Tropospheric ozone. 1. Properties and role in natural and anthropogenic processes

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Current problems, associated with the tropospheric ozone, are overviewed. Questions addressed include: the properties and role of ozone in natural processes; its physical and chemical properties; ozone units of measure; optical characteristics of ozone; radiative effects of ozone; ozone influence on living organisms and environmental objects, including ozone effect on humans, animals, plants, and materials; the use of ozone for positive purposes; safety rules in ozone treatment.

Introduction

Ozone was detected in laboratory air in the middle of the nineteenth century by C.F. Schönbein.[1] Later he also had determined its presence in the atmospheric air.[2]

Further studies have shown that the ozone in the atmosphere is distributed nonuniformly. There is about 90% of all ozone in the stratosphere and, therefore, it is often called the ozone layer. The remaining ozone resides in the troposphere.

The tropospheric and stratospheric ozone are chemically identical. However, their role in the Earth's atmosphere significantly depends on the height of occurrence.

The stratospheric ozone plays a key role in the absorption of hard solar ultraviolet radiation, ensuring quite low and biologically safe level of the radiation near the Earth's surface. The absence of the ozone layer would favor the reaching of the Earth's surface by the most part of the ultraviolet radiation. This would have unclear effect on the evolution of life on the Earth. At least for existing forms of life, this radiation is destructive.

The tropospheric ozone, especially in the near-ground layer, directly interacts with living organisms, exhibiting its toxic properties. This is the substance, which, by Governmental Standard 12.1.005-06, is classified as the first class hazardous species. In large concentrations, ozone strongly depresses the vital activity of plants and has a multiform effect on human organisms. As biological and medical studies have shown,[3] ozone in the troposphere is a virulent poison, having, in addition to its general toxic effect, is mutagenic, carcinogenic, and radiomimetic agent (acting on blood like the ionizing radiation). With regards to the toxicity degree, the ozone surpasses such a well-known poison as the prussic acid. In addition to the effect on the human beings and plants, ozone is also the strongest oxidant, destructing rubber and caoutchouc, oxidizing numerous metals, even of platinum group.[4]

Having an extended (from a few days to a few months) lifetime in the atmosphere and intense absorption lines, the tropospheric ozone may play a significant role in the atmospheric greenhouse effect. By estimates,[5,6] ozone accounts for more than 8% of the total air warming, caused by the absorption of solar radiation by greenhouse gases. More recent estimates suggest that, possibly, the magnitude of this contribution is even greater.

Such a variety of possible negative consequences of the increase of the tropospheric ozone concentration, both for human and environment, calls for an increased attention to the tendency of the ozone content variations in the near-ground air. And, what is strangely enough, the spatiotemporal variations of the tropospheric ozone are studied much poorer than those of its stratospheric counterpart. This fact has several explanations.

First, it was thought over a long period of years that the ozone concentration in the lower atmosphere is not high. Therefore, it was monitored at a small number of stations. And only in the last 30 years, when the danger of ozone increase in the troposphere became apparent, the network of the observation sites started to grow rapidly.

Second, for determination of tropospheric ozone content, the system of satellite monitoring is of little use in view of its orientation to monitoring of total ozone content, the contribution of the tropospheric ozone in which is insignificant.

Third, for a long time there was an opinion among scientists that the major part of the tropospheric ozone is formed in the stratosphere, from which it then is delivered to the near-ground air layer. Therefore, it is necessary to study the ozone transport through the tropopause.

Fourth, the spatiotemporal variations of ozone in the troposphere are caused primarily by dynamic processes, while the photochemical factors play a minor role.

Nonetheless, the analysis of the available non-abundant long term series of the ozone concentration measurements in the near-ground layer has shown an undeniable tendency of ozone increase in the last decades. According to measurements by the chemical method in Paris for period from 1876 to 1986

(110 years), the mean ozone concentration has doubled from 10 to 20 ppb^{-1} [Ref. 7]. The increase of ozone concentration in background regions of Europe by a factor of five for 100 years was marked.[8] Noteworthy, the beginning of the growth of ozone content in the troposphere is dated to 1895. An extensive overview of tendencies of variations of near-ground ozone is given in Ref. 9. On the basis of numerous measurements, the authors conclude that the current growth of ozone content in the troposphere is 1—3% per year and varies depending on the geographic location. In their opinion, the increase of tropospheric ozone concentration will continue in the future at a rate of 0.25% per year. This prediction, among many others, requires a more careful analysis of the regularities in formation and destruction of the tropospheric ozone.

According to the common current opinion, the growth of ozone concentration in the troposphere is favored by photochemical processes, in which the methane, carbon monoxide, nitrogen oxides, and hydrocarbons play a key role. The increase of their concentrations in the troposphere and reactions of these gases with hydroxyl radicals are most important factors, determining the ozone formation and destruction in the lower atmosphere.[10]

This concept of the atmospheric photochemistry has passed a few stages.[11] An impetus for its rapid development was a supposition[12] about relatively large steady-state concentrations of HO and HO$_2$ in the sunlit troposphere. Then, P.J. Crutzen argued that the ozone budget in the atmosphere depended very strongly on nitrogen oxides NO$_x$, which are formed by oxidation of nitrogen dioxide N$_2$O, released from the underlying surface.[13] Then Demerdjian with coauthors formulated the mechanisms of oxidation of hydrocarbons in the presence of NO$_x$ with generation of ozone in the polluted air.[14]

Based on all the aforesaid, Fishman and Seiler came to conclusion that the background ozone content in the troposphere is determined precisely by photochemical processes,[15] while their contribution to the total ozone budget in the troposphere is much larger than the influx of the gas from stratosphere.[16]

Estimates of ozone fluxes from the stratosphere (10^{10} mol·cm^{-2}·s^{-1}) and ozone production in the troposphere are presented in Ref. 17, where it is shown that only 20—25% of ozone in the troposphere are of the stratospheric origin, and its major part is formed just in the troposphere. An inter-hemisphere difference in ozone fluxes also exists. In the Northern Hemisphere, where considerable anthropogenic sources of CO and hydrocarbons are located, the ozone content is 1.7—1.8 times higher than in the Southern Hemisphere. It can be crudely considered that in the troposphere of the Northern Hemisphere the anthropogenic activity produces almost the same ozone amount as natural sources.

It was found in the detailed experiment on determination of tropospheric ozone budget in remote high-latitude regions of the Northern Hemisphere[18] that the dispersed photochemical generation of ozone at a background level of NO concentration (50—10 ppt^{-1}) is the largest source, whose relative contribution is 62%. The influx of stratospheric ozone is 27%, that is the secondary importance. The long-range transport from industrial regions contributes about 9% to the ozone budget and the biomass burning about 2%. Thus, the experimental data[18] turned out to be close to calculations.[17]

The appearance of the smog events in the towns activated the study of the tropospheric ozone. First smog event was described in Ref. 19. A more detailed analysis[20] showed that the main source of ozone-bearing substances were mototransport exhausts.

Despite the fact that the studies of the tropospheric ozone are conducted in many different directions, there remain numerous problems, which should be solved in order to understand the processes determining the ozone variability. These problems are overviewed in Refs. 21—24 and include:

1. Representativeness of data on the annual behavior of tropospheric ozone concentrations and a choice of data characterizing the background conditions.

2. Quantitative estimates of arrival of stratospheric ozone to the troposphere in spring, as well as identification of the possible annual behavior of the stratosphere—troposphere ozone exchange.

3. Analysis of inter-hemisphere asymmetry of ozone concentration and its annual behavior.

4. The existence of meridional gradient of the amplitude in the annual behavior of tropospheric ozone concentration as possible reflection of contributions of different ozone-forming processes, which depend on the latitude.

5. The contribution of the long-range transfer to the ozone concentration variability as compared to the contribution of photochemical processes of *in situ* ozone generation as a factor of annual ozone behavior.

6. Proportion between precursor gas contents and ozone generation as a result of the photochemical processes.

7. Accumulation of long-term series of observations of precursor gas concentrations or anthropogenic tracers for direct monitoring of tropospheric ozone variations under different conditions.

