Tropospheric ozone as a risk factor for crop production in central regions of Russia

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Abstract. Surface ozone is considered as a risk factor for crop production in the territory of central Russia. The known mechanisms of the effect of ozone on plants are given, and the levels of ozone in the surface atmosphere that are dangerous for various groups of plants are discussed. The data of long-term monitoring of tropospheric ozone in central Russia (Vyatskiye Polyany town) are given, which indicate that due to the ongoing climate change and the increase in atmospheric pollution with nitrogen oxides, volatile hydrocarbons, carbon monoxide, even in central Russia with a moderate non-hot climate there is a significant increase in the ozone content of the surface atmosphere. Moreover, the doses of exposure to ground-level ozone, which can be exposed to plants in central Russia, are comparable and even exceed the levels considered safe.

1 Introduction

Molecular ozone is a very active chemical oxidizing agent that adversely affects living organisms and vegetation, contributes to the destruction and degradation of materials. In connection with the ongoing climatic changes and the growth of atmospheric pollution with nitrogen oxides, volatile hydrocarbons, carbon monoxide gas, which are ozone predictors, an increase in ozone concentrations in the surface atmosphere is observed worldwide \cite{1,2}. Ozone is formed under the action of solar radiation in the presence of predictors, and the intensity of formation increases with increasing temperature and intensity of solar radiation \cite{3,4}. The growth of ozone in the surface atmosphere significantly increases the risks to both human health and the entire biosphere of the surrounding person. Due to the climatic features and the specificity of the development of industry and transport, the problem of tropospheric ozone was first encountered 60 years ago by the United States and the countries of southern Europe. In these countries, much attention was paid to studying the effect of elevated concentrations of ozone in the surface atmosphere both on human health and on crop losses in agriculture. In connection with the recent climatic changes observed and the dramatic development of transport, similar problems become relevant for Russia. In particular, we should expect comparable yield losses due to the fault of ozone and in

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Russia. This paper discusses the mechanisms of ozone influence on plants, discusses levels of ozone in the surface atmosphere that are dangerous for different groups of plants, and provides monitoring data on tropospheric ozone in central regions of Russia. The latter indicate that the achievement of high yields of this problem should not be overlooked by agricultural specialists.

2 Mechanisms of the effect of ozone on plants

The negative effect of ozone on vegetation is a long-established fact [5–9]. An increase in ozone concentration can have both direct [7,8] and indirect [10] effects on land plants. The following threshold ozone concentrations for vegetation are given in [11]: 59 μg/m³ for 4-hour exposure, 40 μg/m³ for 24-hour exposure and 400 μg/m³ for 1-hour exposure. Such doses of ozone lead to the death of foliage. The primary effect is due to the sorption of ozone and its chemical interaction with plant material. The consequences of this interaction are discoloration of the affected area and its drying [5,8]. The phytotoxic effect of ozone manifests itself immediately after contact of these gases with vegetation (acute damage). A change in the color of the leaves and needles is a manifestation of lethal cell damage that leads to a loss of the assimilative activity of the plant material. In case of damage to the leaf area of the plant and reduction of the assimilation surface as a result, the death of the plant is also possible.

In clean air, the background equilibrium concentration of ozone in the surface layer of the atmosphere during the summer months at mid-latitudes does not exceed 40-80 μg/m³. These concentrations are harmless to animals and, as a rule, with a short period of exposure do not cause appreciable disturbances in plant cells, mainly due to the presence of antioxidant systems developed during the course of evolution. In the air with a high content of primary pollutants - ozone precursors, the concentration of this gas is often several times higher than the natural background concentration. Often, downwind from industrial centers, big cities and highways, ozone concentration reaches 400 μg/m³ or more. Plant defense systems are not able to neutralize the action of such high concentrations of the oxidizing agent. For plants, the ozone concentration of 80 μg/m³ is considered to be dangerous and can lead to a decrease in productivity and irreversible damage to the leaves with prolonged exposure. Ozone first affects plants at the molecular level. The primary object of its impact is the stomata of leaves and membranes [5]. Ozone contributes to the closure of stomata, but the degree of exposure strongly depends on the magnitude of the background ozone concentration observed before the onset of intensive exposure. The stomata of plants grown in filtered air, when exposed to significant concentrations of ozone, closes at a higher rate.

The first histological changes, which can be observed visually, occur in chloroplasts, which, after a short time, undergo granulation, rupture and acquire a light green color. First of all, the stroma is affected; its granulation may be associated with changes in the composition of ions in chloroplasts or with impaired membrane permeability associated with the action of ozone. The chloroplast membranes are destroyed, chlorophyll is dispersed in the cytoplasm, the cell wall of the cell is damaged and plasmolysis of the cell occurs [5].

Ozone has a very high reactivity, and theoretically it can be expected that it is completely consumed as a result of the reaction with the first molecules with which it comes into contact in the cell membrane and cell membrane. However, in reality, ozone has significant effects on metabolic processes, such as photosynthesis [5].

