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ATMOSPHERIC RADIATION, OPTICAL WEATHER, AND CLIMATE

Air-Temperature Dependence of the Ozone Generation Rate in the Surface Air Layer

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Abstract—The temperature dependence of the atmospheric ozone generation rate was studied based on measurements in a reference area. The type of this dependence is determined by the method based on the comparison of variations in the ozone concentration when a hot or cold wave passes above the measurement post. This approach allowed us to derive for the first time the quantitative, but not qualitative, dependence type. The coefficients of the expression used depend on both the air temperature and initial ozone concentration. Thus, at the long-term minimum of the surface ozone concentration (1999) at a temperature of 30°C, its increase of 5 μg/m^3 corresponded to a temperature change of 1°C. At a maximal concentration (2001) and the same temperature, the increase is almost 25 μg/m^3 per 1°C. In the intermediate periods (1997 and 2010), it was about 14 μg/m^3 per 1°C. The analysis shows that the quadratic character of the given dependence is conditioned by the nonlinear increase in reaction constants and the quadratic increase in hydrocarbon emissions by vegetation with increasing air temperature.

Keywords: atmosphere, dependence, air, ozone, surface air layer, temperature

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INTRODUCTION

Ozone is a trace atmospheric gas. It is not emitted by natural and anthropogenic sources but is generated from precursor gases directly in the atmosphere during photochemical processes. The diversity of the precursor gases and complexity of ozone generation determine the fundamental direction in its investigations. The practical significance of these investigations is conditioned by the properties of ozone. It is a strong oxidant, which has a destructive effect on the environment. In high concentrations, it is a poison contaminating the biosphere. Ozone is a radiatively active gas, the fourth in significance among the gases contributing to the greenhouse effect in the atmosphere.

Ozone is one of the most studied admixtures in air. A voluminous literature is devoted to its study. However, many fundamental problems of its generation and transformation in the atmosphere remain little studied.

In a recently published review [1], composed by an international group of scientists, it is noted that the main variations in the ozone concentration in the troposphere are determined by three basic factors: the emission of the precursor gases and their composition and concentration; solar radiation influx; and meteorological conditions.

Most often, when interpreting ozone measurements and causes that determine variations in the gas concentration, a statistical diagnostic model is built based on correlational relations. The simplest models consider the air temperature, humidity, and pressure; wind speed; and solar radiation [2]. The authors of work [3] neglect solar radiation but introduce precipitation as one of the factors. They found a significant increase in ozone concentration with increasing air temperature, but the form of the dependence is not given. The model [4] includes such meteorological parameters as the maximal air temperature, relative humidity, solar radiation, soil radiative temperature, pressure, wind speed, and general cloudiness. The conclusion was drawn in that work that the dependence of the ozone concentration on meteorological conditions is complex and nonlinear. The strongest connection is between ozone and maximal air temperature. In the model [5], in addition to meteorological parameters, NO_2, SO_2, CO, PM_{10}, cloudiness, and visibility were added. As the result of the analysis, a positive correlation of the ozone concentration variation with the air temperature and a negative correlation with cloudiness were found. A similar result was also found in [6], where it was shown that, on average, the ozone concentration was by 12 ppb lower on cloudy days as compared to clear ones.

Models based on the empirically found relations between the ozone concentration and primary predictors, including meteorological parameters, intensity of solar illumination, characteristics of the atmospheric gas composition, and the ozone concentration in preceding days, began to be used for prognoses. For the first time, such relations were stated at American and West European stations [7–13], when analyzing the ozone concentration measurements, and then they were confirmed by the analysis of observation data from Russian areas [14–20]. These models are based on the same above-described predictors. Taking into account the difficulties in retrieving reliable information on air concentrations of trace gases—ozone predictors—the model can be sufficiently effective in the cases, where anthropogenic emissions of these predictors vary comparatively weakly from day to day and from year to year, while the natural emissions and processes of accumulation and scattering in the surface air layer are conditioned mainly by the meteorological situation. However, prognostic models in no way reveal physical or prognostic patterns.

There is a series of works in which the authors did not build diagnostic or prognostic models but conducted a correlation analysis of individual meteorological parameters, characteristics, or events [21–24].

