PROBLEM OF TROPOSPHERIC OZONE AND SOME RESULTS OF ITS MEASUREMENTS

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This paper presents a review of tropospheric ozone photochemical formation theory and some data on ozone spatiotemporal variability.

INTRODUCTION

Ozone was discovered in 1840 by Schonbein,[1] a chemist from Basel. Since then, as Khrgian[2] noted, the intensity of atmospheric ozone research had a few periods of elevation and fall caused by the appearance of new data on its properties.

It has been revealed to date that the stratospheric ozone is a protective layer of the atmosphere that prevents the hard UV radiation of the Sun from falling on the Earth's surface and killing all biological activity on the planetary surface.

Tropospheric ozone formed *in situ* in the ground air layer is the substance related to the first class of danger. Its high concentration strongly suppresses vital activity of vegetation and variously affects human body. As biological and medical researches shown,[3] ozone is the strong poison that, in addition to its general toxic effect, has such properties as mutagenicity, carcinogenicity, and radiomimetic effect (effect on blood similar to that of ionized radiation). Toxicity of ozone is stronger than that of hydrocyanic acid.

The following classification of ozone toxicity is given by Hoppe[4]: a dose $\geq 120\ \mu g/m^3$ causes the decrease of capacity for work under a heavy physical load; $\geq 160\ \mu g/m^3$ causes deterioration of lungs function; $\geq 200\ \mu g/m^3$ causes cough, hoarseness, and tickle in throat; $\geq 240\ \mu g/m^3$ causes a loss of sensitivity to other irritating substances and allergens; and a dose $\geq 400\ \mu g/m^3$ causes inflammation of lower respiratory ducts with possible lethality.

Apart from the effect on human being and vegetation, ozone is the most powerful oxidant destroying rubber and oxidizing many metals including that of the platinum group.[5]

Tropospheric ozone has the long lifetime in the atmosphere (from several days to several months) and intense absorption lines and hence it must play an important role in the greenhouse effect. According to the estimates made in Ref. 6, its contribution to total heating of air, caused by absorption of solar radiation by greenhouse gases, may exceed 8%. The data of calculations reported by Megie et al.[7] give even greater value, from 25 to 60%.

A variety of consequences of negative effects of ozone on human being and environment has attracted attention to the tendencies of variation of its concentration. According to the data of Ref. 4, ozone content in the troposphere increased by 60%, on average, in the last 30 years. The beginning of the increase of ozone concentration was observed in 1895. It increased five times since that time.[7] Such an increase of the ozone concentration in the troposphere did not occur by itself, it was the result of the increase of the number of ozone-producing photochemical reactions caused by the development of industry in the last 100 years. Industrial emissions (up to 60000 different substances[8]) significantly increased the number of primary air ozone-producing impurities as well as the number of photochemical reactions in the atmosphere in which it can appear or take part. The expert group on chemical kinetics CODATA/IUPAC recommended in the review on atmospheric photochemistry to take into account more than 400 such reactions for numerical modeling.

Thus, ozone, which is the product of photochemical reactions and takes part in them, is the quintessence of all photochemistry of the atmosphere. It is no mere chance that some international organizations such as WMO, WHO, etc. recommend to assess the air quality in populated areas based on the data on the ozone concentration. Many foreign countries included ozone into the list of five substances to be monitored compulsory in the ground atmospheric layer. Russia has not yet done it.

FORMATION OF OZONE AND OTHER SECONDARY IMPURITIES IN THE ATMOSPHERE (CONCISE HISTORY OF THE THEORY DEVELOPMENT)

There were several periods in the development of the ozone formation theory.

At the beginning, Chapman[10,11] proposed the theory of ozone formation in reactions with particles containing only oxygen:

$$O_2 + h\nu \rightarrow O + O, \qquad 150 \leq \lambda \leq 300\ \text{nm}$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + h\nu \rightarrow O_2(^1\Delta g) + O(^1D), \quad 180 \le \lambda \le 300 \text{ nm}$$
$$O_3 + O \rightarrow 2O_2\,.$$

Then the reactions of vibrational and electronic excited states of particles were added to this cycle[12]:

$$\begin{aligned}
&O_3 + O(^1D) \rightarrow 2O + O_2 \\
&\qquad\qquad\quad \rightarrow 2O_2(^1\Delta g) \\
&O_3 + O_2(^1\Delta g) \rightarrow O + 2O_2 \\
&O_2(^1\Delta g) + M \rightarrow O_2 + M \\
&O_2(^1\Delta g) \rightarrow O_2 + h\nu \\
&O(^1D) + M \rightarrow O + M \\
&O + O + M \rightarrow O_2 + M \\
&\qquad\qquad\quad \rightarrow O_2\,(^1\Delta g) + M \\
&O_2(^1\Delta g) + O \rightarrow O_2 + O \\
&2O_2(^1\Delta g) \rightarrow 2O_2\,.
\end{aligned}$$

For a long time the Chapman reaction scheme was sufficient for theoretical analysis of oxygen photochemistry and explanation of well-known facts. The appearance of new experimental data revealed its inadequacy.

For example, in the calculations of the global formation of O_3 taking into account only oxygen reactions, Johnson[13] obtained tremendous surplus of ozone. It occurred that only 20% of newly formed O_3 was destroyed in the reaction of ozone with atomic oxygen, and the transport of O_3 through the tropopause was only 1%. Therefore, the additional reactions resulting in the ozone destruction should run.

In opinion of Tal'roze et al.[14] two cycles of oxidation-reduction conversion are important for the ozonesphere

$$\begin{array}{l} X + O_3 \rightarrow XO + O_2 \\ XO + O \rightarrow X + O_2 \\ \hline O_3 + O \rightarrow 2O_2 \end{array} \quad \text{and} \quad \begin{array}{l} X + O_3 \rightarrow XO + O_2 \\ XO + O_3 \rightarrow X + 2O_2 \\ \hline O_3 + O \rightarrow 3O_2\,. \end{array}$$

Here, the initial substance X, the catalyst, should have a photochemical origin caused by the primary source, i.e., the solar radiation. The photons of solar radiation can take part in the catalytic cycle like

$$\begin{array}{l} X + O_3 \rightarrow XO + O_2 \\ XO + O_3 \rightarrow XO_2 + O_2 \\ XO_2 + h\nu \rightarrow X + O_2 \\ \hline 2O_3 + h\nu \rightarrow 3O_2\,. \end{array}$$

The next stage in the development of photochemical theory of the ozone formation was introduction of the hydrogen (hydroxyl) cycle into the general scheme. History of the discovery of this cycle goes back[3] to 1950, when Krasovskii and Manel showed that the hydroxyl OH is the source of the intense IR radiation of the night sky. Bates and Nicolet[15] in 1950 revealed the important role of hydrogen constituents H and OH as catalysts of photochemical reactions. According to the data of Ref. 16, the source of H and OH can be the photolysis of H_2O with the principal reaction of the following type:

$$H_2O + h\nu \rightarrow H + OH, \qquad \lambda < 242 \text{ nm}.$$

Cadle[17] noted that such particles can be produced through the reactions of $O(^1D)$ with methane, water, and hydrogen.

Hampson[18] and Hunt[19] introduced the hydroxyl cycles identified by Bates and Nicolet

$$\begin{array}{l} H + O_3 \rightarrow OH + O_2 \\ OH + O \rightarrow H + O_2 \\ \hline O + O_3 \rightarrow 2O_2 \end{array} \qquad \begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2 \\ HO_2 + O \rightarrow OH + O_2 \\ \hline O + O_3 \rightarrow 2O_2 \end{array}$$

$$\begin{array}{l} HO_2 + O_3 \rightarrow OH + 2O_2 \\ OH + O_3 \rightarrow HO_2 + O_2 \\ \hline O_3 + O_3 \rightarrow 3O_2 \end{array}$$

into the analysis. This made the theoretical models of ozone distribution in the atmosphere essentially closer to the experimental data. However, many differences remain.

Further development of the theory of photochemical ozone formation was connected with introduction of nitrogen cycles into it.

In the beginning, Konashenok[20] analyzed principal disagreements between theoretical and experimental data on ozone and concluded that the excess decrease of ozone in the layer below 50 km was due to the presence of small impurities, including nitrogen oxides NO and NO_2, and their reactions in the atmosphere. Then Crutzen[21] noted that the ozone budget in the atmosphere depends strongly on the nitrogen oxides NO_x formed by oxidation of nitrous oxide N_2O emitted from the underlying surface. Then Johnston[22] called attention to the potential danger caused by the development of supersonic aviation polluting the air by nitrogen oxides. So, the nitrogen cycle was put into consideration:

$$\begin{array}{l} NO + O_3 \rightarrow NO_2 + O_2 \\ NO_2 + O \rightarrow NO + O_2 \\ \hline O + O_3 \rightarrow 2O_2\,. \end{array}$$

The modern stage of development of the ozone formation theory is divided into two branches. The first branch studies the appearance of ozone holes. It is devoted to the stratospheric ozone destruction on chlorine-fluorine-hydrocarbons and in the course of heterogeneous reactions on polar cloud particles.