8. Role of photochemical processes in the wintertime ozone formation in the entire troposphere.

9. Study of ozone exchange between the atmospheric boundary layer and the free troposphere.

10. Identification and qualitative estimate of the chemical and physical mechanisms of springtime maximum of the near-ground ozone concentration.

11. At last, the smog situations.

According to Ref. 25, the ozone concentration in the troposphere (from ground level to 10—15 km) throughout Europe now is 3—4 times higher than in pre-industrial period. This is due to rapid growth

since 1950s of emissions of nitrogen oxides, whose source is industry and automobile transport. In European Union, the causes of approximately 700 hospital visits for period from March — October, 1995 (75% of which is recorded in France, Italy, and Germany) can be due to ozone concentrations higher than the threshold. And, as a later overview shows,[26] according to observations at 1842 European stations, the situation is not improved.

It is important to note that main properties of the tropospheric ozone can be both adverse and useful for human beings and plants. For instance, being one of the most effective oxidants, ozone kills a large number of bacteria and microorganisms, including pathogenic ones; also it favors the decomposition of different wastes of both natural and anthropogenic origins.[27] Ozone is just indispensable for disinfection of empty buildings, hospital rooms, vegetable stores, refrigerators, trucks, which transport the vegetation production for long distances.

Thus, despite the advances in the tropospheric ozone study, many unsolved problems still remain. The information accumulated to date is dispersed in different papers, or, in the best case, in overviews, which are not always accessible to the ordinary reader. The last monograph, in which the problem of tropospheric ozone was considered comprehensively, was published in USSR in 1980 [Ref. 3]. At the time of its preparation, the photochemical theory of the tropospheric ozone has been only surfaced among the abundant experimental data and theoretical hypotheses; so the authors had to describe this part of the ozone problem with caution. Naturally, it needs more adequate consideration at the current level. In this paper, we summarize the data on the spatiotemporal ozone variability in troposphere and its regularities.

1. Ozone properties

Though the discovery of ozone as a gas is generally considered in association with the name of C.F. Schönbein,[1] the history of the subject is far longer.[2] As early as in 1785, conducting experiments with the electrical machine, Martinus van Marum has noticed that sparks cause the appearance of new smell and augmentation of air oxidizing properties. Then, Krukshenk in 1801 detected a similar smell during electrolysis of water. And only in 1840 Schönbein had linked the change in the oxygen properties in electrical processes to formation of a specific gas. Later, de la Rive and Marignac confirmed that ozone is a modification of oxygen, and Hant in 1848 hypothesized that ozone is the triatomic oxygen (see Ref. 28 for details). And only in 1861 Olding had identified the ozone molecule as a triatomic gas.[28] The final variant was found by J.L. Soret who, on the basis of measurements of the ozone and carbon dioxide diffusion rates, has shown their molecular masses to be in proportion 48:44. These results have made it possible to perform a

purposeful study of ozone properties, and then apply them in different fields of science and industry.

1.1. Physical and chemical properties of ozone

The ozone properties are described in detail in numerous basic publications.[3,4,28,30–32] In this paper, only those of them are mentioned, which are used in the study of ozone behavior in the troposphere.

According to the currently adopted model of O_3 molecule, its atoms are located in vertices of the isosceles triangle.[4] The interatomic distance is $(1.278 \pm 0.003) \cdot 10^{-8}$ cm, and the central angle is $116°50' \pm 30'$. The mass of the molecule O_3^{16} is $7.97 \cdot 10^{-23}$ g.

The ozone molecule may include heavier isotopes of oxygen O^{17} and O^{18}. By crude estimates, there is about 0.21% of molecules of $O^{16}O^{18}O^{16}$ and 0.41% of molecules of $O^{16}O^{16}O^{18}$ in the atmospheric ozone (see Ref. 3). The most recent data suggest[33–35] that it is possible to judge about ozone origin from the ratio $O^{18}:O^{17}$ in the composition of ozone molecule and, as calculations show, in certain situations, the enrichment with the isotopes O_3^{49} and O_3^{50} may vary from 7.5 to 12.5% in comparison with their concentrations under standard conditions.

The gaseous ozone at standard temperature and pressure has a density of $2.144 \cdot 10^{-3}$ g·cm^{-3} and molecular weight of 47.9982 g/mol. The heat capacity of the gas decreases with lowering of the temperature (Table 1).

Table 1

Temperature, K	Heat capacity, $J \cdot kg^{-1} \cdot K^{-1}$
473	904
273	795
100	690

Ozone liquefies at a temperature of (161.3 ± 0.3) K to dark-blue liquid with a density of 1.46 g·cm^{-3}. The evaporation heat of the liquid, according to the different sources,[28] may vary from 11.17 to 16.60 kJ·mol^{-1}. The temperature of solidification of the liquid is (80.6 ± 0.4) K.

The refractive index of ozone varies with wavelength. Some data are presented in Table 2.

Table 2

Wavelength, nm	Refractive index
480	1.0533
546	1.0520
671	1.0502

The diffusion coefficient at a pressure of 1 atm and a temperature of 300 K is 0.157 cm$^2 \cdot$s^{-1}. A permittivity of O_3 at 0°C is 1.0019. The ionization potential of ozone is equal to 12.8 eV; the electron

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affinity, according to different authors,[3] varies from 1.9 to 2.7 eV.

Mixtures of ozone with oxygen, nitrogen, and air are close to ideal ones.[31] Therefore, the densities, viscosities, and other physical parameters of these mixtures vary linearly as functions of the O_3 concentration.

Because of the high excessive energy of the molecules (24 kcal/mol),[4] ozone is extremely explosive in all phases and, therefore, it is used only in the form of diluted mixtures with other gases.[31] Depending on the ozone concentration in these mixtures, four regions in ozone behavior are identified:

1) 0−20% of O_3 by mass is the region of simple decomposition;

2) 20−45% is the region of "self-sustaining" decomposition;

3) 46−50% is the region of nonstationary decomposition;

4) > 50% is the region of detonation.

In this regard, treatment of gas mixtures, containing no more than 15% of ozone by mass is considered safe.

The chemical properties of ozone reflect features of its formation. They include water solubility, instability, and oxidizing capacity.

According to Ref. 28, the determination of the ozone solubility is complicated by its instability and spontaneous decomposition in liquids. In water, ozone is decomposed considerably faster than in gas phase. Noteworthy, an exceptionally large influence on its decomposition rate is exerted by the presence of admixtures, especially, ions of methals.[36]

Table 3 presents the temperature dependence of ozone solubility in water. It is reduced to 100% ozone content at the atmospheric pressure. The data are taken from Ref. 37.

Residing in air in small amounts, ozone is decomposed relatively slowly.[8] The presence of NO_2, Cl_2, and other catalytic gases in air (in the absence of solar light), as well as the catalytic effect of oxides of certain metals (Al, Cu, Fe, Mn), accelerates the ozone decomposition.

Table 3. Solubility of ozone in water

Temperature, °C	Solubility, g/l
0	1.09
10	0.78
20	0.57
30	0.40
40	0.27
50	0.19

As the temperature increases, the ozone decomposition is accelerated. The mechanism of the reaction seems to be as follows:[3]

$$O + M \overset{K_1}{\underset{K_1^1}{\leftrightarrow}} O_2 + O + M, \quad O + O_3 \overset{K_2}{\rightarrow} 2O_2,$$
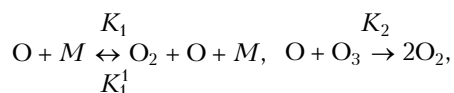
where the rate constants

$$K_1 = 7.8 \cdot 10^{14} \cdot \exp(-23340/RT) \text{ cm}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1};$$

$$K_1^1 = 1.24 \cdot 10^{13} \cdot \exp(-1090/RT) \text{ cm}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1};$$

$$K_2 = (2.9 \pm 0.9) \cdot 10^{12} \cdot \exp(-3700/RT) \text{ cm}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$

Ozone has strong oxidizing properties. At standard temperature, most metals are oxidized by ozone. It was reported[4] even about oxidation of platinum and its analogues by ozone. However, later this was assented a mistake.[28] Below, we will repeatedly return to this issue.