Thus, in [21] the ozone concentration variation was studied as a function of meteorological parameter values, UV–B radiation, and radon. The strongest correlation was revealed between O_3 and UV–B radiation (a correlation coefficient of 0.52). The authors of [22] concluded that the ozone concentration growth was fixed at a low negative humidity, high values of temperature and solar radiation, and dry weather; however, they did not present quantitative criteria. A similar investigation [23] shows that considering meteorological parameters, solar radiation, soot, and aerosol allows description of 91% of variations in the ozone concentration.

Interesting results were found in [24] from the analysis of the event with strong fires in the Moscow region. The correlation coefficient between ozone and air temperature reached 0.82 in 2010 in the lower 300-meter layer. In 2011, it decreased to 0.63. The correlation coefficient in the case of the relative humidity turned out to be negative (–0.66). The transition to the absolute humidity when excluding its dependence on the temperature, showed a lack of the correlation in 2010 and a significant negative correlation (–0.48) in 2011. The role of the wind was distinctly related to the direction of the precursor gas emission. The influence of UV–B radiation under smoke conditions in 2010 was lower than under standard conditions in 2011 (coefficients of 0.56 and 0.74, respectively).

Quite a few works are devoted to investigation of the influence of individual factors on the ozone concentration variation. Among them, air temperature is the most significant. This factor is also important in connection with the prediction of the climate warming, which can stimulate additional ozone generation [25, 26]. Moreover, some authors note that simultaneous increase in the ozone concentration and air temperature is accompanied by an increase in mortality in the population [27–29]. This, possibly, points to the synergetic effect of these processes.

Along with the abovementioned works, the increase in ozone concentration with air temperature is noted in a series of publications [30–35]. However, the type of this dependence is not specified. In [36, 37], the authors tried to determine the type of the dependence of ozone concentration variation on the temperature increase. The approximations derived showed a linear dependence. In [38], the authors also noted the linear character of the relation between temperature and ozone; however, the figure presented clearly showed the nonlinear dependence. The nonlinear variation in the ozone concentration at high temperatures was revealed in [39]. Moreover, it turned out that at temperatures of about 40°C the curve changed its slope downwards to negative. The nonlinear dependence of the ozone concentration on the temperature as the latter increases should be due to two causes. First, in most of the reactions in which ozone is generated have an exponential or quadratic dependence [40]. Second, the dependence of the emission of ozone-forming organic gases from natural sources is also close to quadratic [41–45]. In this case, as shown in [46], organic compounds contribute no less than 50% to the initial compounds from which ozone is generated.

Some scientists called attention to the synchronism in the increase in the ozone concentration and air temperature in heat waves [47–49]. Despite the well-expressed diurnal behavior of both parameters, the increase in ozone and temperature was observed during 5–7 days after a change in air masses. The superposition of plots shows that these processes are almost synchronous [47]. The authors of [49] determined that a 10-ppb-increase in ozone corresponds to a temperature increase of 5°C. They note that the content of organic gases of biological origin increases by 10 ppb per day in heat waves.

We have analyzed the ozone behavior not only in heat waves, but also in cold waves [50]. It turns out that the same processes are observed in cold waves, but with the inverse sign. After a change in air masses, when the air temperature decreases during the same 5–7 days, the ozone concentration decreases. Based on this fact, we have revealed the type of dependence of the ozone concentration variation on the air temperature as the latter is rising or falling.

ANALYTICAL TECHNIQUES

Data from the TOR station (56°28′41″ N, 85°03′15″ E) were used in our analysis. The initial variant of the station is described in [51]. It is an auto-

matic post located in the building of the Lidar Station of IAO SB RAS located at the north-eastern outskirts of Akademgorodok (Tomsk). There are no industrial facilities and highways near the station: therefore, the influence of local sources of gases and aerosols is weak. Since the station is situated in the boreal forest zone, it is surrounded by small zones of coniferous and foliage forests. When air masses are transported from the west, the site is under the influence of air passed above Tomsk city and enriched with industrial and transportation emissions. In all other cases, air comes from reference regions where there is a high proportion of forest mass and they are free of industrial facilities. More detail about this is given in [52].