The second branch, namely, the tropospheric photochemistry, began to develop quickly after the supposition was made about relatively high concentration of OH and H_2O in the troposphere in sunlight and the mechanisms of oxidation of hydrocarbons in the presence of NO_x with formation of ozone in polluted air were first formulated.[9]

Summing up the aforementioned and considering the last review of Crutzen,[23] we can briefly generalize the modern photochemistry of tropospheric ozone as follows. The beginning of photochemical processes in the troposphere is the photolysis of ozone present here

$$O_3 + h\nu \rightarrow O(^1D) + O_2, \qquad \lambda < 310\ \text{nm}$$

that leads to the formation of hydroxyl in the presence of water vapor

$$O(^1D) + H_2O \rightarrow 2OH.$$

According to the Semenov[24] theory of chain reactions, further conversion of substances, CO in particular, can occur in two ways depending on the nitrogen oxide concentration in the atmosphere:

I.
$$\begin{aligned}
&CO + OH \rightarrow H + CO_2\\
&H + O_2 + M \rightarrow HO_2 + M\\
&H_2O + NO \rightarrow OH + NO_2\\
&NO_2 + h\nu \rightarrow NO + O, \qquad \lambda \le 400\ \text{nm}\\
&O + O_2 + M \rightarrow O_3 + M\\
\hline
&CO + 2O_2 \rightarrow CO_2 + O_3
\end{aligned}$$

II.
$$\begin{aligned}
&CO + OH \rightarrow H + CO_2\\
&H + O_2 + M \rightarrow HO_2 + M\\
&HO_2 + O_3 \rightarrow OH + 2O_2\\
\hline
&CO + O_3 \rightarrow CO_2 + O_2\,.
\end{aligned}$$

In the first cycle, for $NO \ge 4{\cdot}10^{-12}$(4 pptv), the ozone concentration increases from 20 to 100 ppbv. The transition to the second cycle occurs for $NO < 2{\cdot}10^{-14}$.

The appearance of excess ozone in the first cycle converts NO to other nitrogen oxides, namely,

in the daytime:

$$\begin{aligned}
&NO + O_3 \rightarrow NO_2\\
&NO_2 + OH + M \rightarrow HNO_3 + M
\end{aligned}$$

at night:

$$\begin{aligned}
&NO_2 + O_3 \rightarrow NO_3 + O_2\\
&NO_3 + NO_2 + M \rightarrow N_2O_5 + M
\end{aligned}$$

Some reactions run only in the presence of HO_2 and produce H_2O_2 in the following cycle:

$$\begin{aligned}
&CO + OH \rightarrow H + CO_2\\
&H + O_2 + M \rightarrow HO_2 + M\\
&HO_2 + HO_2 \rightarrow H_2O_2 + O_2\\
&H_2O_2 + h\nu \rightarrow 2OH, \qquad \lambda \le 350\ \text{nm}\\
\hline
&2CO + O_2 \rightarrow 2CO_2\,.
\end{aligned}$$

Then H_2O_2 takes part in the catalytic reaction

$$\begin{aligned}
&HO_2 + HO_2 \rightarrow H_2O_2 + O_2\\
&H_2O_2 + OH \rightarrow HO_2 + H_2O\\
\hline
&OH + HO_2 \rightarrow H_2O + O_2\,.
\end{aligned}$$

If only inorganic gases were present in the atmosphere, the approximate balance $NO \approx O_3$ would be kept in the photochemical cycles. However, the presence of hydrocarbons of natural and anthropogenic origin disturbs this balance. The most controllable mechanism is the oxidation of methane. This mechanism can also branch[24]:

I. $NO \sim 1$ ppb
$$\begin{aligned}
&CH_4 + OH \rightarrow CH_3 + H\\
&CH_3 + O_2 + M \rightarrow CH_3O_2 + M\\
&CH_3O_2 + NO \rightarrow CH_3O + NO_2\\
&CH_3O + O_2 \rightarrow CH_2O + HO_2\\
&HO_2 + NO \rightarrow OH + NO_2\\
&NO_2 + h\nu \rightarrow NO + O, \ \ \lambda < 400\ \text{nm}\\
&O + O_2 + M \rightarrow O_3 + M\\
\hline
&CH_4 + 4O_2 \rightarrow CH_2O + 2O_3
\end{aligned}$$

II. $NO < 4{\cdot}10^{-12}$ (4 ppt)
$$\begin{aligned}
&CH_4 + OH \rightarrow CH_3 + H_2O\\
&CH_3 + O_2 + M \rightarrow CH_3O_2 + M\\
&CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2\\
&CH_3O_2H + h\nu \rightarrow CH_3O + OH, \quad \lambda < 330\ \text{nm}\\
&CH_3O + O_2 \rightarrow CH_2O + HO_2\\
\hline
&CH_4 + O_2 \rightarrow CH_2O + H_2O
\end{aligned}$$

III. $NO < 10^{-14}$
$$\begin{aligned}
&CH_4 + OH \rightarrow CH_3 + H_2O\\
&CH_3 + O_2 + M \rightarrow CH_3O_2 + M\\
&CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2\\
&CH_3O_2H + OH \rightarrow CH_2O + H_2O + OH\\
\hline
&CH_4 + OH + HO_2 \rightarrow CH_2O + 2H_2O.
\end{aligned}$$

The important point of the first mechanism is that OH, HO_2, NO, and NO_2 are formed simultaneously with two molecules O_3 as catalysts for subsequent cycles.

If the content of NO in the atmosphere is low, the methane reaction of the second type will run, with the formation of such a toxic substance as formaldehyde.

And finally, when the concentration of NO is very small, the alternate mechanism will be realized, in which the OH and HO_2 are expended. This causes the termination of all photochemical reactions.

Admittedly, if UV radiation is present, the sink by the third mechanism can be disrupted due to the oxidation of formaldehyde with the formation of 0.8 HO_2 per $1CH_2O$. This process also can branch

$$\text{I.}\quad \begin{array}{l} CH_2O + h\nu \rightarrow H + CHO, \quad \lambda \le 350\ \text{nm} \\ H + O_2 + M \rightarrow HO_2 + M \\ CHO + O_2 \rightarrow CO + 2HO_2 \\ \hline CH_2O + 2O_2 \rightarrow CO + 2HO_2 \end{array}$$

$$\text{II.}\quad \begin{array}{l} CH_2O + OH \rightarrow CHO + H_2O \\ CHO + O_2 \rightarrow CO + HO_2 \\ \hline CH_2O + OH + O_2 \rightarrow CO + H_2O + HO_2 \end{array}$$

$$\text{III.}\quad CH_2O + h\nu \rightarrow CO + H_2, \quad \lambda \le 350\ \text{nm}.$$

Photochemistry becomes more complex in the polluted atmosphere, and some intermediate products may be formed in the reactions. As an example, Crutzen presents the cycle of formation of peroxiacetylnitrates (PAN) by oxidation of ethane (C_2H_6) and acetaldehyde (CH_3CHO)

$$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$$

$$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$$

$$C_2H_5O_2 + NO \rightarrow CH_3CH_2O + NO_2$$

$$CH_3CH_2O + O_2 \rightarrow CH_3CHO + HO_2$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O$$

$$CH_3C(O) + O_2 + M \rightarrow CH_3C(O)O_2 + M$$

$$CH_3C(O)O_2 + NO_2 \rightarrow CH_3C(O)O_2NO_2\ (\text{PAN}).$$

There are weaker sources of ozone in the troposphere other than the photochemical ones. They are ozone that arrives from the stratosphere due to dynamic processes and ozone formation due to electrical phenomena.

As early as the last century, scientists paid attention to the relationship of ozone with storm phenomena. According to existing ideas,[3] ozone can be initiated in the troposphere by electrical discharges of two types: silent (corona) and storm (lightning).

The lightning initiates a wide spectrum of electromagnetic radiation, including UV. The last with the wavelengths $\lambda \le 250$ nm can excite oxygen molecules in the $O_2(^3\Sigma^+u)$ state. Then they take part in the reaction

$$O_2(^3\Sigma^+u) + O_2 \rightarrow O_3 + O + 41.9\ \text{kJ}\cdot\text{mole}^{-1}$$

that leads to the formation of ozone

$$O + O_2 + M \rightarrow O_3 + M.$$

Preliminary estimates of the ozone amount formed by this scheme[25,26] give very high values comparable with the ozone content in the atmosphere.

However, it was shown further that the principal source is the silent discharge, because the ozone concentration increases long before a thunderstorm.[27] The increase of the electric field intensity under thunderstorm conditions leads to formation of the silent discharge near tree tops, shrubs, and even blades of grass starting from an electric field intensity of 8–9 V/cm. An ozone amount of $3\cdot10^{-5}$ μg/s is produced in 1 l, or 0.03 μg/m^3, on average, in the ground layer for three hours before the thunderstorm. Taking into account the high probability of ozone destruction in the ground layer, we can assume that such a process is of local significance and not to include it into the total budget of tropospheric ozone. The scheme of its formation can be the following.

Electrons with the energy greater than 5.09 eV can dissociate the oxygen molecules in the discharge, silent or lightning

$$1/2O_2 + e \rightarrow e + O.$$

Energy of 109.5 kJ·mole^{-1} is expended in this reaction. Then the classical reaction of the ozone formation runs. The dissociative electron attachment can occur for less electron energy (3–5 eV)

$$e + O_2 \rightarrow O + O^- - 347.8\ \text{kJ}\cdot\text{mole}^{-1}.$$

Then classical reaction or the reaction

$$O^- + O_2 \rightarrow O_3 + e - 41.9\ \text{kJ}\cdot\text{mole}^{-1}$$

should run.

The following reactions may run simultaneously:

$$O^- + O_2 + O_2 \rightarrow O_3 + O_2 + 54.5\ \text{kJ}\cdot\text{mole}^{-1}$$
$$e + O_2 + O_2 \rightarrow O^- + O_3 - 251.4\ \text{kJ}\cdot\text{mole}^{-1}.$$

The ions of atomic oxygen can destroy ozone in the reactions

$$O^- + O_3 \rightarrow O_2 + O_2^- + 347.8\ \text{kJ}\cdot\text{mole}^{-1}.$$
$$e + O_3 \rightarrow O_2 + O^- + 41.9\ \text{kJ}\cdot\text{mole}^{-1}.$$

On the whole, these reactions remain locally significant as verified by more recent researches.[28] So they are not taken into account when calculating the total ozone budget in the atmosphere (see Table I borrowed from Ref. 7).