Ozone acts on the living nature as well. A characteristic smell is felt at a concentration of $10^{-4}\%$. At small concentrations, undoubtedly, ozone is useful; however, at considerable concentrations, as biological and medical studies show, ozone is a virulent poison.

1.2. Ozone units of measure

Ozone in the atmosphere is studied by specialists of many scientific disciplines. As a rule, a specific set of units of measure, convenient for description of the processes, studied by a particular scientific discipline are used in each. As a result, there occur problems with conversion of the units to the form, acceptable by a given discipline. Therefore, it is advisable to present the simplest relations for conversion from one unit of measure to other.

As for any atmospheric gas, the basic unit of measure for ozone is the number concentration, or the number of molecules in the unit air volume. Usually, it is denoted by the subscripted letter N. For ozone, the frequent designation is N_3 or N_{O_3} with units of m^{-3}, dm^{-3}, and cm^{-3}.

Other units of measure for ozone may be obtained using the number concentration[3] on the basis of universal constants of physics: the Avogadro number N_A, the Loschmidt number N_L, Boltzmann constant, and the ideal gas law:

$$P = NkT = \frac{N_L}{N_A}RT. \tag{1}$$

Remind that one mole of gas under standard conditions: at a pressure of $1.013 \cdot 10^5$ Pa = = 1013 hPa and a temperature of 273.16 K, occupies a volume of 22.4136 dm^{-3}. Noteworthy, the number of N_A molecules in this volume is $6.022 \cdot 10^{23}$. The number of molecules in 1 cm^3 is $N_L = N_A / V_0 = 2/6868 \cdot 10^{19}$, V_0 is the mole volume. The universal gas constant is

$$R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{kmol}^{-1}, \; k = 1.3806 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}.$$

To characterize the specific amount of ozone or any other atmospheric gas, the density (partial density) and partial pressure are used. The partial pressure of ozone in air is the pressure, at which the ozone would be, all the other gases being removed from air and the volume and temperature remaining

unchanged. The partial pressure is denoted by the letter P indexed as P_3 or P_{O_3}. The partial density of ozone is often denoted through ρ subscribed as ρ_3 or ρ_{O_3}, and has the units of $\mu g/m^3$. Relation between the density and partial pressure of ozone is derived from equation of state of ideal gas[38]:

$$\rho_3 = \frac{\mu P_3}{RT}, \qquad (2)$$

where μ is the molar mass, equal to $47.998\ kg \cdot kmol^{-1}$ for ozone; P_3 is in mPa; and T is the ozone temperature in K.

The ozone mass concentration, or ozone density, depends on the air temperature and pressure. Therefore, in a number of disciplines, the specific content of ozone or some other atmospheric gas is characterized using relative units: the molar mass and volume concentration, usually denoted through ppm, ppb, and ppt.

Molar concentration of ozone or any other gas is meant the ratio of the density of ozone or other gas to the air density:

$$r_i = \rho_i / \rho = (N_i \mu_i) / \mu. \qquad (3)$$

Here the subscript i denotes ozone or any other gas, and the absence of subscript is for air. It is important, that thus obtained concentration does not depend on the temperature and pressure.

The volume concentration of ozone or any other gas means the ratio of mole pressures or the ratio of mole volumes

$$R = N_i / N = P_i / P = V_0 / V_{0i}. \qquad (4)$$

Here, as in Eq. (3), the index i indicates ozone or other gas and the index absence means air. This concentration is also independent of air pressure and temperature.

The volume concentration is often confused with the notion of mixing ratio, which is defined as follows: the ratio of the ozone density (or some other gas) to the density of air, free of this gas:

$$r_i^* = \rho_i / (\rho - \rho_i) = r_i / (1 - r_i). \qquad (5)$$

It is clear that for minor components of air, formulas (3) and (5) are in fact identical. Seemingly, this explains the confusion of the notions.

The ozone characteristics, which depend on the temperature and pressure should be reduced to standard conditions ($P_0 = 1013\ hPa$ and $T_0 = 273.16\ K$) in order to facilitate the comparison of the data, obtained under different conditions. In this case, the following formula is commonly used:

$$\rho_0 = \rho_i \frac{P_0 T_i}{P_i T_0},$$

where i refers to the measurements, performed under conditions other than standard.

Below, we will use both ozone mass and volume concentrations. Because conversion from one parameter to another requires the knowledge of P

and T, which are not always available in the original work, we will leave the units indicated by the authors.

1.3. Optical characteristics of ozone

The start of the studying of optical properties of the atmospheric ozone refers to the nineteenth century. The history of formation of this field of knowledge has been described by Khrgian [Ref. 39]. To date, the spectral coefficients of ozone absorption are determined quite accurately. There are detailed overviews of the subject,[40,41] and specialized databases are built (see, e.g., http://ozone.iao.ru); therefore, we will give here only most general characteristics of spectral coefficients of ozone absorption, which are required for further presentation.

It is seen in Fig. 1 that ozone has several absorption bands: from vacuum ultraviolet to microwave spectral range.
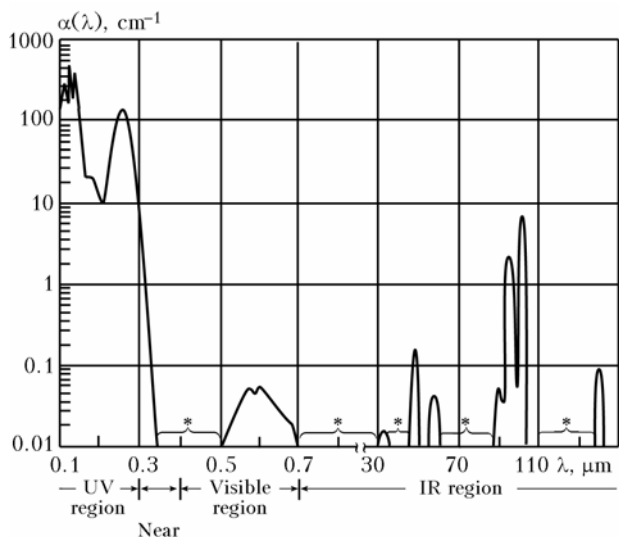
Fig. 1. Ozone absorption coefficients in different regions of the spectrum (asterisk indicates the regions where the absorption coefficients are less than 0.01 cm^{-1}) (see Ref. 3).

The band in the vacuum UV spectral range ($\lambda < 0.2\ \mu m$) is insignificant for the troposphere, because the absorption in this band takes place in the upper atmospheric layers, therefore, the solar radiation at $\lambda < 0.295\ \mu m$ does not reach the troposphere in practice. The Hartley band, though located in the solar blind region, is used in most UV ozone analyzers. The Higgins band ($\lambda = 0.295-0.320\ \mu m$) is of importance for dynamics of the tropospheric ozone, in which the ozone photolysis proceeds, which initiates the photochemical process. The ozone absorption band near $\lambda = 9.57\ \mu m$ is used for satellite sensing of ozone.[42] (For more detail, refer to the site http://ozone.iao.ru, which, in addition to database, gives an extensive bibliography on the subject).

1.4. Radiation effects of ozone

The presence of absorption lines of electromagnetic radiation in different parts of the solar spectrum augments the ozone significance for the energy balance of the Earth's atmosphere. The tropospheric ozone, in particular, absorbing the solar radiation, enhances the greenhouse effect of the planet. Intensification of the greenhouse effect may cause global climate changes and, as a consequence, natural catastrophes.[43] As is suggested in Ref. 43, the change of the influx of the solar radiation by 1% increases or decreases the temperature of the lower atmospheric layer approximately by 1.5°C. In this regard, we analyze the tropospheric ozone contribution to the radiation balance of the Earth's atmosphere.

The numerous estimates of the radiation effect of the tropospheric ozone are summarized in Ref. 44. These estimates suggest that the total amount of O_3 in the troposphere since 1850 has increased by 36%, which is primarily explained by anthropogenic emissions of a few groups of ozone-forming gases and corresponds to the positive radiation effect, equal to $0.35 \ W \cdot m^{-2}$. Noteworthy, the O_3 effect appreciably varies from one region to another and responds much faster to variations in emissions than long-living greenhouse gases in the atmosphere, such as CO_2.

At present, estimating the radiation effects continues. Certain estimates are presented in Table 4.