As a measure of the surface ozone concentration, we use a 3-02P semiluminescent gas-analyzer (OPTEK Ltd., St. Petersburg) and a TEI UV ozonometer, model 49 (United States). They are regularly calibrated with the help of the GS-024-2 generator of the same manufacturer. The earlier conducted intercalibration of the ozonometers [53] showed the UV ozonometer to overestimate the ozone concentration under smoke conditions. At the TOR station, air intake is performed through Teflon tubes from an altitude of 5 m. Measurements at the post are conducted hourly around the clock. Readings are taken with a frequency of 1 Hz and then are ten-minute averaged. The station has been working from December 1993 to now.

Earlier [54], we studied the ozone concentration variations during the passage of atmospheric fronts. In that case, significant temperature variations accompanied by high gradients of the ozone concentration were also observed. However, such processes are connected with a change in air masses, having various origins and, consequently, various temperatures and air compositions. Therefore, such events are unsuitable for revealing correlations between the air temperature and ozone concentration. Under anticyclone conditions, long periods (of several days) are observed where temperature decreased or increased. This process is accompanied by an increase or decrease in the ozone concentration in the surface air layer. Similar processes were also observed in [47–49].

As an example, Fig. 1 shows periods with heat and cold waves recorded at the TOR station in August 1997.

Figure 1a shows that in the period from August 1 to 7, 1997, a heat wave was observed near Tomsk, during which the maximum air temperature increased from 24 to 30°C, despite well-expressed diurnal behavior. This temperature increase was accompanied by the increase in the surface ozone concentration from 92 to 121 μg/m^3. The start and terminal points of the process are connected by arrows. The inverse process is shown in Fig. 1b, which shows a five-day cold wave from August 19 to 24, during which the air temperature decreased from 27.8 to 21.2°C, the ozone concentration, from 160 to 80 μg/m^3.

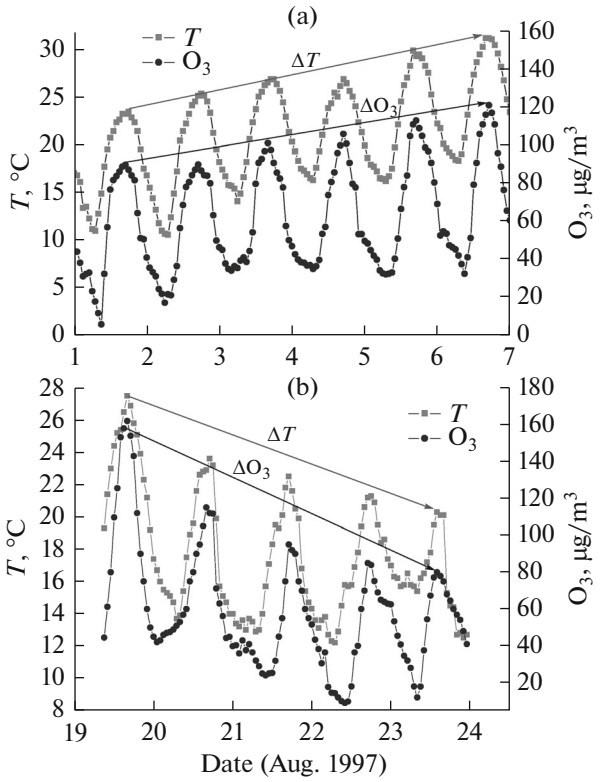

Fig. 1. Variations in the air temperature (T) and surface ozone concentration (O_3) in Tomsk during (a) heat and (b) cold waves.

Cold and heat waves differ in length. Consequently, the differences between temperatures and ozone concentrations also differ even with a linear dependence between them. However, based on data mentioned in the Introduction, it should be assumed that they must nonlinearly depend on the temperature and increase with it. Therefore, to compare differences in ozone concentration values at different temperatures, ozone differences were normalized to temperature differences $(O_{3t} - O_{3s})/(T_t - T_s)$ (indices "t" and "s" denote terminal and start values of the corresponding parameters). During the processing, the normalized differences were correlated with the mean temperature of the particular cold or heat wave $(T_t + T_s)/2$.