It is seen from Table I, that according to Megie et al.[7] about 15–25% of ozone comes from the stratosphere. Since this source, as a rule, is assessed from indirect data, the reliability of its intensity estimates casts some doubt for many scientists. In particular, Khrgian[2,3] thinks that the descending motion of stratospheric ozone along isentropic surfaces passing through the front plane is practically impossible and should be accompanied with the significant (up to 40°C) air temperature rise.

The issue on the temperature rise can be resolved when radiative cooling is considered.[29] Nobody has observed the descending motion yet. So the viewpoint of Reiter[30] that only half the ozone layer takes part in such an exchange is preferable. The ozone layer remainder is fixed by the photochemical equilibrium.

Turning back to Table I, we note that the bulk of tropospheric ozone is formed during the photochemical processes. The initial impurities listed in the Table for the northern hemisphere are not only sources, but also sinks of ozone simultaneously. So below we consider in detail the peculiarities of some photochemical processes in the troposphere.

TABLE I. Balance of ozone generation and sink in the troposphere (10^{10} mol·cm^{-2}·s^{-1}).

Process	Northern hemisphere		Southern hemisphere	
	Generation	Sink	Generation	Sink
Transport from the stratosphere	6.5	–	4.5	–
Photolysis	–	– 10	–	– 7
Photochemical formation	29	–	15.5	–
CO	15.5	6.2	–	–
CH_4	5.5	5.3	–	–
Hydrocarbons	8	4	–	–
Photochemical sink	–	– 12	–	– 8
Sink on the surface	–	– 13.5	–	– 5
Total	35.5	– 35.5	20	– 20

ROLE OF HYDROXYL IN TROPOSPHERIC PHOTOCHEMISTRY

The division of tropospheric photochemistry devoted to the study of the role of hydroxyl is now vigorously developed. This is caused by its particular significance for photochemical processes, because hydroxyl has the extreme reactivity. If we look at the diagram[31] shown in Fig. 1, we see that ozone interacts with practically all substances present in air. Here, RH denotes hydrocarbons and R denotes radicals.

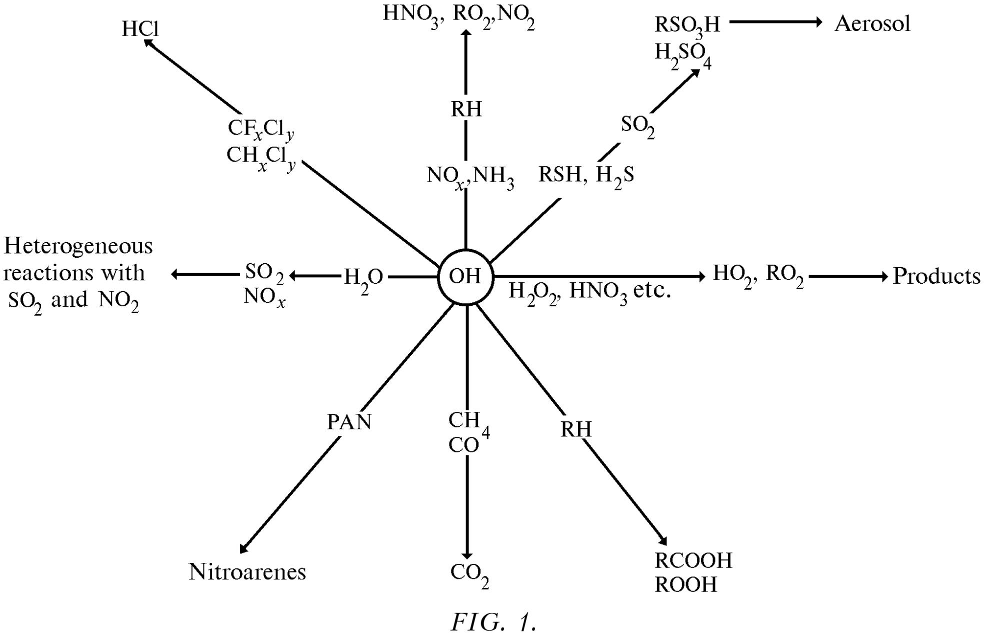


FIG. 1.

According to Campbell et al.[32] 90% of CO in ambient air is oxidized by the radical OH, and only the remaining 10% are oxidized by other oxidants. According to Wayne,[33] 70% of OH formed in the atmosphere is expended in the reactions with CO and 30% with CH_4. It is no mere chance that hydroxyl is called “cleanserB of the troposphere.[34]

The formation of OH in the troposphere starts from the reaction[35]

$$O_3 + h\nu \rightarrow O_2 + O(^1D), \quad \lambda < 320 \text{ nm},$$

which then branches. Approximately 90% of $O(^1D)$ passes to the lower state $O(^3P)$ after interaction with the molecules of air and then converts to ozone again

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2$$
$$O(^1D) + O_2 \rightarrow O(^3P) + O_2$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M \ (M = N_2, O_2)$$

About 10% of $O(^1D)$ reacts with water vapor under normal conditions with formation of OH

$$O(^1D) + H_2O \rightarrow H_2O_2 \rightarrow OH + OH.$$

This occurs because the rate constant of the last reaction is 10 times greater than that of the previous ones.

According to Ref. 36, OH also can be formed in a number of reactions of $O(^1D)$ with other gases:

$$CH_4 + O(^1D) \rightarrow CH_3 + OH$$
$$H_2 + O(^1D) \rightarrow H + OH.$$

Then OH reacts with atmospheric impurities, forming new cycles. One of the aforementioned cycles is the oxidation of CO, during which OH is reduced and ozone is formed[37]:

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O, \quad \lambda < 410 \text{ nm}$$
$$O + O_2 + M \rightarrow O_3 + M$$

$$CO + 2O_2 \rightarrow CO_2 + O_3.$$

The compounds OH and HO_2 produced in these reactions undergo mutual change in the troposphere when they take part in reactions with oxygen[34]

$$O_3 + OH \rightarrow HO_2 + O_2$$
$$O + HO_2 \rightarrow OH + O_2.$$

Since OH is a highly reactive compound, it reacts with more complex compounds. So, Kharchilava and Amiranashvili[28] suppose that the oxidation of CH_4 by hydroxyl is the central point of all tropospheric photochemistry.

The simplified diagram of methane oxidation is shown in Fig. 2.

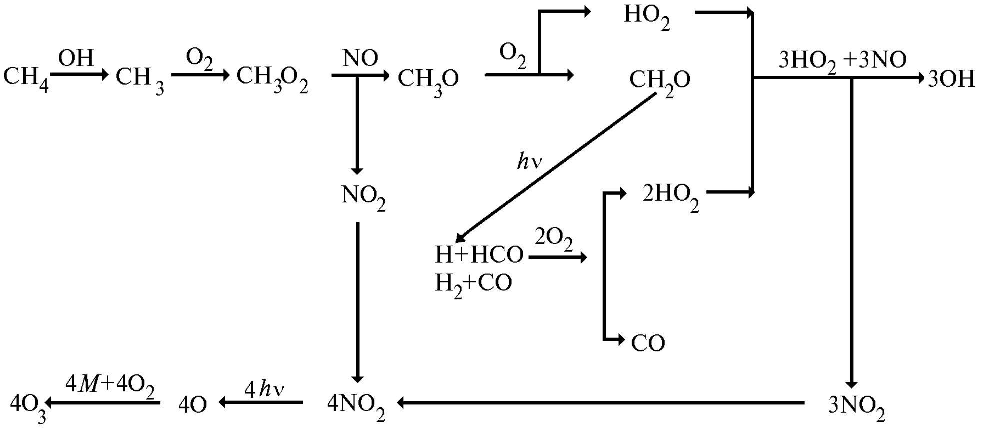


FIG. 2.

It follows from this diagram that three hydroxyl radicals and four ozone molecules can be formed when one CH_4 molecule is oxidized. Another molecule of O_3 can be formed from CO by the aforementioned reactions. Thus, the theoretically possible ozone yield is five molecules per one molecule of CH_4.

One can extend this diagram to other components of the hydrocarbon series present in air subject to intensive anthropogenic influence. For example, the following sequence of reactions was proposed for the oxidation of ethane[34]:

$$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$$
$$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$$
$$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$$
$$C_2H_5O + O \rightarrow CH_3CHO + HO_2$$
$$CH_3CHO + h\nu \rightarrow CH_3 + CHO$$

and then by the methane oxidation scheme.

Hydroxyl radicals are not only formed, but also destroyed in the real atmosphere. Principally, this occurs in the reactions in which the molecules of H_2O are formed[34]

$$OH + H_2O_2 \rightarrow H_2O + HO_2$$
$$OH + HO_2 \rightarrow H_2O + O_2$$
$$OH_2 + HO_2 \rightarrow H_2O + O_2,$$

in the reactions with nitrogen and sulfur oxides[33]

$$OH + NO + M \rightarrow HNO_2 + M$$

$$OH + NO_2 \rightarrow HNO_3$$

$$OH + SO_2 \rightarrow HOSO_2 \xrightarrow{H_2O} H_2SO_4$$

$$\hookrightarrow HOSO_2 \times H_2O + O_2 \rightarrow H_2SO_4 + HO_2,$$

and in the reactions of formation of hydroperoxide[39,40]

$$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M.$$

However, the reactions written above do not always lead to the sink of hydroxyl radicals. According to Ref. 41, they can repeat the cycle in the process of photolysis of the products by the reactions

$$HNO_2 \xrightarrow{h\nu} NO + OH, \lambda < 400 \text{ nm}$$

$$HNO_3 \xrightarrow{h\nu} NO_2 + OH, \lambda \le 335 \text{ nm}$$

$$H_2O_2 \xrightarrow{h\nu} OH + OH, \lambda \le 300 \text{ nm}.$$

Thus, numerous acts of interaction of different chemical compounds occur in the real atmosphere. They form a number of cycles in which the same substances can repeatedly return to the beginning. This is most vividly illustrated by Fig. 3, where the estimated amounts of interacting substances[35] are also given.

