuous ambient air monitoring data over each year must not exceed 80 ppb

Areas were to be designated under the new standard in the year 2000, and State Implementation Plans were to be due in 2003. Areas would have ten years from designation to attain the standard, meaning 2010 would serve as the attainment date.

**Table 3.** Ozone Standards in Canada (Source: Environment Canada, National Ambient Air Quality Standards on PM and Ozone, 1997.)

Pollutant	Averaging Time	Permissible Pollutant Concentrations ( $\mu\text{g}/\text{m}^3$ )		
		Acceptable Level	Canadian Objectives	
			Newfoundland	British Columbia
Ozone	1-Hour	82	82	82
	8-Hour	—	—	—

In Russia ozone is included in the group of the most dangerous chemical agents according to the hygienic and sanitary standards which were approved by the State Standard of Russia and Ministry of Health of the Russian Federation

[1, 2].

At present in Russia the 2 standards of the maximum concentration limits for ozone content in the surface layer are established. The first standard is the one-time maximum (average for 20-30 minute) concentration limit which is  $160\mu\text{g}/\text{m}^3$  or about 80 ppb. In Russia (USSR) the 20-30 minute time interval of measurement was established when the ozone content was determined by chemical method (by absorption) and to a great extent manually. This standard is kept till now in spite of the fact that modern techniques of ozone determination in the air can determine ozone concentration automatically and more often.

**Table 4.** Maximum concentration limits for ozone content in the surface layer in Russia [1, 2]

Set by	Description	Criteria	Value
Russia			
GOST 12.1.005–88. “Air of working area. General hygiene and sanitary requirements”	Protection of health of workers	one-time maximum	$100\mu\text{g}/\text{m}^3 \approx 50\text{ ppb}$
“Maximum concentration limits of air pollutant in atmosphere air of populated area” GN 2.1.6.1338-03	Protection of population health	one-time maximum 24 hour average	$160\mu\text{g}/\text{m}^3 \approx 80\text{ ppb}$ $30\mu\text{g}/\text{m}^3 \approx 15\text{ ppb}$

According to our estimations, the difference between the mean hourly and the mean for 30 minute interval ozone concentrations are only several ppb (for example, the difference for Lovozero is less than 1 ppb). Hence, the one-time maximum concentration limit is close to mean hour standard of air quality, which was approved by the EU (see table 1).

The second standard is the maximal mean daily concentration limits, which is  $30\mu\text{g}/\text{m}^3$  or about 15 ppb. The mean daily ozone concentrations abroad are not limited. It may be caused by the following fact. The highest concentrations of ozone in the surface layer occur in the daytime and it is caused by Intensive reaction between oxides of nitrogen (NOx) and volatile organic compounds (VOC) in presence of the sunlight. However, ozone concentrations decrease during the night as the decomposition reaction of ozone occurs with the same NOx and VOC. As a result the mean daily ozone concentration can appear to be little and not revealing the fact of excess by ozone the one-time maximum concentration limits in the afternoon.

Both indices are equivalent and the air is considered polluted if any of these indices is exceeded.

There are no standards for vegetation in Russia similar to EU.

### 3. Results and discussion

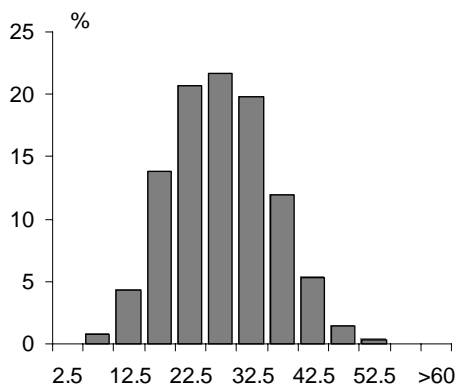
In Russia the long-period and regular measurements have been implemented by divisions of Federal Service for Hydrometeorology and Environmental Monitoring in seven federal centers and the organizations of the Russian Academy of Science in Moscow, Tomsk, Ulan-Ude, Kislovodsk and in Lovozero (Murmansk Oblast) and some other regions.