Many authors called attention to the complex dependence of the ozone concentration differences on the air temperature. The dependence is affected by such factors as the season, local properties, presence of local sources of the ozone-forming gases, etc. Therefore, we have preliminarily selected data before processing.

Earlier investigations near Tomsk showed that even the annual average ozone concentrations can vary severalfold [52, 55]. The same is seen in Fig. 2, supplemented by the later data. Therefore, we processed data for four years, shown in Fig. 2 by circles, when the observation-period absolute minimum (1999) and

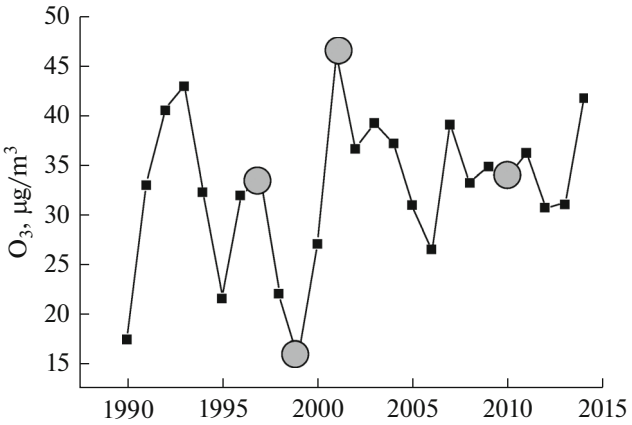

Fig. 2. Variations in the annual average surface ozone concentration near Tomsk between 1990 and 2014.

absolute maximum (2001) and mean values (1997 and 2010) of the surface ozone annual average concentrations were recorded.

INVESTIGATION RESULTS

Data on the amount of the ozone generation processed by the above-described technqiue are shown in Fig. 3 versus the air temperature. To build the plots, we selected 43 heat and cold waves in 1997 and 1999, 55 in 2001, and 44 in 2010.

Figure 3 allows us to draw few conclusions. First, the dependence of the amount of generated ozone on the air temperature has a nonlinear character in all the years considered and is best described by the second-order exponent.

Second, the amount of the generated ozone at various temperatures significantly changes from year to year. Thus, at the minimum of surface ozone concentration in 1999 [56], at a temperature of 30°C, its change of 1°C corresponds to a concentration increment of 5 μg/m^3. At the concentration maximum (2001), the increment can be almost 25 μg/m^3 per 1°C. For interperiods (1997 and 2010), this value is equal to ~14 μg/m^3 per 1°C.