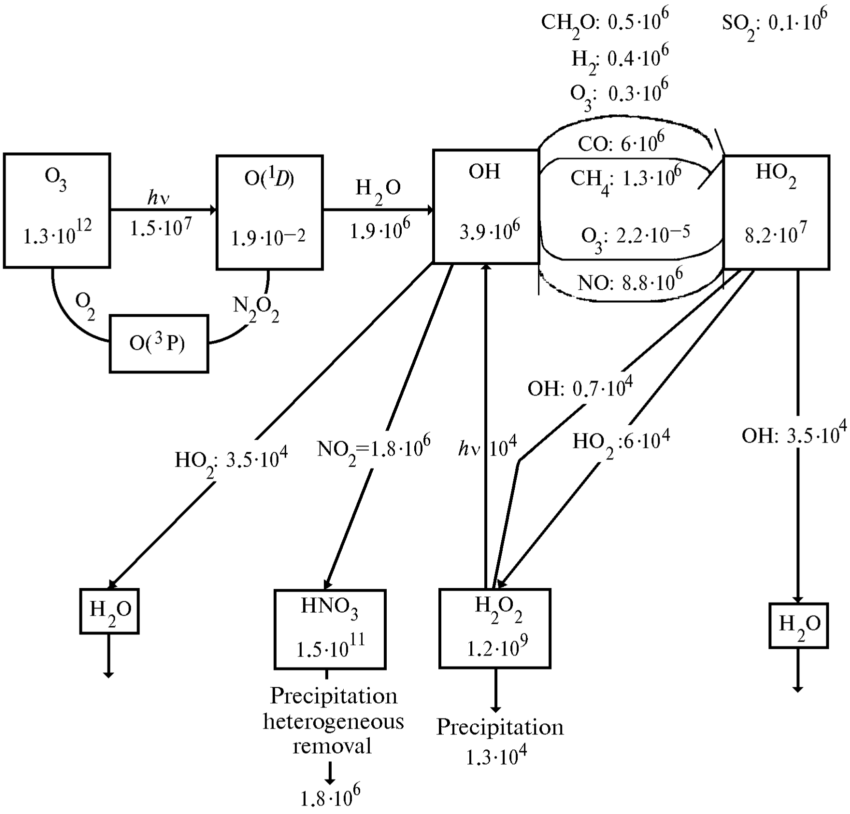


FIG. 3. Reaction cycles of OH *and* HO_2.

Direct measurements of OH, HO_2, and H_2O_2 concentration[42–44] gave the following values: $1...7 \cdot 10^6$ cm^{-3}, $1...2 \cdot 10^8$ cm^{-3}, and 0.4...1.8 ppbv, respectively. They are close to the results shown in Fig. 3 and the estimates of other authors.[45,46]

“CleansingB the troposphere, hydroxyl OH also reacts with more complex hydrocarbons that are not shown in Fig. 3. According to different estimates, only emissions of forests contain more than 70 organic compounds.[47] Isidorov[41] observed more than 170 organic volatile compounds in urban air. Interaction of the majority of them with OH was observed. Such reactions usually form no cycles. The ozone was produced in some of them. The data on oxidation by OH of *n*-butane, toluene, propene, and benzene are given in Ref. 47; butane, propane, ethylene, propylene, *trans*-2-bytene, β-pinene, α-pinene, 3-karene, β-pheladrene, γ-terpinene, limonene, and myrcene in Ref. 41; isoprene in Ref. 48; Δ^3-karene and sabinene in Ref. 49; and kamchene and terpinolene in Ref. 50.

Naturally, the aforementioned substances and the other oxidized by OH and present in the troposphere have different values of reactivity. The data on these characteristics are given in the detailed study carried out by Killus et al.[51] at the California coast from onboard an aircraft. They are collected in Table II.

TABLE II. Chemical reactivity of hydrocarbons in relation to the OH radical ($ppm^{-1}\cdot min^{-1}$).

Substance	*R*	Substance	*R*	Substance	*R*
α-terpinene	53280	styrene	9620	*n*-nonane	1644
myrcene	32880	4-methyl-1-pentene	9500	*n*-octane	1613
isoprene	29896	3-methyl-1-butene	9413	2-methylheptane	1573
γ-terpinene	26048	1-pentene	8880	3-methylhexane	1543
2-methyl-2-butane	25722	1-hexene	8633	cyclopentane	1539
trans-2-butene	23569	1,3,5-threemethylbenzine	7893	3,3-dimethylbutane	1529
α-limonene	22200	α-pinene	7874	*n*-heptane	1522
2-methyl-2-pentene	21953	ethylene	6320	3-methylpentane	1381
trans-3-methyl-2-pentene	21707	1, 2, 4-threemethylbenzine	5427	*n*-hexane	1376
cis-2-butene	20757	*m*-xylene	4533	2-methylpentane	1357
terpinolene	20000	*p*-xylene	2812	ethylbenzine	1314
trans-2-pentene	19832	*o*-xylene	2720	toluene	1309
cyclopentane	19832	ethylcyclohexane	2405	*n*-pentane	1202
cis-2-pentene	19241	methylcyclopentane	2319	*i*-pentane	1154
J-butene	19018	methylcyclohexane	2178	*s*-butilbenzine	1036
2-methyl-1-pentene	18000	2, 3, 4-threemethylpentane	2035	*n*-propylbenzine	970
2-methyl-1-butene	17760	1-ethyltoluene	1973	*n*-butane	936
trans-2-hexene	16580	2-ethyltoluene	1973	2, 2, 3-threemethyl-pentane	900
cis-2-hexene	16000	cyclohexane	1820	*i*-butane	877
propene	12975	2, 3-dimethylhexane	1813	2, 2-dimethylbutane	641
Δ^3-karene	12876	2,3-dimethylpentane	1755	propane	582
1-butene	11618	3-ethylhexane	1740	acetylene	577
β-pinene	11574	2, 4-dimethylhexane	1721	benzine	316
				ethane	241

As noted above, when higher hydrocarbons oxidize, ozone can be formed. The number of ozone molecules formed by one atom of hydroxyl for some gases in urban air according to Chameides et al.[52] is given below:

ethylene	0.95	*i*-butane	0.48	*i*-pentane	0.34
propene	0.85	*o*-xylene	0.46	ethyl-benzine	0.19
isoprene	0.70	CO	0.45	cyclohexane	0.19
ethane	0.61	propane	0.34	toluene	0.17
isobutane	0.50	*n*-butane	0.34	benzine	0.11.

Thus, although there are no ecological requirements normalizing the hydroxyl OH and its derivatives, they play a dominant role in the formation of cycles of photochemical reactions in which ozone and secondary impurities are formed.

ROLE OF NITROGEN OXIDES IN PHOTOCHEMICAL REACTIONS

A dominant role of nitrogen oxides in tropospheric chemistry is reduced to the fact that in most cases in the daytime the photochemical equilibrium is established between NO, NO_2, and O_3 [53,54]:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O, \quad \lambda < 395\ \text{nm}$$

$$O + O_2 + M \rightarrow O_3 + M.$$

The sources of nitrogen oxides in the atmosphere are evaporation from the underlying surface and anthropogenic activity.[55,56] Nitrogen oxides can be present in the atmosphere in the following forms: N_2O, NO, N_2O_3, NO_2, N_2O_4, NO_3, and N_2O_5. Some of them, such as NO, NO_2, and NO_3 are free radicals.[57]

Many authors think that the principal source of nitrogen oxides is the oxide N_2O formed during natural biological processes. It is converted to NO through the reaction

$$N_2O + O(^1D) \rightarrow NO$$

with subsequent participation in photochemical cycles. The other more exotic cases of N_2O formation in the atmosphere were considered in Ref. 58. However, their significance under natural conditions is little.

Apart from N_2O, NO is also evaporated from the underlying surface; admittedly, according to Mooney et al.[55] its amount is less than that of N_2O. Another source of NO in the atmosphere is the processes of combustion[57] that produces nitrogen oxide by the scheme

$$N_2 + O \rightarrow NO + N \quad \text{or} \quad N + O_2 \rightarrow NO + O.$$

In the troposphere, NO is converted to NO_2 by ozone or in the following reactions[59]

$$NO + OH \rightarrow HONO$$

$$NO + HO_2 \rightarrow NO_2 + OH$$

$NO + RO_2 \rightarrow RO + NO_2$,

where R denotes the organic radical. The reaction

$2NO + O_2 \rightarrow 2NO_2$.

runs when the concentration NO > 1 ppm.

Then nitrogen dioxide undergoes photolysis in the aforementioned reaction with generation of ozone or takes part in the subsequent reactions[60–62]:

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_2 + OH \rightarrow HNO_3$

$NO_2 + NO + H_2O \rightarrow 2HONO$

$NO_2 + NO_3 \rightarrow N_2O_5$

$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$.

Some products of this cycle also react[63–64]:

$NO_3 + M \rightarrow NO + O_2 + M$

$NO_3 + NO \rightarrow 2NO_2$

$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$

$N_2O_5 + H_2O \rightarrow 2HNO_3$

$N_2O_5 + NaCl \rightarrow NO_2Cl + NaNO_3$.

Not all products are stable. They undergo photolysis or thermal decomposition in the real troposphere.

The molecule N_2O_5 is not stable and is decomposed in the reaction[60]

$N_2O_5 \rightarrow NO_2 + NO_3$

The reduced molecule NO_3 may undergo photolysis in the daytime

$NO_3 + h\nu \rightarrow NO + O_2, \quad 500 < \lambda < 700$ nm.

The atom Cl is produced by photolysis[64]

$NO_2Cl + h\nu \rightarrow NO_2 + Cl, \quad \lambda < 700$ nm.