The rupture of the cell membranes leads to a sharp change in the normal metabolic processes, causing an increase in water loss and disrupting the balance of ions. It is established that ozone is able to modify amino acids, change the mechanism of protein metabolism, affect the composition of unsaturated fatty acids and sulfhydryl residues.
addition, there is an obvious link between the concentration of impurities with oxidative properties and a decrease in the content of chlorophyll and some soluble proteins. Under the action of ozone, an almost instantaneous decrease in the ATP content is observed. This may be a primary reaction or be associated with an ionic imbalance [5].

Ozone also has a strong inhibitory effect on the CO₂ fixation process, although at low concentrations it is likely to be completely consumed as a result of reactions in the outer shells and will not fall into chloroplasts. Many researchers believe that the residues of unsaturated fatty acids in lipid membranes are the areas on which ozone acts in the first place. However, lipid oxidation products are formed mainly after cell death [5].

It is possible that all changes in lipids are associated with the oxidation of sulfhydryl, which is also considered as an object of the primary attack of ozone [5].

The most important consequence of exposure to ozone, both separately and mixed with nitrogen and sulfur oxides, may be a decrease in crop yields. According to estimates by American scientists, for example, in the United States, the damage caused by the action of ozone is 90% of the total yield losses attributable to atmospheric pollutants. According to existing estimates, with an average of 7 hours of ozone concentration of 120 μg/m³, the damage to agricultural products for the three main crops would be 5.6% of income, which in 1978 was 3 billion US$. With an average 7 hour ozone concentration of 160 μg/m³, the damage would have amounted to 10% of the income [9].

In Europe, the damage from increased ozone background for wheat in 1993 was 2065 million US$, and for rye 223 million US$; total damage of 2288 million US$ [8]. This is the minimum damage assessment. Later updated estimates give a value of 1.89 to 3.3 trillion US$ annually. The economic damage to the wheat harvest in 1993 in Russia amounted to 149 million US$ [8].

Depending on the type of plant and environmental conditions, the symptoms of damage from ozone exposure can be quite varied. Since the assimilation layer is primarily affected by damage — small patches of cells on the upper part of the leaf, small spots on the upper side of the leaf are most often visually detected. Spots form between small streaks, their color can vary from fawn to dark brown or even to purple-reddish in the case of plants in which ozone stimulates the formation of anthocyanin pigment [5]. Pigmentation of lesions with anthocyanins and the resulting formation of dark green, purple or red spots is a common symptom for woody plants. The discoloration of the upper leaf surface in woody plants occurs less frequently than in herbaceous plants. In case of severe injuries, damage can spread through the sheet, as a result, symptoms appear on both surfaces.

As a result of the increase and coalescence of the affected areas, a large part of the outer surface of the sheet acquires a straw and sometimes a bronze color. With more severe injuries, the cells of the spongy parenchyma are also exposed on the lower surface of the leaf, where visible symptoms also appear [5].

In cases where the ozone concentration only slightly exceeds the threshold of visible damage, damage to the chloroplast can occur even before the cell dies. Its symptom is chlorosis, i.e. yellowing leaves. Particularly characteristic chlorotic stains appear when exposed to ozone on pine needles. Chlorosis was also observed on herbs, and in some cases on alfalfa. Chlorosis is usually accompanied by premature wilting and loss of leaves [5].

The characteristic symptoms for conifers include the appearance of chlorotic spots on old needles, which are replaced by reddish-brown necrosis extending from the tips of the needles. Reduced photosynthesis causes stress leading to terminal dieback. In the initial stage of damage, chlorotic spots of silvery, pinkish or reddish shades appear on the needles of 1-6 weeks. Then these lesions develop into a burn of the tips of the needles, which ultimately leads to the deformation and shrinkage of the trees.

For diagnosis, it is important that the symptoms first appear on the older leaves of the plant. Damage to leaves that are in the initial, most sensitive stage of development, first
occurs without visible symptoms. It is reported that leaves that are 65-95% of their full size are most sensitive to damage [5].

Currently, the term “sensitivity” is widely used to characterize the level of plant response to an increase in ozone concentration [8]. For this purpose, a number of generalized characteristics of the effect of ozone on plants for any period are used. The most common are: the dose which is the integral of the external concentration; average concentration; maximum concentration; and the AOT (accumulated over threshold) indicator meaning the integral of exceeding the threshold concentration and over the exposure period [8].

Critical levels of ozone are determined for plant protection in accordance with [12]. They are expressed as cumulative effects that exceed the threshold ozone concentration of 40 ppb and are designated as AOT40. AOT40 is calculated as the sum of the differences between the hourly concentration and 40 ppb for each hour when the concentration exceeds 40 ppb.