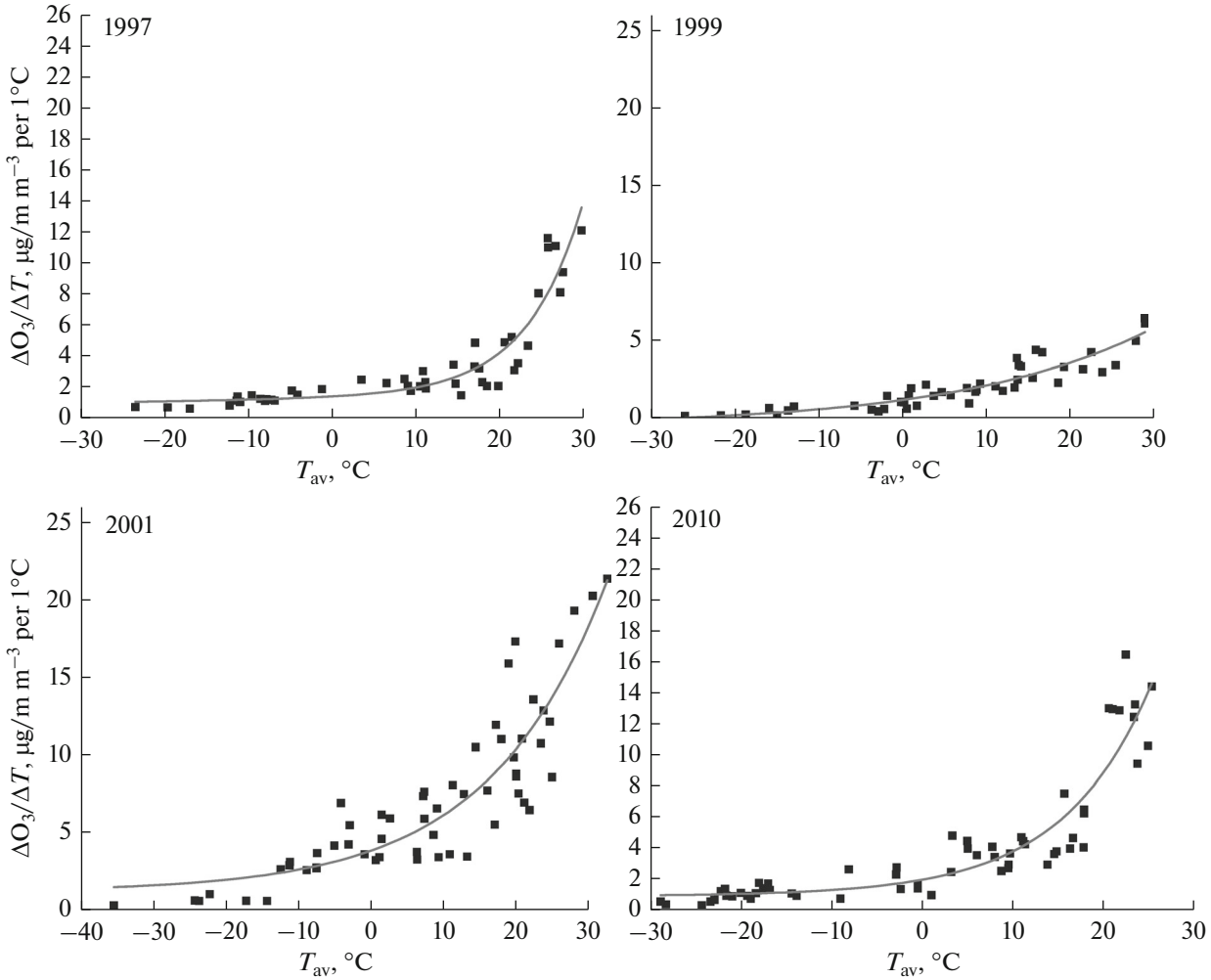

Fig. 3. Variations in the amount of generated ozone as a function of air temperature (T_{av} denotes the average temperature during a heat/cold wave).

Third, the change in the ozone generation volume with the temperature increase from –40 to 0°C is near linear. The nonlinear increase (almost quadratic) begins at positive temperatures. The process activates at an air temperature of >10°C. For climate conditions of Tomsk, this means that ozone is intensively generated, when the underlying surface is free of snow. Correspondingly, the active change by gaseous components between the atmosphere and the surface should be observed.

DISCUSSION

To analyze the processes which can result in a nonlinear relation between the ozone generation rate and air temperature, let us consider the empirical formula for its photo-chemical generation in the form [57]:

$$CO + CH_4 + RH + NO \xrightarrow{h\nu,\ H_2O,\ O_2} fH_2CO + KO_3 + NO_2 + P,$$

where f is the stoichiometric coefficient of transformation of hydrocarbons; K is the ozone yield factor, which depends on the concentration of nitrogen oxides that reverse chains of the ozone generation; and P denotes products of photochemical reactions, i.e., aerosol particles, generated by the interaction of gaseous components.

The empirical formula has a clear physical sense: initial admixtures (CO, CH_4, RH (nonmethane hydrocarbons), and NO), being emitted into the atmosphere, which contains N_2O and O_2, are transformed into more toxic compounds under the action of UV solar radiation ($h\nu$)—H_2CO, O_3, NO_2, and P.

Thus, the amount of the generated ozone depends on the composition and concentration of precursor gases and the solar radiation influx. The processes can branch [57] during photochemical reactions, and different compounds can be involved in the reactions [58]. In this case, the reactions' constants, most of which depend on the air temperature, should also change.