Nitric and nitrous acids may undergo photolysis in the daytime[65]:

$HNO_3 + h\nu \rightarrow NO_2 + OH$

$HONO + h\nu \rightarrow NO + OH$.

Since the rates of the aforementioned reactions and the concentration of individual components are different in the daylight and night time, the scheme that gives a general idea of the principal and secondary important reactions between nitrogen oxides was presented in Ref. 62. It is shown in Fig. 4.

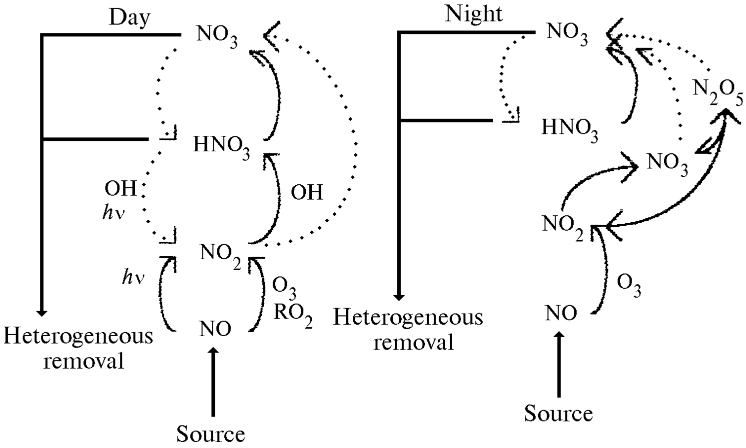


FIG. 4.

Similar to hydroxyl, nitrogen oxides interact with organic substances. However, unlike hydroxyl that “cleansesB the troposphere, nitrogen compounds form the secondary more toxic substances.

The data on such mechanisms were presented in Ref. 16. They are:

$NO_2 + CH_3CO_3 \rightarrow PAN$

$NO + CH_3CO_2 \rightarrow NRAT$

$NO_2 + CH_6H_5O \rightarrow NPHN$,

where PAN denotes peroxiacetylnitrates, NRAT denotes alkilnitrates, and NPHN denotes nitrophenols.

According to the data of Ref. 66, complex oxidants are produced in parallel with the formation of ozone, because they have the similar temporal behavior. Evidently, this is the reason why high ozone concentration is accompanied by the haze of photochemical origin.

According to the data of Ref. 67, the character of reaction of oxides with hydrocarbons depends essentially on the type of hydrocarbons, because the yield of PAN can change from few to several tens of per cent.

Le Bras and Poulet[68] and Platt et al.[69] have revealed that nitrogen oxides also take part in oxidation of dimethylsulfates, alkenes, and volatile hydrocarbons not only in the daytime.

Thus, nitrogen oxides play an active role in tropospheric photochemistry and, depending on their concentration, are the “switchesB of the branches of chain reactions.

OTHER PHOTOCHEMICAL SOURCES OF OZONE

As is well known, there is a certain amount of sulfur dioxide even in the background troposphere. Brickard[70] has identified the following possible mechanism of ozone generation through photochemical oxidation of this gas:

$$SO_2 + h\nu + O_2 \rightarrow SO_2^{+}, \quad \lambda < 390 \text{ nm}$$

$$SO_2^{+} + O_2 \rightarrow SO_3 + O_3 .$$

A similar mechanism was described in Ref. 71. It begins from excitation of molecules SO_2 to the active state in the reaction

$$SO_2 + h\nu \rightarrow SO_2\ (^3B_1), \quad 340 < \lambda < 400 \text{ nm}.$$

Then it interacts with O_2SO_4:

$$SO_2(^3B_1) + O_2SO_4 \rightarrow SO_3 + O_3$$

or

$$SO_2(^3B_1) + O_2 \rightarrow SO_3 + O(^3P)$$

with subsequent ozone formation:

$$O(^3P) + O_2 + M \rightarrow O_3 + M.$$

Evidently, the mechanisms of sulfur dioxide oxidation are inefficient for the troposphere. There are no estimates of their significance in the literature. These mechanisms were not manifested in a number of experiments.

A lot of papers are devoted to the study of a role of halogens in the ozone destruction in the stratosphere associated with the ozone hole formation. It was revealed in some papers that ozone may be formed in the reactions with bromine compounds under conditions close to tropospheric ones. The reaction

$$HO_2 + BrO \rightarrow HBr + O_3$$

that runs at room temperature was presented in Ref. 72.

Niki et al.[73] studied the oxidation of ethylene and acetylene in the presence of bromine oxides. It occurred that, in addition to organic products, OH and O_3 are formed in a number of chain reactions. The measurements carried out in Alert show that C_2H_2, C_2H_4, and O_3 have synchronous behavior. It can be evidence of the significance of such a mechanism for the polluted troposphere.

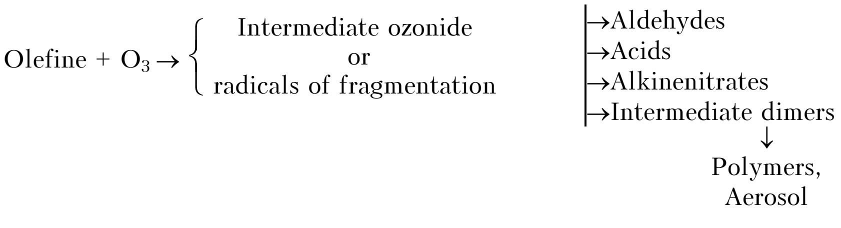
SINKS OF OZONE AND OZONE-PRODUCING GASES

Photochemical origin of tropospheric ozone supposes not only numerous acts of its formation, but also destruction of its molecules. The result is the balance of concentration in one or another place. The value of concentration is determined by the content of ozone-producing gases, intensity of solar radiation, and ozone-destroying substances. According to modern conception, the sink occurs in the troposphere on the underlying surface and immediately in the atmosphere due to photolysis and interaction with gases and aerosols.

One usually estimates the ozone sink on the underlying surface by means of special chambers[74] or by the gradient technique.[75–76] According to generalized data,[3] the values of the ozone flow to the surface can vary by two orders of magnitude, from 10^{10} cm^{-2}s^{-1} for sea water up to 10^{12} cm^{-2}s^{-1} for juniper shrubs.

We have already considered the mechanism of ozone photolysis and its destruction due to interaction with principal tropospheric gases. So it is not expedient to repeat their consideration.

Investigations of some authors[41,47,77] show that ozone accumulation depends on the relationship between the values of initial concentration of organic compounds, being precursors of peroxide radicals, and nitrogen oxides. The rate of conversion of NO to NO_2 is low for small value of this relationship, and nitrogen oxide takes part in the process of ozone destruction. Ozone is not accumulated at a very high value of this relationship by two reasons: due to interaction of NO_2 with organic radicals and the reaction of newly formed O_3 with hydrocarbons. The reactions of O_3 with hydrocarbons usually lead to the formation of the aerosol being the active source of the ozone destruction.[78–81] According to the data of Ref. 82, the organic component makes up about 30% of submicron fraction of the atmospheric aerosol. The general scheme of interaction of ozone with hydrocarbons is given on the example of olefine[81]



Investigations of the chemical activity of hydrocarbons in relation to O_3 show great dispersion of their values. Table III, in which the rate constants of the reactions of some terpenes with ozone are presented, is constructed from the data of Ref. 41.

TABLE III.

Hydrocarbon	k, O_3 $cm^3/mol\cdot s$	Hydrocarbon	k, O_3 $cm^3/mol\cdot s$
isoprene	$1.2\cdot10^{-17}$	limonene	$6.5\cdot10^{-16}$
β-pinene	$3.6\cdot10^{-17}$	myrcene	$1.3\cdot10^{-15}$
α-pinene	$1.4\cdot10^{-16}$	ocimene	$2.0\cdot10^{-15}$
3-karene	$1.2\cdot10^{-16}$	terpinolene	$1.0\cdot10^{-14}$
β-phelandrene	$1.8\cdot10^{-16}$	α-phelandrene	$8.9\cdot10^{-14}$
γ-terpinene	$2.4\cdot10^{-16}$	α-terpinene	$8.9\cdot10^{-14}$

It follows from this Table that the rate constants of ozone addition to β-pinene and α-terpene differ more than 2000 times. Hence, one can expect very high ozone concentration and its complete destruction even in the background regions with different types of vegetation.

An important role of hydrocarbon compounds in the photochemical smog formation leads to the idea of inhibition of smog-producing substances. To this end, some authors[83,84] suggested injecting diethylhydroxylamine (DEHA) into the atmosphere. Laboratory experiments showed the efficiency of such a mechanism. However, the field experiments were not carried out because the ecological consequences were uncertain.

The ozone sink on tropospheric aerosol is one of the poorly studied ways of its destruction.

It has been established to date that the intensity of the sink depends on the presence of some chemical substances in the composition of particles. It is shown in Refs. 85–87 that the presence of bromine ions in the composition of particles leads to the ozone destruction. Laboratory determination of the coefficients of ozone sink on some substances modeling natural solid aerosol particles leads to the conclusion that Al_2O_3 can effectively favor the heterogeneous break of the ozone molecules.[88,89] The proof of the ozone destruction on water droplets was given by Marenco.[90] Some authors[91,92] note that the ozone sink occurs on the finely dispersed aerosol fraction. It is important to note that the problem of aerosol-gas relationships is relatively young, because the ozone sink on aerosol particles was considered to be insignificant until Pittack[93] had published his results. Let us note in conclusion that, according to the data of Ref. 94, the molecules OH and HO_2, playing a determining role in the photochemical cycles of ozone formation in the lower troposphere, are also destroyed on aerosol particles.