![Fig. 1. Variations of ground-level ozone concentrations (SOC) throughout 2016 year in Vyatskiye Polyany.](image1)

![Fig. 2. Variations of the average hourly SOC during July and August of 2016 in Vyatskiye Polyany.](image2)

Numerous studies on the estimation of the AOT40 value for plants (see, for example, [8, 10, 12-14]) indicate that in most cases this value is justified. Although, for some cultures it
is necessary to introduce AOT30 or even AOT20. In addition to AOT, there are other approaches to rationing the effects of ozone on plants. Thus, in New Zealand, the following thresholds have been established: 200 μg/m$^3$ at 1 hour, 65 μg/m$^3$ for 24 hours, and 60 μg/m$^3$ for 100 days of the growing season [14]. In [15], similar values are given for Uzbekistan - 61 μg/m$^3$ per hour and 29 μg/m$^3$ for the day.

3 Tropospheric ozone in central regions of Russia

Consider, which is the real level of pollution of the surface atmosphere with ozone in the central of Russia and whether tropospheric ozone can affect vegetation in this region. We have established a monitoring station of tropospheric ozone in the background plain region in central Russia in the city of Vyatskiye Polyany, in the south of the Kirov region (latitude: 56°13′N, longitude: 51°4′E). For continuous long-term monitoring of ground-level (surface) ozone concentrations (SOC), we used a 3.02 P-A chemiluminescent ozone analyzer manufactured by OPTEC Ltd., St. Petersburg, Russia, which is internationally certified by the US Environmental Protection Agency [16]. Observations at this station are carried out by us since 2010. The figures below show fragments of our data that can characterize the current situation.

Figure 1 shows typical variations of SOCs observed throughout the year. For illustration, the data of 2016 was chosen, since this year was distinguished by high ambient temperatures (summer maximums exceeded 30°C) and the observed SOC values were also quite high. It is seen that especially high concentrations of ozone are observed in the spring and summer, when the air temperature and the intensity of solar radiation are maximum. Maximum values of SOC exceed 200 μg/m$^3$. Figure 2 shows the course of the average hourly SOC during the summer months (July and August) of 2016. The figure clearly shows the alternation of night minima and daily maximums of SOC, when ozone concentrations were in the range of 150–200 μg/m. The average SOC over these two months was 102.6 μg/m$^3$. Figure 3 shows variations in per-minute SOC values for 3 days, from August 1 to 3, 2016. The typical daily passages of the SOC, due to variations in both light and ambient temperature, are clearly visible. The average daily SOC over these three days was more than 130 μg/m$^3$. As can be seen, the exposure time with the SOC value of more than 150 μg/m$^3$ was on these days from 6 to 8 hours.

Fig. 3. Variations of SOC values for 3 days, from August 1 to 3, 2016 Vyatskiye Polyany.
Thus, the values of SOCs and doses of the hazardous effects of ozone, observed in central Russia, can significantly exceed the threshold ozone concentrations for vegetation, which were given above.

Consider what the trend of this problem. As mentioned above, the last decades in Russia, as well as on the entire planet, there have been noticeable climatic changes. In particular, record high values of air temperature are recorded in spring and summer, the frequency and duration of heat waves increase. In addition, air pollution by road is growing. Figures 4 and 5 show the growth dynamics of the ozone content in the surface layer of the atmosphere over the past decades. They are usually observed in the summer months. Figure 4 shows the dynamics of the maximum observable SOC in the Moscow region for 20 years. They are usually observed in the summer months. If in 1996 the maximum values were at the level of 200 μg/m$^3$, then after 2010, the values exceeding 500 μg/m$^3$ regularly began to be observed.

Fig. 4. Dynamic of the year maximum hourly averaged SOC over the past decade in Moscow region.

Fig. 5. Daily course of the SOC averaged over the year in Vyatskiye Polyany for 2010-2016.
Figure 5 shows the daily averaged SOC averaged over the year, obtained in Vyatskiye Polyany. When analyzing these data, it is necessary to take into account that the averaging of daily variations over the year leads to a significant decrease in the average values obtained due to the relatively low ozone content in the surface atmosphere during the autumn and winter months (see the annual course of SOC in Figure 1). As can be seen from Figure 5, from 2010 to 2016, there was a gradual increase in the average annual values of SOC. In particular, the maximum average annual SOC increased by almost 2 times, from 53 to 92 μg/m³. Thus, the above results of long-term tropospheric monitoring in one of the background regions of central Russia show that the problem of the impact of ground-level ozone on crops and the decrease in yields due to this factor may become relevant in the near future both in the middle lane and in the southern regions of Russia. The results are in good agreement with the results of studies by other scientists [17-27].

4 Conclusions

The results of long-term monitoring of tropospheric ozone in central Russia (Vyatskiye Polyany, Moscow) indicate that due to the ongoing climate change and the growth of atmospheric pollution with nitrogen oxides, volatile hydrocarbons, carbon monoxide, even in central Russia, which is characterized by moderate The climate is not hot, there is a significant increase in the ozone content in the surface atmosphere. Moreover, there is both an increase in peak values of surface ozone concentrations and a duration of episodes of significant excess of safe ozone levels. At the same time, the doses of exposure to ground-level ozone to which plants can be exposed in central Russia are comparable and even exceed the levels considered safe. Thus, the problem of the impact of ground-level ozone on plant crops and yield reduction due to the action of this factor may become relevant in the near future both in the middle lane and in the southern regions of Russia.

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