The monitoring of UV-B and total radiation conducted simultaneously with ozone measurements, did not show any significant distinctions between data of 1997, 1999, 2001, and 2010, used in this work [59]. Earlier, it was revealed that solar radiation can cause long-term (5–6 years) [60] or 1–2-month [61] variations in the ozone concentration. Consequently, variations in solar radiation can hardly lead to nonlinear dependence of the ozone generation on the air temperature within a heat or cold wave.

Recall that the photochemical ozone generation begins with photolysis in the ozone troposphere [62]. It is noted in a series of works that the photolysis rate depends on the air temperature [63–65]. This dependence is plotted in Fig. 4 by data [65] in relative units. It is seen that the photolysis rate linearly increases with the temperature. This cannot explain the above-revealed nonlinear correlation.

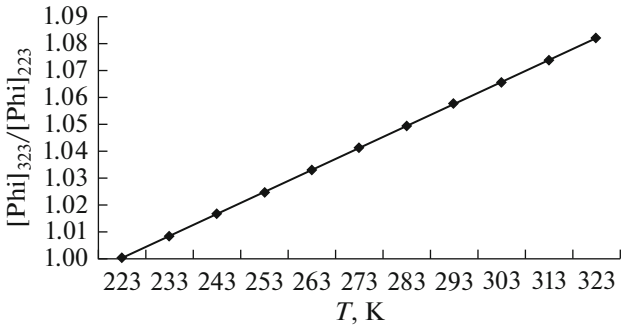

Fig. 4. Dependence of the photolysis rate on air temperature.

Let us consider how the reactions' constants vary under variations in the air temperature. To do this, let us select the most characteristic reactions for ozone cycles from the available database [40]. The selected reactions, resulting in ozone generation in the troposphere, are gathered in Table 1. Figure 5 shows the reaction rates calculated by formulas from Table 1 for the temperature range that occurs in the actual atmosphere (–50° to +50°C). To compare constants at different temperatures, their values are normalized to their magnitudes at a minimal temperature of –50°C.

The computations showed that the reaction rate can both increase and decrease as the temperature increases. Therefore, all selected reactions were divided into two groups: those rates of which decrease (Fig. 5a) and increase (Fig. 5b) with the temperature increase.

It is seen in Fig. 5 that the deceleration of reactions with the temperature increase is almost linear and the reaction rate can change by up to three times within the temperature range –50° to +50°C. On the contrary, rates of certain reactions increase by up to 95 times in the same range. This points to the fact that depending on the composition of precursor gases, the amount of the generated ozone can nonlinearly increase with the air temperature.

Alongside with the ozone generation in the process of photochemical reactions, its depletion takes place, as in the course of other nonphotochemical reactions omitted here, and during the ozone interaction with atmospheric gases and aerosols [66]. Reactions, taking part in the ozone sink from the atmosphere, are gathered in Table 2. Figure 6 shows results of computation by these formulas with the constants tabulated; the data are also normalized to the constant values, corresponding to the minimal temperature.

The curves in Fig. 6 show that at interaction with different compounds the rate of the ozone destruction nonlinearly varies and can increase up to 38 times within the temperature range from –50° to +50°C. Consequently, the ozone sink can also nonlinearly depend on the air composition.