ENERGY SUPPLY OF PHOTOCHEMICAL REACTIONS IN THE TROPOSPHERE

When describing the processes of activation of gas molecules and their photolysis, the spectral range of radiation, in which these processes occur, was given. It is the UV radiation with $\lambda \le 400$ nm for the majority of reactions. Since atmospheric air is the strongly absorbing medium, the question arises whether or not the conditions of photochemical processes occurring by the aforementioned schemes are provided in the lower troposphere.

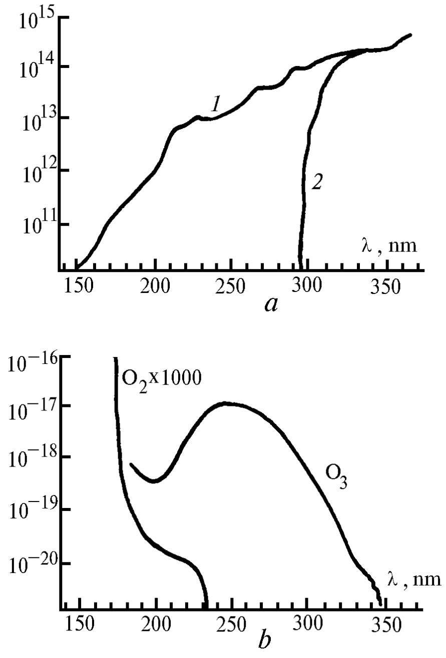


FIG. 5. Photon flux ($cm^2\cdot s^{-1}\cdot nm^{-1}$) *(a) at the upper boundary of the atmosphere (1) and at the ground (2); absorption cross sections* (cm^2) *of oxygen and ozone (b).*

As is well known,[94] the rate of photolysis of gases in the atmosphere is determined by the convolution of the form

$$j_{A\to B} = \int\limits_{\Delta\lambda} \sigma_\lambda^A \, q_\lambda^{A\to B} \, F_\lambda \, d_\lambda \, (d\lambda),$$

where Δλ is the spectral range of photodissociation,

σ_λ^A is the absorption cross section of the gas A at the wavelength λ, $q_\lambda^{A \to B}$ is the quantum yield of the reaction, and F_λ is the intensity of the monochromatic radiation flux.

The intensities of radiation flux at the upper boundary of the atmosphere and near the underlying surface, as well as the absorption cross sections of oxygen and ozone borrowed from Ref. 35 are shown in Fig. 5. It is seen that all conditions for ozone photodissociation as initial stage of the photochemical processes are provided in the lower troposphere.

GENERAL SCHEME OF TROPOSPHERIC OZONE FORMATION

In the closing stage of our analysis of the processes of photochemical ozone formation in the troposphere, following Ref. 95, let us write the brutto-formula of its budget in the following form:

$$RH + CO + NO \xrightarrow{h\nu,\, O_2,\, H_2O} NO_2 + f\, H_2CO + kO_3 + P,$$

where f and k are the stoichiometric coefficients of hydrocarbon conversion and P denote the product of the reaction being the sink of photochemical reaction.

It is seen from this brutto-formula that, entering into the real atmosphere with oxygen and water vapor, which is illuminated by the Sun, the initial impurities of air, including hydrocarbons of different nature (RH), nitrogen, and carbon oxides convert to nitrogen dioxide, formaldehyde and ozone in the course of the photochemical processes. The nongaseous products (P) are also produced in the reactions and then are removed from the atmosphere. It seems that the brutto-formula gives the simple scheme of the photochemical processes in the troposphere. Really, it is not so simple, taking into account back reactions. Let us consider the scheme (Fig. 6) presented in Ref. 96 as an example.

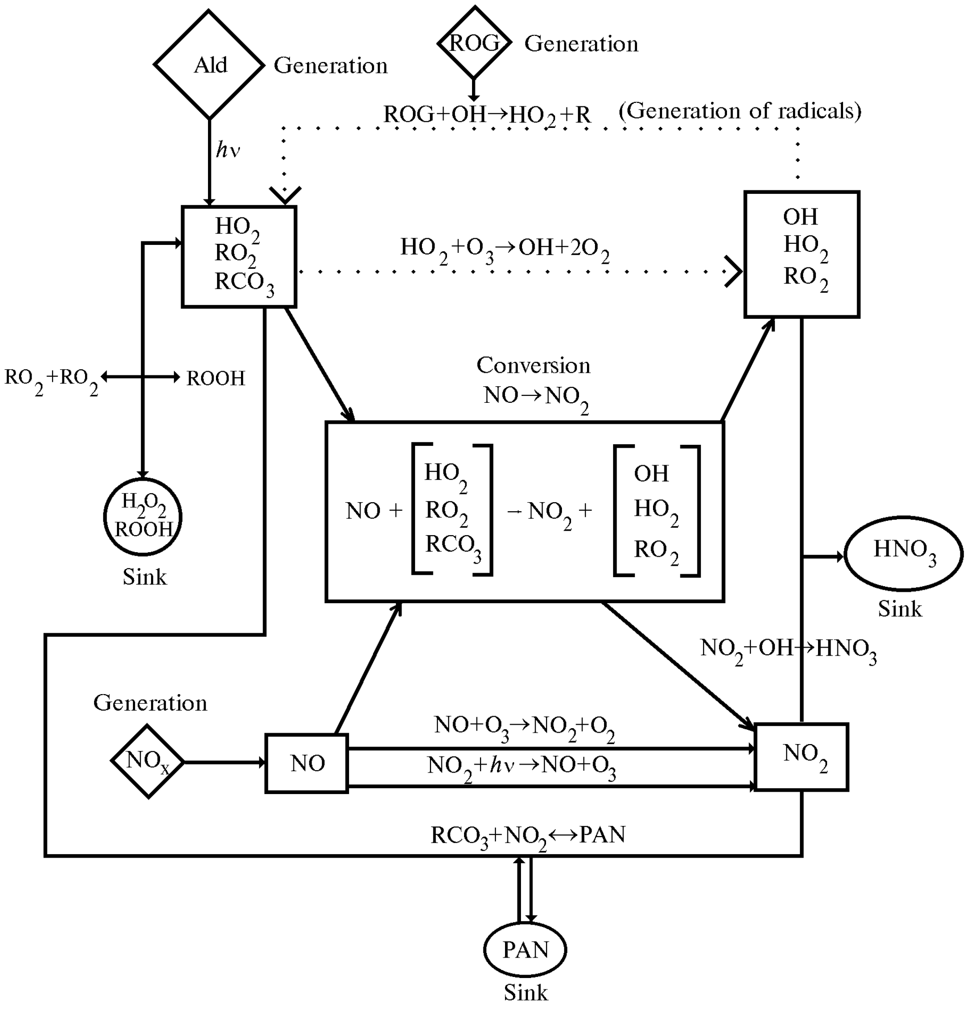


FIG. 6. Generalized diagram of ozone sources and sinks in the troposphere. Here ROG *denotes reactive organic gases,* Ald*–aldehydes,* PAN*–peroxiacetylnitrates, and* R*–radicals.*

Alkenes of biological origin and isoprene belong the OLE3 group that principally consists of hydrocarbons with seven carbon molecules. Carbonyls are represented by formaldehyde (H_2CO), acetaldehyde

(C_2HO), propionaldehyde (RCHO) and methyl-ethyl-ketone (MEK). The individual impurities such as carbon oxide, methane, and ethane were also taken into account in the calculations. The results of calculations for this model are shown in Fig. 7.

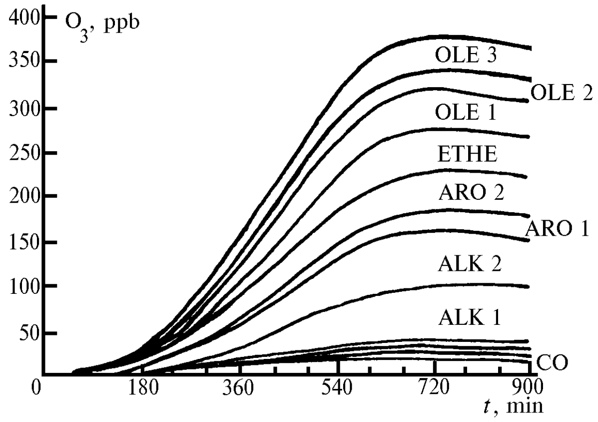


FIG. 7. Ozone generation depending on the nature of hydrocarbons for the ratio $RH/NO_x = 8.2$.

Such number of sources and sinks of substances participating in photochemical processes makes the simple estimate of the contribution from each of them to the total ozone budget impossible. To this end, one should perform a very complex experiment with monitoring of all components of the ozone cycle shown in Fig. 6. Another way is numerical modeling of the photochemical processes.[31, 97,98]

The most detailed estimates of the contribution from individual components of the ozone cycle to the total ozone budget were performed in Ref. 99 for the SAPRC–90 model. The following compounds were taken into account in the calculations: alkenes ALK1 containing four carbon molecules, alkenes ALK2 with eight carbon molecules; all aromatic compounds ARO1 including principally toluenes; aromatic compounds ARO2, mainly xylenes; olefines OLE1 with four carbon molecules; alkenes OLE2 with five molecules. It is seen from Fig. 7 that the hydrocarbon compounds ALK1, ALK2, ARO2, OLE1, and ethane make the primary contribution to the ozone formation in the troposphere. The contribution of all other compounds is less than a half. It is no mere chance that the maximum of the ozone concentration in the troposphere is observed in spring, when the vegetation generates a lot of terpenes.

Figure 8 gives an idea of the role of nitrogen oxides in ozone formation in the presence of the same initial hydrocarbons. As is seen, there is the optimum ratio RH/NO_x, for which the ozone generation is maximum. This confirms the conclusion of Ref. 77 that the ozone generation is absent when the oxide concentration is either low or high, i.e., emphases the switching role of oxides in the chain reactions.