As is seen, the estimates of the radiation contribution of the tropospheric ozone are close in value and fall in the range $0.1-1.1 \ W \cdot m^{-2}$. They may increase by $0.27 \ W \cdot m^{-2}$, once the emissions of automobile transport are taken into account.

The equivalent change of the near-ground temperature is generally estimated from the formula[58]:

$$\Delta T_0 = k\Delta F,$$

where ΔF is the radiative forcing; k is the parameter of climate sensitivity, which varies from 0.3 to $1.4 \ K \cdot m^2 \cdot W^{-1}$, depending on the used model. These estimates are presented in Table 5.

It follows from Table 5 that the air temperature should increase by 0.2−0.4 K, and even by 0.8 K in some regions.

A somewhat different approach to the calculation of temperature change is presented in Ref. 63, where it is suggested to calculate by the formula

$$\Delta T = 0.7[N_3(t) - N_3(t_0)]/15,$$

where $N_3(t_0)$ is the ozone concentration in 1980; and $N_3(t)$ is the ozone concentration in subsequent years.

Table 4. Radiation effects of ozone in the troposphere

Conditional estimates	Radiative forcing, $W \cdot m^{-2}$	Refs.
Change of ozone from 1850 to 2000	0.25 … 0.45	45
Calculations for different regions	0.3 … 1.1	46
Annually mean global forcing The same for subtropical latitudes	0.54 1.0	47, 48
Forcing from 1950 to the present The same from 1850 to the present	0.38±0.10 0.70	49
Annually mean global forcing	0.53	50
The same	0.49	51
Calculation for 1990−2100	0.43	52
Annually mean global forcing The same for tropical latitudes	0.1 … 0.4 0.5 … 1.0	53
Annually mean global forcing The same for the pre-industrial period Additional radiative forcing due to growth of ozone in 2050 Total forcing in 2050	0.40 … 0.78 0.43 0.26 0.69	54 55
Globally mean annually average forcing The same for tropics and subtropics	0.30 0.6 … 0.8	56
Globally mean annually average forcing The same for 2100	0.22 0.57	57
Annually mean global forcing	0.50	58
Additional forcing due to global vehicle exhausts	0.27	59
Changes with taking into account the climate dynamics and emissions by 2100	0.76 … 0.93	60

Table 5. Change of near-ground temperature due to radiative forcing of the tropospheric ozone

Conditions of calculation	ΔT_0, K	Refs.

Globally mean temperature growth:
    Northern hemisphere
    Southern hemisphere
	
	0.4
	0.2
		61

Temperature growth in the flow from Europe, Asia, or North America	>0.8	
Globally average temperature growth	0.3	62
Springtime growth in Arctic	0.4−0.5	

In contrast to the radiative heating due to tropospheric counterpart, the stratospheric ozone has a negative effect on the change of the near-ground temperature. By data from Ref. 64, this value is −0.4 … −0.5 K. Nearly the same conclusions are drawn in Ref. 65.

2. Effect of ozone on living organisms and environmental objects

The negative action of ozone on the living organisms was recorded in 1857 in Germany by Werner and Siemens [Ref. 66]. Further studies have shown ozone negatively action on many other environmental objects.[8,17]

Later, positive role of ozone was also revealed and ozone has found its wide application in medicine, technology of refinement, etc.[66]

In this section, we consider both negative and positive ozone effects on environment.

2.1. Ozone impact on human being

Ozone influences on human being directly and indirectly. The result of direct influence is tiredness, headache, vomiting, irritation of respiratory tract, cough, disorder of breath, chronic bronchitis, emphysema of lungs, asthma attacks, pulmonary edema, and hemolytic anemia.[67]

Indirectly, ozone, like some other gases, affects the blood analogously to the ionizing radiation.[3] This is the so-called radiomimetic effect. According to Ref. 68, a 30-minute inhalation of ozone at a concentration of 0.8 mg/l is equivalent to exposure to 100 REM.

To date, it is found that, in addition to the general toxic, irritating action, ozone has carcinogenic, mutagenic, and genotoxic effect on the human being.

Studies of ozone effect on the human[69–71] have made it possible to conclude that:

1. Ozone causes irritation of respiratory tract, cough, and chest tightness. These effects may last for a few hours and pass to the illness stage.

2. Ozone decreases the lung function. When working outdoors, the breath rate increases and the breathing depth decreases.

3. Ozone favors development of asthma and increases the amount of asthma attacks.

4. Ozone causes allergic response to most widespread substances: dust, pollen, as well as to domestic animals and insects.

5. Ozone damages the lung tissue.

6. Ozone leads to aggravation of bronchitis and emphysema of lungs.

7. Ozone considerably reduces the immunity to infections.

These conclusions are supported by subsequent studies. Let us present some examples.

Based on the study of a group of Mexican children at the age of 5–13 years, suffering from mild asthma, it has been shown that as the hour ozone concentration increases up to 50 ppb, the cough repetitiveness increases by 8% and the respiratory symptoms − by 11% [Ref. 72].

In Ref. 73 it has been reported that the increase of the hour ozone concentrations up to 44 ppb and of 8-hour concentrations up to 38 ppb causes 18.7% and 21.8%, respectively, increase in the number of visits to physicians by patients older 64 years.

A considerable reduce of automobile traffic[74] during the Olympics in Atlanta (1996) resulted in decrease of mean ozone concentrations by 27.9% and the following decrease in the number of asthma attacks by 41%.

Strong aggravation of lung function and rapid tiredness of cadets during their training was noticed in New Jersey, when the ozone concentration there reached 100 ppb.[75]

The high incidence of asthma attacks (by 3.3 times) among students playing sports was marked at the University of the Southern California School of Medicine, at the exceeding of the level of the ozone maximum permissible concentration (MPC).[76]

A number of papers present more detailed estimates of the effect of ozone on the health of the population (see Table 6).

The mechanism of action of ozone is determined by its strong oxidizing properties, formation of free radicals and peroxide oxidation of lipids. The state of the cell and sub-sell membranes is broken, and the permittivity of alveoli increases.[85]

The ozone intoxication leads to imbalance of biogenic amines in the organism, distortion of the chromosomal system of lymphocytes and metabolic processes, decrease of infection-related stability, which is associated with depression of production of antibodies due to distortion of the thymus function.[86,87]

Table 6. Effect of ozone on the health of the population (the number of incidents in April − October)[83,84]

City	Respiratory hospitalization	ER visits for respiratory problems	ER visits for asthma	Asthma symptoms	Weak symptoms	Refs.
Birmingham	170	510	64	24	320	78
Minneapolis	470	1410	150	64	900	78
Alabama	1000	3000	350	130	1700	79
Detroit	930	2790	310	130	1800	80
New York	4100	12300	1200	510	6900	81
New Jersey	2000	6000	600	240	3400	82

Since ozone is not characterized by the presence of strong smell, there appears a problem of identification of the causes of the human intoxication. The ozone effect symptoms are given in Table 7.

Close in value are air quality standards, established by Environmental Protection Agency in USA.[89,90] Noteworthy, these characteristics are regularly verified in the experiments.[91-96]

In view of the ozone strong toxicity (ranked as the first class), it is given quite stringent requirements in Russia:

$MPC_{w.z}$ in the working zone air is 100 μg/m^3 [Ref. 97].

MPC_{da} (daily-average in the atmospheric air) is 30 μg/m^3 [Ref. 98].

MPC_{MS} (maximum single in the atmospheric air with a probability of 0.1%) is 160 μg/m^3 [Ref. 98].

The serious character of the problem is admitted by many countries and organizations as well (Table 8).

The standards indicated in Table 8 are constantly reconsidered and updated. For instance, California plans to lower the MPC thresholds as follows: a 8-hour threshold — to 70 ppb and 1-hour threshold to 0.095 ppb in the framework of the California Air Resources Board (CARB) Project. Based on the results of studies,[100] the developers anticipate to decrease ozone effect on the population, as seen from Table 9.

On the basis of the performed evaluations of reduction of disease incidents, the authors of the Project used the available methods[101,102] estimated the possible economic benefit for USA from introduction of the new standard as 2.6 trillion dollars per year. These calculations assumed that the cost of the human death for the country is 6.5 million dollars, the cost of hospitalization is 18000 dollars, and the cost of 1-day school non-attendance is 75 dollars.