Table 1. Reactions and constants from cycles of photochemical ozone generation

Reaction	Constant
$O + O_2 + M \rightarrow O_3 + M$	$6.0 \times 10^{-34}(T/300)^{-2.6}$
$H + O_2 + M \rightarrow HO_2 + M$	$5.4 \times 10^{-32}(T/300)^{-1.8}$
$O + HO_2 \rightarrow HO + O_2$	$2.7 \times 10^{-11}\exp(224/T)$
$O + H_2O_2 \rightarrow HO + HO_2$	$1.4 \times 10^{-12}\exp(-2000/T)$
$HO + HO + M \rightarrow H_2O_2 + M$	$6.9 \times 10^{-31}(T/300)^{-0.8}$
$O + NO + M \rightarrow NO_2 + M$	$1.0 \times 10^{-31}(T/300)^{-1.6}$
$O + NO_2 \rightarrow O_2 + NO$	$5.5 \times 10^{-12}\exp(188/T)$
$HO + CH_4 \rightarrow H_2O + CH_3$	$1.85 \times 10^{-12}\exp(-1690/T)$
$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$	$8.6 \times 10^{-29}(T/300)^{-3.4}$
$HO + C_2H_6 \rightarrow H_2O + C_2H_5$	$6.9 \times 10^{-12}\exp(-1000/T)$
$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$	$8.0 \times 10^{-27}(T/300)^{-3.5}$
$HO + C_3H_8 \rightarrow H_2O + C_3H_7$	$7.6 \times 10^{-12}\exp(-585/T)$
$HO + \alpha$-pinene $\rightarrow$ products	$1.2 \times 10^{-11}\exp(440/T)$
$HO + CO \rightarrow H + CO_2$	$9.1 \times 10^{-19}T^{1.77}\exp(580/T)$
$NO_3 + C_2H_4 \rightarrow$ products	$3.3 \times 10^{-12}\exp(-2880/T)$
$NO_3 + C_3H_6 \rightarrow$ products	$4.6 \times 10^{-13}\exp(-1155/T)$
$NO_3 + n\text{-}C_4H_{10} \rightarrow$ products	$2.8 \times 10^{-12}\exp(-3280/T)$
$NO_3 + \alpha$-pinene $\rightarrow$ products	$1.2 \times 10^{-12}\exp(490/T)$

Thus, depending on the air composition, a nonlinear increase in ozone generation and depletion with air temperature is possible. Because of competing processes acting in the atmosphere, which lead to both generation and destruction of ozone [57], its final content is determined by the balance of these processes. Therefore, the question is how the atmospheric composition depends on the air temperature.

The earlier published review [67] on sources and sinks of ozone precursors and components participating in ozone cycles, failed to reveal the dependence of their sinks on the air temperature. The only exception

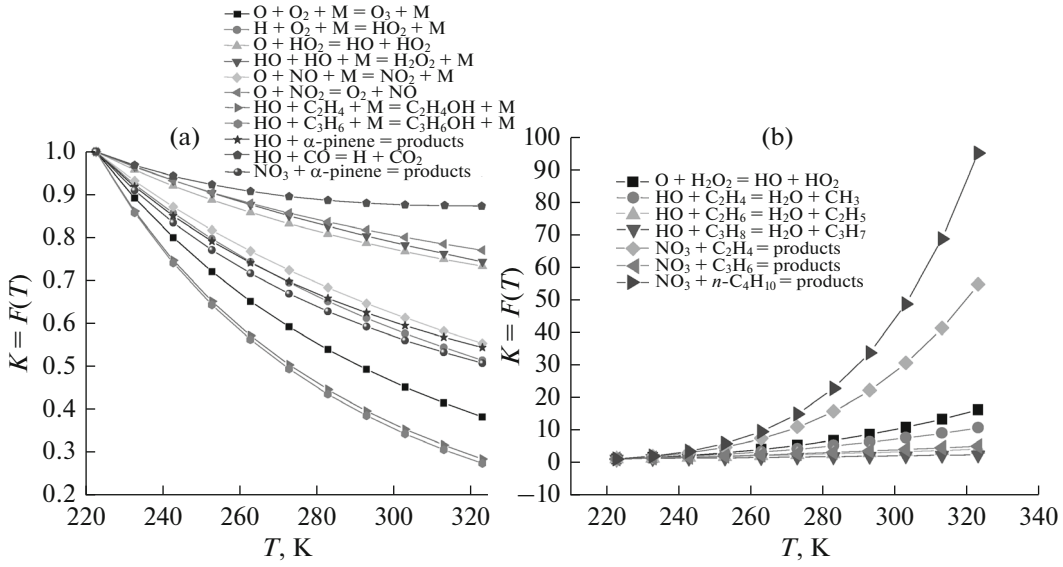

Fig. 5. Rates of ozone cycle reactions at different temperatures.