The results of ozone measurement show that there were cases of exceeding by ozone of the one-time maximum concentration limits. The episodes of increased ozone concentration in the surface layer occurred on the day with a maximal air temperature  $>28^\circ\text{C}$  and an average wind speed  $<3\text{ ms}^{-1}$ . However, as a rule such episodes are observed less than 10 times in the course of year and not every year. In some region (for example, in the Northwest Federal District) there was not any case of exceeding by ozone of the one-time maximum concentration limits at all [3].

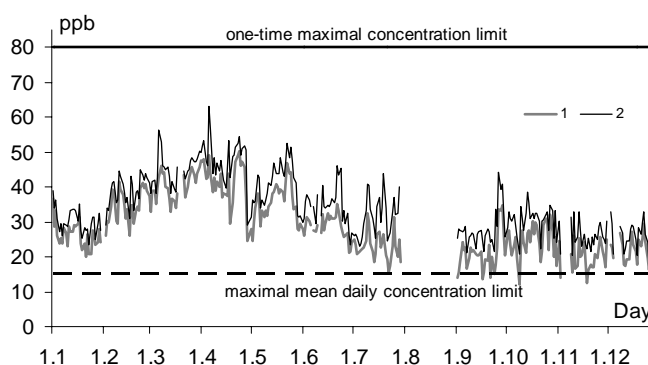
At the same time the state of affairs with the mean daily ozone concentration limit is absolutely different. In Moscow the mean daily ozone concentration exceeds the maximum concentration limit about 50% of days in the course of year. The similar index takes place in Novosibirsk also. In Lovozero (rural site) the mean daily ozone

concentrations exceed the maximum concentration limit for about 95 % of days in the course of year while the maximal one-time ozone concentrations do not approach the maximum one-time concentration limit (figure 1 and 2).

The results of ecological monitoring of ground-level ozone are reciprocally contradictory. For example, in Lovozero we can indicate that the ozone concentration in the surface layer does not exceed the maximum concentration limits, if the one-time maximum concentration limits are used as the main air quality standard. The standards of the WHO and EU are being kept also. That is the ground-level ozone is not a dangerous pollutant of atmosphere air in the region. At the same time here the mean daily maximum ozone concentration limit is exceeded during the most part of the year. It is obvious that in this case we must alert the people to undertake the measures for population protection practically every day.



**Fig. 1** Percentage distribution of mean daily ozone concentrations in Lovozero (1999-2005)



**Fig. 2** Mean daily (1) and maximal one-time ozone concentration (2) in Lovozero, 2005

In much the same the sanitation service demands the accurate observance of requirements for the ozone content in the air of a work area, but it ignores completely the cases of the practically every day exceeding by ozone concentration the mean daily maximum concentration limit.

The contradictory result is caused by non-coordination of the national standards.

It is important that the exceeding of the maximal concentration limits occurs in the rural sites, where the ozone sources in the surface layer are natural. This fact indicates that national standard for the ozone content in the surface layer, which is being calculated on the basis of mean daily values, had been proved insufficiently as the values of the maximum concentration limit must exceed the natural background.

There is the necessity of the abrogation or numeric revision of value of the mean daily maximal concentration limits taking into account the international standards and the WHO recommendations. The decision of this problem is the barest necessity as the ozone is a chemical agent of the greatest hazard rating.

#### 4. Conclusions

1. The cases of exceeding of the one-time maximum concentration limits of ozone in the surface layer ( $160\mu\text{g}/\text{m}^3$ ) occur in the territory of the Russian Federation. For example, these episodes occurred in the Central Federal District (including of Moscow) and the West Siberian Federal District. The duration of the periods with increased ozone concentrations is several days. However such episodes are not observed every year and everywhere.
2. The cases of exceeding of the mean daily maximum concentration limit of ozone ( $30\mu\text{g}/\text{m}^3$ ) occur routinely and everywhere. The number of these cases in most regions (including rural sites) exceeded 300 during of the year.
3. The results of long-term ground-level ozone measurement in the rural sites prove the necessity of addressing the Ministry of Health of the Russian Federation with the purpose of revision of the present maximum concentration limits of ozone in the surface layer.

**Acknowledgments.** This study was supported by RFBR, grants No 05-05-64271 and No 06-05- 64427

#### References

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