It should be noted that the threshold of ozone concentration for the lethal case remains to be found.[103] A short-term (0.5 h) exposure of human to ozone concentration of 50 μg/m^3 has been documented. At the same time, cases of human being reaction (headache, giddiness, distortion of eyesight, etc.) to ozone concentration of 200 μg/m^3 are not uncommon. Serious functional distortions of different organs are characteristic of workers concerned with production of perhydrol as long as 7 years at ozone concentration of 0.5—0.8 μg/m^3.

Table 7. Symptoms of ozone intoxication for people[88]

Concentration, μg/m^3	Duration of inhalation, h	Consequences
4—15	—	Threshold of smell perception in the clean air
>120	8	Reduction of working efficiency at high loads
>160	24	Degradation of lung function
>200	8	Cough, hoarseness, tickle in throat
>240	3	Loss of sensitivity to other toxicants and allergens
>400	8	Inflammation of the lower respiratory tract with a possible lethality

Table 8. Maximum permissible concentrations of ozone

Document, organization, country	Criterion	Concentration
EU Directive 2002/3/EC European Council	Mean 1-h concentration Information threshold for population Average concentration over 3 h Alarm threshold	180 μg/m^3 240 μg/m^3
World Health Organization	Running 8-h maximum as a guide to health protection	120 μg/m^3
National air quality standard NAASQS, USA	Maximum average 1-h concentrations Average 8-h concentration	120 ppb 85 ppb
CEDRM, 1992, Chile	Maximum average 1-h concentration Average 24-h concentration	160 μg/m^3 100 μg/m^3
Turkey[99]	Maximum average 1-h concentration	240 μg/m^3

Table 9. Consequences of exposure of population to ozone at MPC variation, %

Consequences	MPC = 85 ppb	MPC = 70 ppb	Rarer ER visits
Death	0.17	0.06	0.11
Hospitalization for respiratory diseases	0.71	0.28	0.43
Asthma attacks	1.26	0.49	0.77
School non-attendance	0.87	0.34	0.53

Death estimates rely upon data of statistics. It is meant that the increase of the ozone content with a step of 10 ppb augments the risk of death by 0.5%. In parallel, this increases the mortality from cardiovascular and respiratory diseases by 0.65% per day.[104–106] These calculations are sooner estimative. However, to some or another degree they reflect the cause-effect relations.

In addition, it is proved[98] that ozone also has a summing effect; that is, in combination with other admixtures its action is amplified.[107–110]

2.2. Influence of ozone on animals

Studies suggest that ozone increased concentrations make animals to experience the same symptoms as human beings.[111,112]

Three- to four-hour exposure of mice to air mixture, containing 1.6–3.0 mg/m^3 of ozone, caused the increase of the lung mass and decrease of the liver mass, decrease of the level of creatine phosphokinase and ascorbic acid in the serum of blood and in the liver.[112] The 3-h exposure of rats to 6.5 mg/m^3 of ozone decreased the irritation of their central nervous system, decreased the consumption of oxygen, content of hemoglobin and erythrocytes in blood, as well as the 24-h inhalation of ozone at a concentration more than 2 mg/m^3 led to distortion of the function of thyroid gland and metabolism of thyroid hormones. The 1-h exposure of dogs to ozone at a concentration of 0.2–1.5 mg/m^3 caused damage of parathyroid glands; and a 3-h exposure of sheep to ozone at a concentration of 1.0–1.45 mg/m^3 triggered the decrease of the level of SH groups and amount of erythrocytes, as well as increase of the methemoglobin content.[113–116]

Different types of animals similarly respond to ozone impacts. They exhibit irritation of the mucous membranes, lachrymation, and damage of the lung tissue. In addition to the negative effect on the lung function, there may also take place biochemical changes at the cell level. Damage (destroy) of the cells in these cases may be caused by high chemical activity of free radicals, formed in the cell exposed to ozone.[117] Ozone concentration of 200–250 μg/m^3 may drastically accelerate the process of ageing of cells of animals and human beings.[118]

An inhalation by mice and rats of ozone at a concentration of 2.0–2.4 mg/m^3 for 3–5-day increases their lung mass and the content of Zn, Cu, and Mn in lungs, as well as decrease of the mass of liver, spleen, and kidneys.[119–121] A 4–7-day exposure of monkeys to ozone with a concentration of 1.2–1.5 μg/m^3 for 4 h daily was accompanied by damage of mucous membrane of trachea, as well as by decrease of the level of recovered glutathione in erythrocytes, increase of the peroxide oxidation of lipids, and decrease of the concentration of vitamin E in lungs.[122–125] The 6-week exposure for 4 h daily of sheep to ozone with a concentration of 9.5 mg/m^3 has led to rapid distortion of the structure and function of the glands of the mucous membrane of the bronchi, properties of secretion of the glands and the process of its excretion.[126]

In addition to the direct effect, ozone also leads to decrease of resistance of organism of animals to a number of infection diseases.[127]

Of interest is the adaptation of animals to the effect of large doses of ozone. After a pre-exposure to mixtures with low ozone concentration (not leading to visible effects), the resistance of animals to the effect of higher concentrations increased; at the same time, the control group of animals experienced damage of the lung tissue.[128–131]

Present generalized data from Refs. 111–131 (Table 10) on ozone concentrations, hazardous for animals.

The effect of polluting substances is characterized by synergism both for animals and human beings.[132]

Figure 2 is plotted in accordance with the classification of Thorp [Ref. 133]. Data for small animals are borrowed from Ref. 134.

Table 10

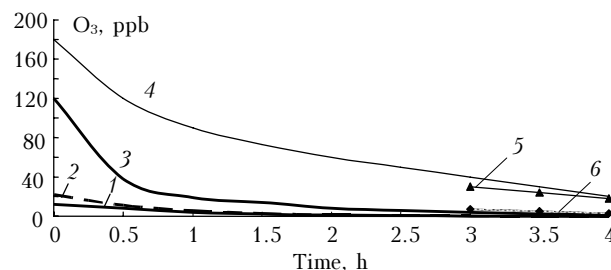| Animal species	Ozone concentration, mg/m^3	Exposure, h	Lethality, %
Mice	40	3	50
Rats	30	1	80
	5	3	58
	0.5	1	17
Guinea-pigs	1–10	3	50
Rabbits	7.4	3	»
Cats	7	3	»

Fig. 2. Physiological effect of ozone on animals: symptomatic effect (curve *1*); irritating effect (curve *2*); poisonous effect (curve *3*); lethal dose (curve *4*); lethal dose for small animals (curve *5*); symptomatic effect on small animals (curve *6*).

It is seen that the increase of the exposure time leads to considerable decrease of the level of ozone concentration affecting animals to some or another degree.

2.3. Ozone effect on plants

The negative effect of ozone on plants is a fact established quite long ago.[135, 136]

An increase of ozone concentration may cause both direct[136–138] and indirect[139] effects on terrestrial plants.

Primary effect is in sorption of ozone and its chemical interaction with plant material. Consequences of such interaction manifest themselves in the change of color, loss of color in the damaged part and its drying.[140] Phytotoxic action of ozone shows up itself right after the gas contact with plants (acute damage). Change of leaf and needle color is the manifestation of lethal damages of cells, which lead to the loss of assimilation activity of the plant material. In the case of the damage of vegetative leaf area and, correspondingly, the decrease of the assimilation surface, the plant death is quite possible.

The secondary action of the toxic gases on the plant is caused mainly by the effect of the products of their chemical conversions on the acidity characteristic and the character of metabolic processes proceeding in soil.[140]

According to Ref. 141, the response of plants to the action of ozone is associated with the function of stomata. Increase of humidity, which favors opening of stomata, increases the damage of the plants by ozone[142]; whereas in the case of closed stomata, no or almost no damage occurs.[143] Noteworthy, the peak of the plant sensitivity is not associated with the number of stomata and their resistance on both leaf surfaces.[143]

Ozone affects the breath of the plant diversely, and may either stimulate[144] or inhibit it.[145,146] However, in opinion of many scientists,[147–149] this process still needs a further study.