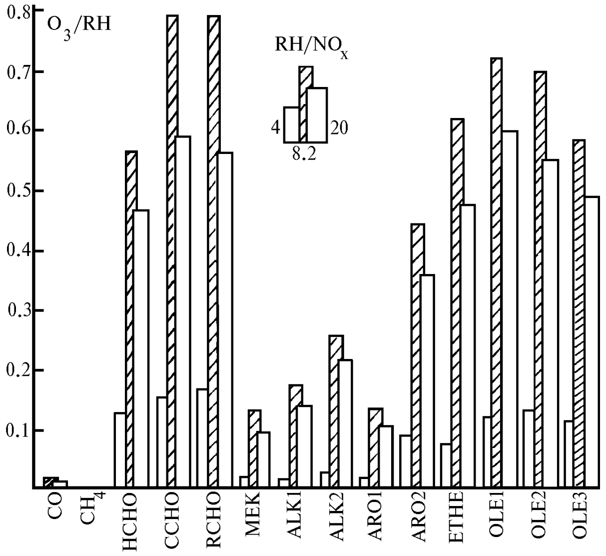


FIG. 8. Formation of ozone from hydrocarbons for different values of concentration of nitrogen oxides.

In conclusion of this section, let us remind that the data shown in Figs. 7 and 8 are the results of theoretical calculation that gives an idea of the contribution from different substances to the total ozone budget. However, as I know, the experiment that considers all factors has not yet been performed, though the study of the ozone-producing property of some substances has been carried out in papers listed above.

SOME DATA ON THE SPATIOTEMPORAL VARIABILITY OF TROPOSPHERIC OZONE

In spite of the long history of atmospheric ozone investigations, the data on its spatiotemporal variability are incomplete. By now, only its characteristics in the stratosphere and ground layer have received more or less study. So let us briefly consider the ozone dynamics in the lower troposphere.

The material for an analysis is the result of sounding of the atmosphere from onboard the IL–14 (see Ref. 100) and AN–30 (see Ref. 101) aircraft-laboratories as well as the data of measurements in the ground air layer at the TOR-station.[102]

Let us consider in the beginning where (at which altitude) and how (in space) the generation of tropospheric ozone occurs. To this end, look at Fig. 9, where the vertical profiles of ozone concentration measured at latitudinal and meridional sounding of the atmosphere during one day are shown.

Curves *1*, *2*, and *3* were obtained in flight Tomsk–Ufa–Donetsk on February 5–6, 1989. Profiles *4*, *5*, and *6* were obtained in flight Tomsk–Balkhash–Niznevartovsk on March 23–24, 1989.

It is seen from Fig. 9 that the ozone generation in both cases occurs primarily in the atmospheric boundary layer (H = 1200 m). The ozone vertical profiles above the boundary layer are similar to each other. It is especially well seen in February. Taking into account that the distance between Tomsk (86° E) and Donetsk (38° E) is 48°E, and that the curves in the free atmosphere practically coincide in the same manner as for the Ufa region, we can conclude that the ozone generation occurs only in the boundary layer. The tendencies in March were the same, although the total ozone concentration increased. There is the ozone generation in the boundary layer and similarity of ozone profiles in the free atmosphere. Whereas the latitudinal behavior does not reveal any differencesabove the boundary layer in different regions, the meridional behavior does not show such a similarity. The ozone concentration in the free atmosphere over Balkhash (46°N) is noticeably less than that over Tomsk (58°N) and Nizhnevartovsk (61°N). Therefore, the ozone is formed in the boundary layer independently of the geographical position and then enters into the upper layers. One can estimate the last item from the comparison of profiles obtained in February and March. Geographical position of the measurement site affects the meridional section stronger than the latitudinal one.

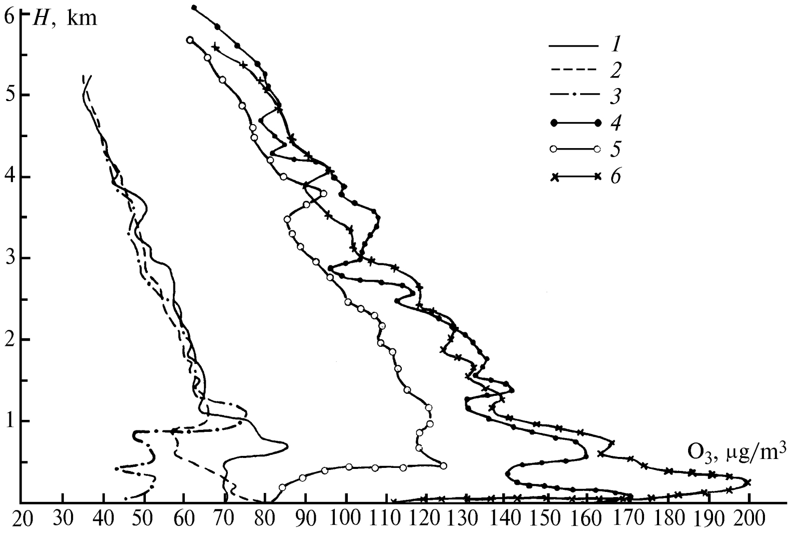


FIG. 9. Vertical ozone distribution over the cities: 1) Tomsk, February 5, 1989; 2) Ufa, February 5, 1989; 3) Donetsk, February 6, 1989; 4) Tomsk, March 23, 1989; 5) Balkhash, March 23, 1989; 6) Nizhnevartovsk, March 24, 1989.

There are some salient features of the ozone generation within the boundary layer. It is most pronounced in the mixing layer rather than at the Earth's surface.[103] This result is natural considering the intense sink of ozone on the underlying surface.

The data obtained in February and March were specially selected from the total data array. It is precisely this period in which the intense ozone generation begins due to the effect of natural factors.[104] In particular, a lot of phytoncides containing hydrocarbons, the basis for ozone generation, enter into the atmosphere.[105–108] In addition, the underlying surface gets rid of the snow cover, thereby increasing the rate of arrival of nitrogen oxides into the atmosphere.[109–112] The influx of solar radiation also increases. The results obtained in Refs. 104–112 allow one to suppose that ozone formation should be the greater, the more intense is the generation of the initial components.

The data shown in Fig. 9 confirm such supposition. It is seen that the ozone concentration in the ground layer is a few times greater in the forest regions (Tomsk and Nizhnevartovsk) than in a steppe (Donetsk) or a desert (Balkhash). The city of Ufa, situated at the south of the Urals, takes an intermediate place.

The next question attracting our attention is the rate of recovery of the photochemical equilibrium in the process of ozone generation. Let us consider the data obtained in airborne sounding over such an ecologically unfavorable region as Komsomol'sk-on-Amur. Emissions of enterprises of this city lead to the situation in which the photochemical smog of different intensity is present over the city practically always.[113] The ozone is formed in winter too.

Two periods, winter and summer, when the atmospheric front passed and cleansed the atmosphere over the city from impurities practically completely, were selected for the analysis. The vertical profiles *1* and *4* in Fig. 10 show the initial ozone distribution established in the course of photochemical processes. Profiles *2* and *5* were obtained just after the passage of atmospheric fronts. And finally, profiles *3* and *6* show the distribution of the ozone concentration over the city a day after passage of the front. It is seen from the comparison of these curves that the ozone concentration is recovered during a day. This means that the photochemical processes generate the amount of ozone optimum for this period under specific physical-geographical conditions in a few hours (night should be excluded) in the presence of the sources of the ozone-producing substances.

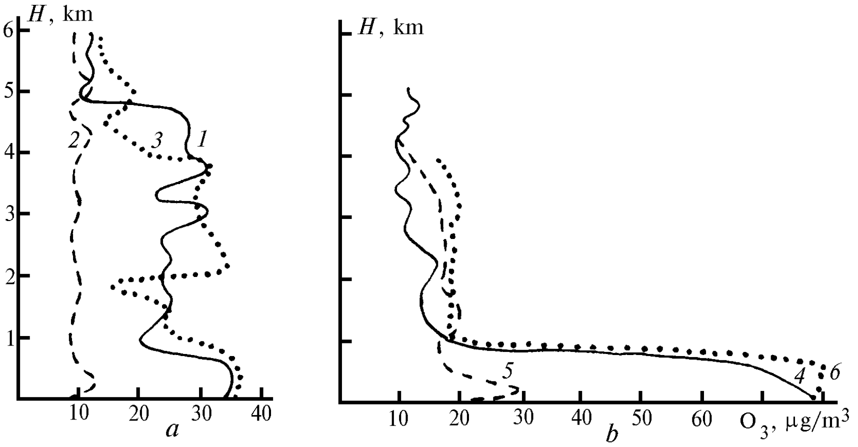


FIG. 10. Ozone vertical distribution over Komsomol'sk-on-Amur in summer (a): 1) June 20, 1990; 2) June 28, 1990; 3) June 29, 1990; in winter (b): 4) December 12, 1990; 5) December 18, 1990; 6) December 19, 1990.

It is also seen from Fig. 10 that the ozone generation occurs only in the mixing layer across the whole its thickness. As its height increases, the absolute value of the ozone concentration decreases, although the total ozone content remains approximately the same. Evidently, this is the manifestation of the constant intensity of anthropogenic ozone-producing sources present in the city. Ozone generation in winter, when natural sources practically do not act, is the primary evidence of their anthropogenic nature.[104]

This phenomenon – the ozone formation in the internal mixing layer – has a continuation that has the negative significance for the biosphere, especially in cities. This is the ozone sedimentation on the ground at night, when turbulent mixing essentially weakens. Such sedimentation was observed in Khabarovsk and Komsomol'sk-on-Amur[113] and is manifested through the appearance of the night maximum of concentration, i.e., during the period when the photochemical processes do not occur and there is no ozone generation. Kharchilava et al.[114] also reported about the presence of the night maximum. Possible consequences of the ozone impact on the biosphere have been discussed in the introduction.