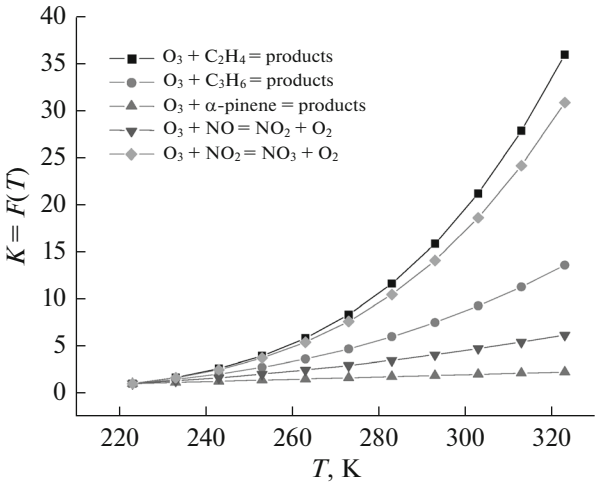

Fig. 6. Rates of ozone reactions with gaseous components at various temperatures.

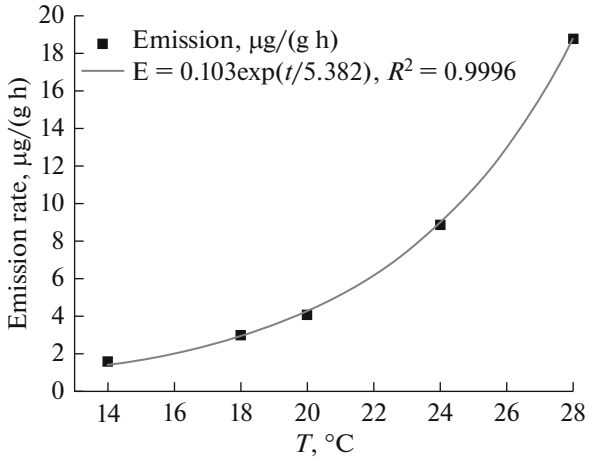

Fig. 7. Rate of terpene emission by pine needles versus air temperature.

are organic gases of natural origin. Figure 7 shows the example of terpene generation by pine needles depending on the air temperature. The plot is built from data in the Table, published in [41].

Figure 7 shows the positive nonlinear dependence of the terpene emission rate by pines on the air temperature. Thus, at a temperature of 14°C the rate is 1.6 μg/(g h), and at 28°C it is even 18.8 μg/(g h). The change in temperature by 14°C leads to an emission increase by 11.75 times.

Table 2. Reactions and constants determining the ozone sink from the atmosphere

Reaction	Constant
$O_3 + C_2H_4 \rightarrow$ products	$9.1 \times 10^{-15}\exp(-2580/T)$
$O_3 + C_3H_6 \rightarrow$ products	$5.5 \times 10^{-15}\exp(-1880/T)$
$O_3 + \alpha$-pinene $\rightarrow$ products	$6.3 \times 10^{-16}\exp(-580/T)$
$O_3 + NO \rightarrow NO_2 + O_2$	$1.4 \times 10^{-12}\exp(-1310/T)$
$O_3 + NO_2 \rightarrow NO_3 + O_2$	$1.4 \times 10^{-13}\exp(-2470/T)$

Many studies of the emission rate of organic gases by vegetation are currently being conducted. A part of them is devoted to the dependence of the emission on air temperature. All of them show the nonlinear increase in the emission rate with temperature (see, for example, [42–46]).

CONCLUSIONS

The dependence of the ozone generation rate in the atmosphere on the air temperature is studied using measurement data from the reference region. The nonlinear character of the dependence is revealed. Thus, at the long-term surface ozone concentration minimum in 1999 at a temperature of 30°C an ozone concentration increment of 5 mg/m^3 corresponds to a temperature change of 1°C. At the concentration maximum (2001) at the same temperature, the increase can be about 25 μg/m^3 per 1°C. For intermediate periods (1997 and 2010), this magnitude is about 14 μg/m^3 per 1°C.

The analysis of possible causes of the nonlinear character of the dependence shows it to be conditioned by a nonlinear increase in the reactions' constants with the air temperature and a quadratic increase in hydrocarbon concentrations.

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