Most part of the surface mesophyll is the medium for dissolution of gas-phase ozone.[150,151] However, now it is little known on the processes of diffusion and chemical ozone conversion in this tissue.

Ozone in plants is the source of superoxide radical O_2^-, which, in its turn, forms in them such reactive radicals as OH and H_2O_2. These radicals may oxidize different cellular metabolites.[152,153] Ozone also acts on many components of membranes such as SH groups, amino acids, proteins, and unsaturated fatty acids.[150,151] At the same time, the possible oxidation of these components is the result of free radical attack.[152,153]

Under impact of ozone, the permeability of plant tissues for water, glucose, and ions changes.[143,154,155]

The direct ozone effect suppresses the growth and productivity of plants, whereas the indirect effect leads to decrease of the growth of roots in comparison with above-ground plant parts. This occurs because ozone inhibits the assimilation of carbon and somehow inhibits the transfer of metabolites to the root system. For instance, chronic exposure to ozone leads to 40–60% reduction of the total symbiotically fixed nitrogen in fodder, stubble, and roots of lucerne.[156] Under influence of 0.1–0.15 ppb ozone, the roots of haricot develop slower than those of the control plants, growing in the filtered air.[157] Moreover, the roots and hypocotyls of ozone-exposed plants have more colonies of fungi than the control plants.[158]

Therefore, the roots respond to ozone identically, and sometimes even stronger than, the above-ground plant part. The reduction of the amount of assessable hydrocarbons or other organic energy-producing species in the roots leads to inhibition of symbiotic ties between microorganisms and host plant.[159–160] These conditions may intensify the development of pathogenic fungi and increase their population on the root surface of ozone-damaged plants.

External manifestations of ozone-damage plants can be summarizes as follows.[161–168]

For deciduous trees and certain grassy plants the initial damage is often restricted to localized group of palisade cells. Development of the damage leads to appearance of spots and granular-shaped damages, whose size may vary from microscopic scale, which corresponds to damage of a few cells, to macroscopic scale, with appearance of spots up to 2 mm in diameter. The color of leafs may change from light-green to white or dark-brown, which corresponds to the necrosis of cells.

In monocotyledonous plants, such as grass, the damages may have the shape of chlorotic strips or dashes, located between the parallel ribs. Noteworthy, the damages are visible on both leaf sides. Often, the strongest damages appear at the bents of maize, onion, and grasses, and this may cause full destroy of inter-rib tissues of the damaged plant part.

First symptoms of damage in wood plants have the shape of the isolated discrete dimly-green colored spots. With increase of the number of damaged cells, the spots increase in size, merge, and so become chlorotic, colorless, or dark. Color loss for the upper leaf surface in the wood plants occurs rarer than in grass plants. In the case of strong damages, the injuries may spread across the leaf and, as a result, the symptoms appear on both leaf surfaces.

For coniferous species, the characteristic symptoms include the appearance of chlorotic spots on old needles, which then evolve into reddish-brown necroses spreading from the ends of the needles. Reduction of photosynthesis causes the stress, which leads to terminal crown drying. At the initial injury stage in 1–6 week old needles there appear silvery-, pinkish-, or reddish-colored chlorotic spots. Then, these injuries evolve into burns of the needle ends, which leads to the deformation and drying of trees. This disease, known as the "chlorotic dwarfness," was described as early as in 1908, but until 1960s its cause was not determined.

At present, for characterization of the level of plant response to increase of ozone concentration the term "sensitivity" is widely used,[140] and a number of the generalized characteristics of ozone effect on the plants over a certain period (t_1, t_2) is used. Most widespread characteristics are:

dose, which is the integral of the external concentration N_3:

$$D = \int N_3(t)\mathrm{d}t;$$

mean concentration

$$\overline{N}_3 = D/(t_2 - t_1);$$

maximum concentration

$$N_{3\max} = \max\{N_3(t)\};$$

index

$$\text{AOT} \int [N_3(t_m) - N_3(t_0)]\mathrm{d}t,$$

which means the integral of above-threshold excess of the concentration over the exposure time N (AOT is abbreviation for accumulated over threshold).

In accordance with Ref. 169, the critical ozone levels for plant protection are defined. They reflect the total effect of ozone abundance in excess of threshold concentration equaling to 40 ppb, and are designated as AOT40. AOT40 are calculated in the form of the differences between hourly concentration and 40 ppb for every hour when the concentration exceeds 40 ppb.

Numerous studies devoted to estimation of AOT40 for plants[170-181] indicate that in most cases this value is justified. Though, for certain species, AOT30 and even AOT20 should be introduced.

In addition to AOT estimation, there are some other approaches to rating the ozone effect on the plants. For instance, New Zealand ecologists have established the following thresholds[182]: 200 μg/m³ for 1 h, 65 μg/m³ for 24 h, and 60 μg/m³ for 100 days of the growing season. The corresponding values for Uzbekistan are: 61 μg/m³ in 1 h and 29 μg/m³ for 1 day.[183]

Plants differently respond to increase of ozone concentration. Most sensitive species are summarized in Table 11 from Ref. 140, where the corresponding references can be found.

Table 11

Wood plants	Agricultural species
Sugar maple	Cultivated onion
Weeping birch; white birch	Peanut
Red ash; American ash	Swede, rape
Liquidambar	Turnip
Tulip-tree	Soy, lettuce
Weymouth pine; loblolly pine; Virginia pine	Tomato, tobacco
Poplar	Haricot
Almond-tree	Wheat
Oak	Corn

The response of plants to increased ozone concentration by a decrease of crop productivity is illustrated in Table 12 from Ref. 184.

It should be underlined that the decrease of crop productivity results in serious economical losses Estimate, obtained for the USA gives the value from 1.89 to 3.3 trillion dollars annually.[185] This problem is treated in many publications.[186-190]

Table 12. Decrease of productivity (in % relative to the control group) of certain species in USA, caused by ozone

O_3 concentration, μg/m³	Wheat	Corn	Soya beans	Spinach	Turnip
120	8.7–14.2	3.8	7.8–21.7	18.5–21.0	26.8–31.0
200	18.6–34.0	8.1	26.4–46.5	40.0–44.8	57.4–66.4

One of the features of the effect of phytotoxic gas admixtures of the atmosphere on the plants is the phenomenon of synergism, i.e., when the total effect of two or many gas components on the plants is not equal to the net effect of each gas separately.[191] The total effect may be either stronger or weaker than the effect of each gas.

A 2-h exposure to air mixture, containing 0.24 ppm of sulfur dioxide and 0.03 ppm of ozone, leads to injure of tobacco leafs.[192] However, in case of sequential fumigation with air mixture, containing solely sulfur dioxide and then solely ozone in the same concentrations, for the same time interval no visible leaf injury was observed.

The nitrogen dioxide has distinctly pronounced stimulating effect on the growth of plant crown, whereas exposure to solely ozone markedly inhibits the growth. Sequential impacts of these compounds leads to simple net effect, influencing the plant growth rate (negative ozone effect is neutralized by positive effect of nitrogen dioxide).[193] Moreover, the estimate of the consequences of exposure of the plant to a mixture of these gases is masked by a pronounced difference in the effects on individual plant organs. Overall, the net effect of plant treatment with O_3 and NO_2 does not exceed the total effect.

Similar result was reported[194] for the mixture of carbon dioxide and ozone. Table 13, borrowed from Ref. 194, shows that ozone can significantly modify the positive effect. The increase of O_3 concentration can substantially reduce the stimulating effect of CO_2, totally suppress it, or even lead to the negative effect. In this regard, the authors call their attention to adopted tendencies of future CO_2 change in creation of scenarios of global climate warming.