In addition to the ozone generation from emissions of anthropogenic sources (in Khabarovsk and Komsomol'sk-on-Amur), the situations were observed in airborne sounding of the atmosphere over some cities in which the ozone was not formed in the presence of all necessary conditions for photochemical processes. This fact is illustrated by Fig. 11 that shows the vertical distribution of gases over Nizhnevartovsk in August 1991 in the daytime.

It follows from Fig. 11 that the ozone vanishes (the detection threshold was 1 μg/m^3) at an altitude of 400 m, where the concentration of hydrocarbons, NO, and CO is maximum. The ozone concentration is also low near the ground. The vertical distribution of NO$_2$ is in the opposite phase with ozone. This possibly indicates its destruction in the reaction

$$NO + O_3 \rightarrow NO_2 + O_2$$

and, since the concentration of NO is significantly greater than that of O$_3$, this leads to its complete consumption.

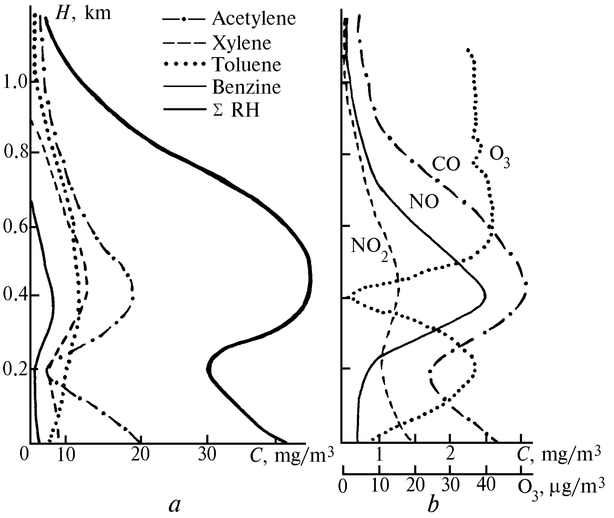


FIG. 11. Vertical distribution of gases over Nizhnevartovsk (average) in August 1991.

Alternative explanation of the decrease of ozone concentration is also possible. When analyzing ozone interaction with heavy hydrocarbons, it was repeatedly noted that its reactivity varied more than 2000 times. A lot of plumes of burning natural gas were observed in the region of Nizhnevartovsk during the experiment. One can suppose that many hydrocarbons leading to the ozone destruction are emitted into the atmosphere in gas combustion. Figure 12 borrowed from Ref. 115 confirms such a possibility. It shows the conversion of initial fuel hydrocarbons in combustion as well as their relative composition observed in air. According to Refs. 41 and 99, production or sink of ozone in its interaction with hydrocarbons essentially depends on their type.

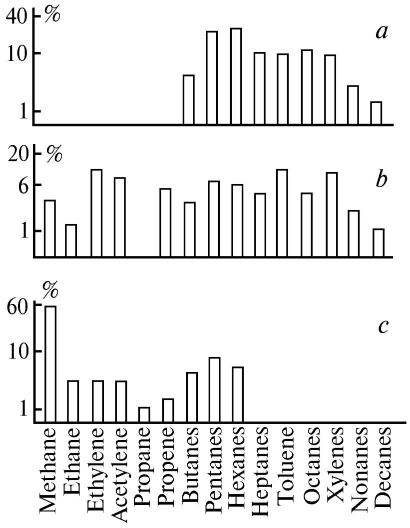


FIG. 12. Percentage (by mass) of different hydrocarbons in fuel (a), motor transport exhausts (b), and urban air (c).

Ozone monitoring in the ground layer was started at the Institute of Atmospheric Optics in September 1989 and then continued at the TOR-station.[102] It is being carried out now. The 3–02P ozonometers periodically tested by means of the GS–2 ozone generator are used as principal measuring means.

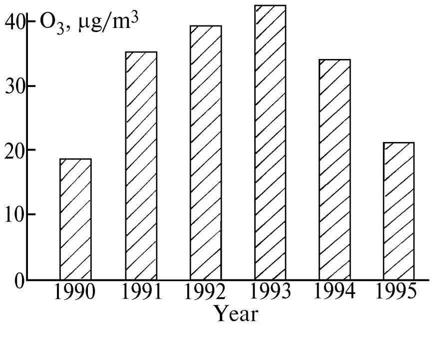


FIG. 13. Average annual ozone concentration in Tomsk.

Measurements carried out during the first four years (Fig. 13) revealed the significant decrease of the ozone concentration, which was also observed by other authors.[4,7,116] However, the average annual ozone content decreased almost down to the initial values in the subsequent years. Neither measurement site no environment was changed. Tests of ozonometers did not reveal any change of their metrological characteristics. So the nature of the ozone behavior in the ground layer in the region of Tomsk is not clear yet.

Two reasons of such year-to-year behavior of ozone concentration are possible. The first is that it reflects the natural atmospheric processes that have long-term trends.[116] The second is the decrease of the anthropogenic contribution due to the decrease of the industrial activity in the last few years, which reached 70% of the total ozone concentration in 1993 (see Ref. 117).

Annual behavior of the ozone concentration during different years is unambiguous (Fig. 14). The majority of authors note that it should have well-pronounced annual amplitude with the maximum in spring caused by the vital activity of vegetation.[118–120]

It is seen from Fig. 14 that such a situation was observed in 1991 and 1992. The annual behavior of ozone concentration in 1993 and 1994 had two maximums of almost equal significance. Maximum in 1995 was observed in the middle of summer.

One can explain in part the above-noted differences by the variability of climatic characteristics of Tomsk.[121] They are principally caused by the general circulation conditions. The matter is that the position of the planetary frontal zone changes abruptly from the southern regions of Western Siberia to the Arctic coast in spring.[122,123] Hence, the weather that determines the ozone generation rate[2,3,41] sharply changes.

One of the sink mechanisms is interaction of ozone with the aerosol. However, the relationship between these air components was studied insufficiently. Putting into operation of the TOR-station, where the aerosol disperse composition is also measured, makes it possible to address to this problem.

It is seen from Table IV that the relationships between ozone and aerosol in the Tomsk region in cold and warm seasons are opposite to each other. Let us remind that a correlation coefficient of 0.1038 is significant for such a sample[124] at a confidence level of 0.9995. The ozone sink in winter occurs on the submicron aerosol fraction (the correlation coefficients are negative). One can explain the high positive correlation with the average-sized aerosol fraction in this period by arrival of warmer air masses enriched by “oldB aerosol.[125,126] Ozone and aerosol generation occurs synchronously in summer. This is manifested through the significant positive correlation coefficients for submicron particles. Correlation of ozone with the average-sized fraction is significant only at a confidence level of 0.95. This possibly reflects aging of aerosol particles in the course of photochemical processes.

Let us note in conclusion that the purpose of this paper is not comprehensive description of the tropospheric ozone problem. More likely it is a guide for the beginners in this field, because it is based on overlapping sciences: physics, chemistry, and meteorology that require the corresponding amount of knowledge. Several hundreds of papers devoted to this direction have already been published. The authors, dealing with an individual very special problem, stated only a part of the general problem from their own viewpoint, and overestimated or underestimated the significance of separate factors or cycles. As a result, in the process of conversance with the literature the sensation is created that almost all substances in the atmosphere can interact with each other forming infinite cycles. Since the photochemical theory is still being developed and many statements require experimental verification, this paper is not, under any circumstances, to be considered as final. Many aspects of photochemical ozone formation in the troposphere have only been touched or briefly considered.

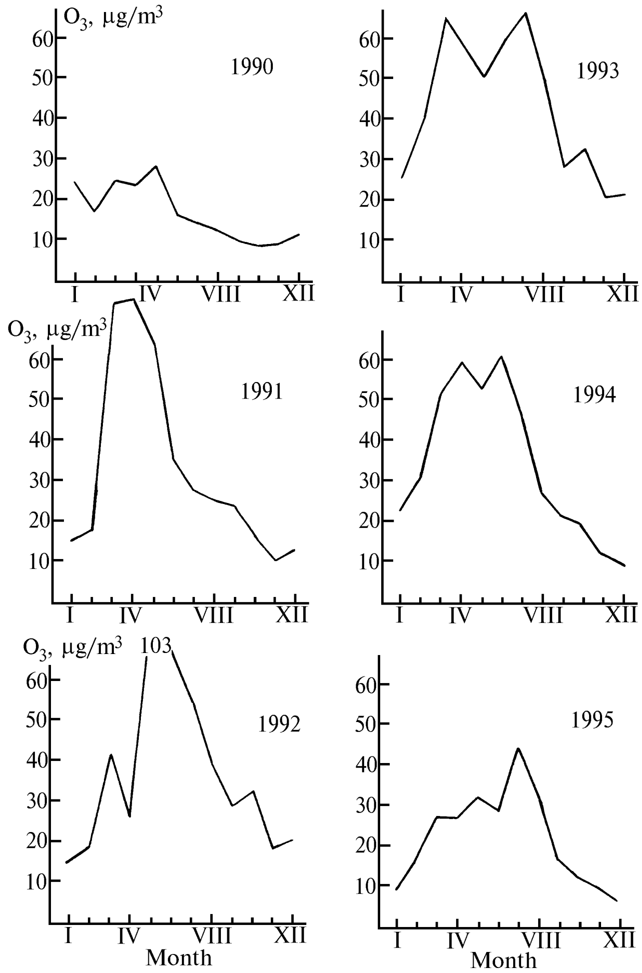


FIG. 14. Annual behavior of ozone in the ground atmospheric layer in Tomsk.

TABLE IV. Correlation coefficients between ozone and aerosol.

Particle size d, μm	0.4	0.6	0.8	1.0	1.5	2.0
Winter ($n > 2800$)	– 0.436	– 0.230	– 0.141	– 0.088	0.331	0.331
Summer ($n > 3500$)	0.221	0.190	0.156	– 0.057	0.018	– 0.053

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