Noteworthy, most significant synergic effect is observed for ozone in combination with peroxyacetyl nitrates (PANs). PAN, like ozone, is the product of photochemical reactions, proceeding in the atmosphere, and is present in the air simultaneously with ozone, though its concentration, on average, is 10 times lower. It was found that the joint effect of ozone and PAN on poplar and haricot leaves exceeds the net effect of each component separately.[195,196]

The synergism effect serves the basis for methods of reduction the negative ozone effect on plants.[197-202] For this, the antiozonant N-[2-(2OXO-I-imidazolidinyl)ethyl]-N'phenylurea is used (EDU). It either is used to treat the plants themselves or their root system. The negative ozone effect can be almost completely eliminated.[197-202]

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Table 13. Change of biomass production of agricultural species (%) for cultivation period due to change of CO_2 and O_3 concentrations

Increase of CO_2 concentration, ppm	Increase of O_3 concentration, ppm			
	0.0	0.010	0.020	0.024
	Corn			
0	0.0	−5.4	−11.6	−12.6
50	7.9	2.1	−4.6	−5.7
100	16.5	10.2	3.0	1.8
150	25.8	19.0	11.2	9.9
	Legumes			
0	0.0	−22.2	−39.5	−45.2
50	14.1	−11.2	−31.0	−37.5
100	30.2	1.3	−21.4	−28.7
150	48.6	15.6	−10.1	−18.6

The problem of influence of the pollutants on the plants is very serious, and this brief overview cannot elucidate it completely. A large amount of information can be found in the literature on the subject or in databases.[203,204]

2.4. Influence of ozone on materials

At standard air temperature, most metals are oxidized by ozone. Silver is blackened in the ozone-containing air; and reaction of ozone with mercury results in formation of the monoxide HgO.[4] Ozone can form ozonides of alkali metals, most familiar of which are potassium and ammonium ozonides. They are red-colored, paramagnetic, and can be considered as stable radicals.

Reactions of ozone with surfaces are of interest because of the following problems: transport of ozone-containing gas mixtures, selection of catalysts for ozone destruction, and protection of materials from corrosion.

Glass, fluoroplastic, and certain metals and their oxides (Ni, W, CrO_3, CdO, Bi_2O_3) have comparatively little influence on the ozone destruction rate.[4] Such compounds as NiO, NiO − Fe_3O_4, and hopcalite increase the ozone destruction by a factor of 10 … 100 in comparison with the above-mentioned species. Ozone is destructed most vigorously in reactions with activated charcoal carbon, metals of variable valence (Mn, Co, Fe), phosphoric anhydride P_2O_3, and barium peroxide BaO_2.

When studying ozone passage through the tubes from different materials,[205] it was found that the teflon tubes transported ozone without losses, glass tubes required short-term pre-exposure to ozone, and tubes from stainless steel, aluminium, and mylar had to be exposed to ozone at 0.01 ppm for a few hours before they could ensured the ozone safety up to 90% of the initial level. Therefore, it is recommended to use the teflon tubes when operating with ozone,[205] though it is reported[206] on the ability of the teflon to interact with ozone, yielding CO_2 and CF_2O.

A number of works pointed out to the joint effect of ozone and other oxidants on corrosion of metals.[207–209] However, the attempts to separate out the individual role of ozone failed.

Ageing and destruction of the natural caoutchouc was always associated with atmospheric effects. It has been thought for long time that these processes are the result of the action of the solar light. Then it was shown that just the ozone is the primary factor causing atmospheric ageing.[210]

Influence of atmospheric phenomena on elastomers and its economic consequences, as well as creation of compliments for rubbers, which increase the resistance to the ozone effect, is discussed in Ref. 211. The rapture of the natural caoutchouc is initiated by the reaction of ozone with double bond. As a consequence, the synthetic elastometers, such as styrene-butadiene, polybutadiene, polyisoprene, are also sensitive to ozone action.

The dependence of the degree of rubber damage on ozone concentration was a subject of many researches. Mostly, such experiments were performed at a high ozone concentration with the use of unstable (antiozonant-free) rubber types.

One of the rare exceptions is the studying of the effect of ozone at about 490 $\mu g/m^3$ concentration on two styrene-butadiene caoutchoucs at several concentrations of antiozonating additives.[212] In climatic chamber measurements, the samples of caoutchouc, used for fabrication of the lateral surfaces of the armed automobile tires, were exposed to ozone at concentrations of 160 and 1000 $\mu g/m^3$ and at two values of deformation (10 and 20%) for 1000 h. The test results are presented in Table 14.
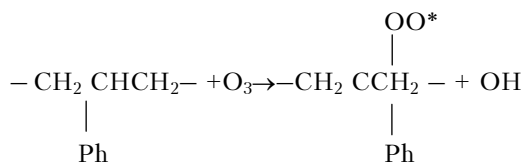
Table 14. Tire sample destruction rates

Ozone concentration, $\mu g/m^3$	Deformation, %	Average destruction rate ± SD, $\mu m/yr$
160	10	10.36 ± 7.76
	20	11.70 ± 7.22
1000	10	19.80 ± 9.64
	10	24.09 ± 6.24

As is seen, the destruction rate depends on ozone concentration and, to a certain degree, on the value of the deformation.

The studies of the ozone effect on the cotton fabrics in test chambers was reported in Ref. 213. The obtained data suggest that, as the ozone concentration increases from 40 to 120 $\mu g/m^3$, the fabric strength decreases by approximately a factor of three. However, the rate of ozone-induced fabric destruction depends on the fabric type. Most intense destruction occurs for fabrics from polyester and nylon[214]; therefore, to decrease the ozone-induced losses in the course of fabrication of synthetic fabrics, the special additives, namely, antiozonants (antioxidants), are used.

There is an evidence for destruction of plastics by ozone. The polysterene is typical to exemplify this process[215]:

$$-CH_2\ \overset{\displaystyle |}{\underset{\displaystyle |}{CHCH_2}}-\ +O_3 \rightarrow -CH_2\ \overset{\displaystyle OO^*}{\underset{\displaystyle |}{\underset{\displaystyle |}{CCH_2}}}-\ +\ OH$$
$$\qquad\qquad Ph \qquad\qquad\qquad\qquad Ph$$

As is seen, ozone initiates the reaction of growth of oxidation chain.

Interaction of ozone with some types of dyes leads to their destruction, formation of crystals, and loss of color in the colored goods. Most prone to ozone impacts are dyes having the organic compounds in their composition.[216, 217]

In some cases, even the addition of antioxidants ends in failure. For instance, a case is reported,[218] when specially developed blue dyes, resistant to NO_2 effect, lost their color either partially or completely after exposure to ozone.

The initial effect of ozone on dyes consists in intensification of erosion of the paint-and-varnish surface. This parameter is generally determined from the mass loss for a certain time interval.

Laboratory and field experiments were conducted with five paint types[219]: oil and latex paints for home building, urea-alkyd coatings for wires, nitrocellulose acrylic automobile paints, and alkyd industrial coatings. In the experiments, both light-protected and light-exposed samples were exposed to ozone. A significant erosion was observed at an ozone concentration of 2000 $\mu g/m^3$. The maximum erosion rate is characteristic for oil paints. For industrial coatings, an intermediate level is recorded. The minimum erosion was observed for latex and automobile paints, as well as coating for wires. In the absence of protection from light, the erosion rate was higher. The results of field experiments were not unambiguous. They have shown a dependence on the location of experiments.

Four dye types were studied in the climatic chamber[220]: oil paint for home building, vinyl acrylic latex for home building, and vinyl and acryl insulation for wires. The purpose of the experiment was to separate the contributions of SO_2, O_3, and NO_2 and to identify some other environmental factors. The statistically significant effects, associated with ozone exposure, were revealed for vinyl and acrylic insulation of wires. Since the oil paint includes $CaCO_3$ as a filler, which rapidly interacts with moisture and SO_4, the effects associated with ozone have been masked and attempts to separate them have failed. The damage rate of acrylic coating for wires at a 90% relative humidity is described by the empirical formula

$$dx/dt = 0.159 + 0.000714 O_3,$$

where dx/dt is in $\mu m/yr$; and O_3 concentration is in $\mu g/m^3$.

Because the ozone effect is statistically significant for an average ozone concentration of 100 $\mu g/m^3$, it has been found with the help of this equation[220] that the service life of 20-μm thick paint-and-varnish coating is about 80 years.

2.5. The use of ozone in technological purposes

Ozone is applied most actively and broadly in medicine. A detailed overview of establishment of ozonotherapy as a branch of medicine is presented in Ref. 221. Let us use this overview to highlight the main milestones in this way.

In 1873, J. Foket observed dying of microorganisms, exposed to ozone. The inventor N. Tesla patented the first ozone generator on September 22, 1896. In 1901, "Siemens" built first power plant with ozonizer installation in Wiesband.

Unique ozone properties attracted attention of physicians as yearly as in beginning of nineteenth century. In 1911, Eberhart used ozone in treatment of tuberculosis, anemia, pneumonia, diabetes, and other diseases. During the First World War, A. Wolf applied the oxygen-ozone mixture to treat festering wounds, complex fractures, phlegmons, abscesses of injured humans.

Studies of the medicinal ozone effect continued until the Second World War. In 1921, H. Kleinmann applied ozone to a general treatment of "cavities of the body." In 1930s, the dentist E. Fish described his rich experience in ozone application in this area in Italian, French, and German publications, and then in 1950s he wrote an extended dissertation on the basis of this material. Fish began treatment with ozone in practice. In the application form for invention of the first laboratory device, Fish proposed the term "CYTOZON," which even today is the name of ozone generators used in dental medical practice. Y. Henzler created first medical ozone generator, which allowed the precise dosing of ozone-oxygen mixture and, thereby, created the possibility for wide application of ozone therapy. P. Auborg revealed the effect of cicatrization of ulcers of large intestine after ozone exposure and concentrated his attention on the character of its general effect on the organism. During the Second World War, the studies of the medicinal effect of ozone were actively continued in Germany. German physicians successfully applied ozone for local treatment of wounds and burns. However, after war, the studies were interrupted for almost 20 years, primarily because of advent of antibiotics, the absence of reliable, compact ozone generators and ozone-resistant materials.

In the early 1970s it had been clear that the antibiotics are incapable to solve completely the problem of purulent-septic diseases. Recognition of this fact motivated the development of the methods of ozone therapy at a new scientific and technical level. Extensive and systematic studies in the field of ozone therapy had begun in the mid-1970s when there appeared ozone-resistant polymer materials and

user-friendly ozonizer setups in the everyday medical practice.

Interest in ozone therapy had increased as more and more data on biological ozone effect on organism have been accumulated, and as more and more clinics in the world reported on the successful use of ozone for treatment of a number of diseases.

At present, the ozone therapy is widely used all around the world, especially in Germany, Russia, Switzerland, Cuba, Italy, and France. In USA, many private medical associations turned to study the applicability of this method in AIDS treatment. H. Wolf and S. Rilling have founded the German Medical Society for ozone therapy and developed the Society regulations. All medical and research activity of H. Wolf was devoted to ozone. He had many publications devoted to ozone therapy, and was tireless to spread the method around the world.

In November 1973, the International Ozone Institute was founded as a public-scientific and enlightening organization. In 1979, the International Medical Society for ozone therapy begins to work. At present, the association performs widespread operations and actively holds international congresses, whose participants are physicians of different specialties from Germany, Austria, USA, Cuba, Russia, France, Italy, and Japan. In 1983, the Italian Association for ozone therapy was created.

The detailed description of the modern methods in medicine is given in Ref. 222. The authors primarily underline the antimicrobial ozone activity, unique in many respects. The destructive ozone effect manifests itself at concentrations, which the tissue cells of multicell organisms survive relatively easily. It is approximately the same for all types of bacteria, viruses, funguses, microbes, and spores, and even more pronounced for microbial species, possessing the means of an additional protection, in the form of capsules, spores, etc., from environmental factors.

The main reason for such a high sensitivity of unicellular organisms to ozone is the absence of quite developed systems of antioxidant protection. In contrast to more complex organisms, microbes have no mechanisms of recovery of broken nucleotide chains. The second important factor is the large area of the contact with cell surface, where ozone has the possibility to simultaneously attack all external membrane, including its functionally important elements, such as excrescences, creeps, flagellums, cilia, etc.

Ozone appears far more effective than other compounds, applied in the sanitation. This is clearly seen in Fig. 3, plotted by data from Ref. 223.

Figure 3 shows the ozone effect on the death of bacteria *Escherichic coli* in water in comparison with exposure to chlorine. At small ozone concentrations, the ozone effect is insignificant; however, starting from a certain critical point, ozone is much stronger suppresses the bacteria than chlorine.
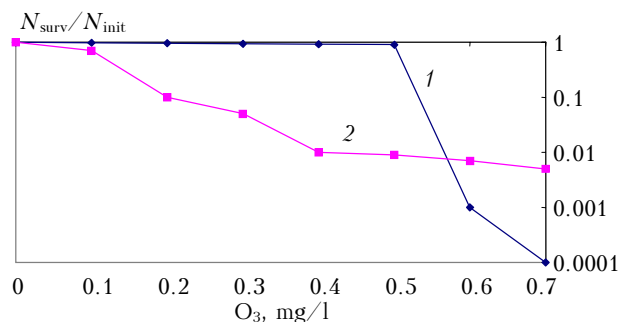

Fig. 3. Survival of microbes for different exposure types: ozonization (curve *1*) and chlorination (curve *2*).

A number of studies[224–228] showed that ozone at a concentration from 1 to 5 mg/l already after a few minutes causes almost 100% death of all pathogenic microfloral species, including gram positive and gram negative bacteria, blue pus bacillus, proteus, microbacteria of tuberculosis, all hydro- and lipophylous viruses (including hepatite of the groups A, B, and C), and all known forms of fungi and primary microorganisms.

The technical implementation of the sterilization methods is described.[222]

Very effectively ozone is used for purification of air in living and industrial buildings.[229,230] The performed experiments revealed that at a concentration between 50 and 100 μg/m³ ozone reduces the microbial semination of air down to the pollution level, characteristic of the clean atmospheric air. Experiments, with conditioners have shown[231] that the addition of ozone at a concentration of 15 μg/m³ to the conditioned air significantly improved the air quality in living and office rooms, made it more comfort for habitants.

Ozone finds increasingly broader application in other branches of economy. For instance, the use of ozone in drying of grain makes it possible to increase the drying rate by 20—25%, as well as to reduce the energy consumption by 20%.[232] In addition to drying, ozone also kills many bacteria, which is widely used for many loose, finely dispersed materials such as grain, seeds, mixed fodder, flour, etc.[233]

2.6. Safety conditions in ozone treatment

Ozone toxicity manifests itself primarily in the inhaled air.[222] In view of its high chemical activity, a minimum of ozone concentration is sufficient to show up its toxic effect. The ozone smell is discernible at sub-toxic concentrations of ~ 20 μg/m³. Ozone markedly complicates the free breath even at a concentration level of 1—2 μg/m³.

In the case of the rapid increase of ozone concentration in closed rooms, it is necessary to switch off the ozone source, ventilate the room, leave it and try to breath the fresh air outdoors.[28] The rooms, where ozone is used constantly in technologic purposes, should be equipped with ozone sensors, and

generators should be placed into draft hoods.[222] The pertinent rules are available in manuals.[235]

High ozone concentrations may also occur in the open air, especially in smog situations. In USA and West Europe, population is given detailed recommendations of how to behave in these cases.[83,84,236,237] At summer time, in periods of hot fair weather, the wind speed is small; therefore, it is necessary to limit the stay in the open air in period from 13.00 to 18.00 LT. Especially strict limitations concern children, elderly, people with lung diseases, and people sensitive to ozone. It is necessary to avoid outdoors physical and labor-intensive exercises at the above-indicated time of the day. In the suburban zone, it is advisable to account for the wind direction and take safety measures in the case of wind from the direction of the town.

In the period, when this overview was under preparation, new publications on the subject appeared. Since they may be interesting to reader involved in the problem, we present the list of such publications.[238-261]

In conclusion, let us briefly inform on the relation of different countries to the problem of growth of ozone concentration in the troposphere. For instance, there are more than 10 thousands of stations of monitoring of ozone and ozone precursors in Europe.[262] The obtained information is used by authority decision-makers. It is very important that this information is brought to public notice. The site in Germany providing for the real-time data on ozone concentration in the atmosphere is most visited. The USA and Europe have already managed to reduce ozone concentration in the atmosphere. There is still no station of monitoring of ozone and ozone precursors in Russia. An exception is the Moscow Ecological Monitoring network, to be built in Moscow; but, of course, it will not solve the problem throughout the country.

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