natural environment and which have no harmful effect on the environment.

Information on the state of natural systems especially in regard to chemical and other kinds of contamination is of enormous importance for the protection of the environment. Most of the operative information on the biosphere is currently provided by the Earth's artificial satellites which have a resolving power of better than 10 m. However such information is suitable for "the monitoring of areas" but is inadequate for "the monitoring of the state" of natural systems. The elaboration of convenient techniques, equipment, and instruments for obtaining quantitative measurements of environmental parameters is of great importance for attaining progress in terrestrial monitoring. In this regard the design of instruments and the development of techniques which employ chemical or physicochemical principles will play an important role. The design of novel and readily obtainable instruments and techniques will improve the accuracy, validity, and range of measurable parameters in natural systems.

These are merely a few of the directions for research into the field of chemical ecology and they will undoubtedly be supplemented by new directions in the elaboration of a chemical ecology programme.

On account of the sharp increase in potential hazards to man and nature posed by the accumulation of xenobiotics in the environment, special national programmes have been organised on this aspect of chemical ecology by the industrially developed countries and through international collaboration. For example since 1980 international conferences on dioxin have been held. Of the major producers and users of chlorine products only the Soviet Union is not participating in the international collaboration on this problem and so far has no kind of programme for engaging in research into this problem. Extension of international collaboration on questions of chemical and other aspects of ecology is also an urgent necessity and should constitute a significant part of the programmes being prepared and projects targetted towards the protection of the environment.

The main objective of chemical ecology is the conservation of the vital qualities of the biosphere and the prevention of progressive pollution of the natural environment by reorganisation of anthropogenic activity which would promote the growth of industrial and agricultural output and which would exclude any unfavourable effect on nature. Ultimately the problem concerns the elaboration of conditions and measures which would promote the further development of human civilisation and the survival of humankind.

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The chemical physics of the ozone layer

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The ozone layer exerts a significant effect on the properties of the middle atmosphere and creates the conditions under which the flora and fauna can exist on the Earth's surface. These features of the ozonosphere are in a sense caused by the unique physicochemical properties of ozone. The ozone molecule absorbs solar radiation intensely in the wavelength region below 290 nm, which is harmful to biological matter, and also (although less intensely) the "terrestrial" infrared radiation at a wavelength of 9–10 μm thereby enhancing by 10% the greenhouse effect caused by carbon dioxide and other radiatively-active components of the atmosphere. On the other hand ozone molecules are highly reactive on account of the low value of the energy bond between the "third" oxygen atom and the oxygen molecule. It is correct to say that the chemistry of the atmosphere and the troposphere and particularly the chemical processes associated with anthropogenic contaminants and their destruction in the atmosphere are controlled by ozone, albeit with the loss of the molecule itself.

As regards the effect of atmospheric ozone on global ecology it can be ascertained that the ozone layer is important as a factor providing a biologically safe level of ultraviolet radiation close to the Earth's surface and is involved in the conservation of the Earth's overall climate and controls the content of certain anthropogenic and natural contaminants in the atmosphere. It is noteworthy that the latter usually is under the shadow of the opposite problem, the effect of anthropogenic impurities on the ozone content. However these problems are evidently closely associated.

The stratification of the middle atmosphere caused by the change in temperature and distribution of ozone with altitude is shown in Fig. 1. The stratosphere contains the main reserves of ozone. The maximum concentration is found at an altitude of 20–25 km. At these altitudes the relative content of ozone in the atmosphere is about 1 ppm, and the total quantity of ozone in the atmosphere is equivalent to 3.3 billion tonnes. This quantity would correspond to a gas layer 3 mm in depth at normal temperature, and pressure. It should also be mentioned that ozone is not uniformly distributed over the Earth. On average there is less ozone in the tropics and more at the poles. In addition at all latitudes the total content of ozone changes with the seasons.

The above-mentioned aspects of the ecological significance of ozone will now be discussed.

I. The role of the ozone layer as a filter for biologically harmful ultraviolet radiation

This effect is caused by the fact that short-wave radiation at $\lambda < 300$ nm is harmful to many biological molecules, especially for DNA. The ozone layer which exists at present successfully fulfils a radiation protective function which may be judged according to the change in the intensity of sunlight in the 210–290 nm wavelength range with altitude. There is a distinct dip in the intensity of

sunlight in the above-mentioned wavelength range. However, in the 300 nm wavelength region ozone does not so effectively absorb light and the light intensity rapidly increases with increase in wavelength.

It is generally agreed that the increase in skin cancer diseases in people living at low latitudes and other biologically unfavourable consequences for the fauna and flora which have not been fully investigated is the result of a decrease in the ozone content of the atmosphere (possible also as a result of the influence of anthropogenic factors).

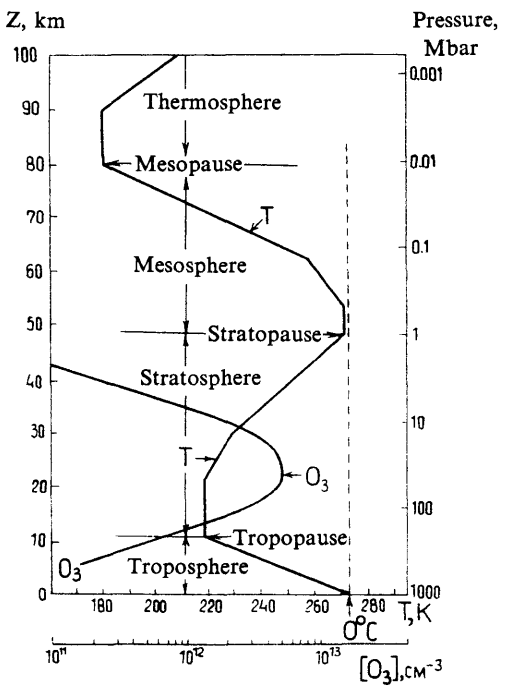


Figure 1. Stratification of the Earth's atmosphere.

II. The ozone layer as a climate-forming factor

The effect of the ozone layer on the climate is also associated with the absorption of light not only in the ultraviolet but also in the infrared region. It has already been mentioned that in absorbing infrared radiation emerging from the Earth's surface the ozone layer intensifies the greenhouse effect. However the question of the link between ozone and the climate is much more complex, because of the significantly larger number of physical and chemical factors which may affect the content of ozone in the atmosphere, since the effect of ozone on the temperature of the Earth's surface and climate is dependent on the altitude at which a change in the content of ozone occurs.

When the ozone content changes, the overall temperature effect is dependent on the absorption of short-wave and long-wave radiation. The plot in Fig. 2 illustrates how the temperature of the Earth's surface will change if the ozone content increases at different altitudes within a narrow range of altitudes when there is 3% change in temperature throughout the entire column. It is evident that up to an altitude of 30 km an increase in the content of ozone will lead to a warming of the Earth's surface and at altitudes above 30 km there will be a cooling of the Earth's surface. In this case the maximal effect will occur, when the ozone content changes in the tropopause region. At these altitudes the effect may be attributed to absoption and over-irradiation by the "terrestrial" infrared radiation at a wavelength of 9–10 μm.

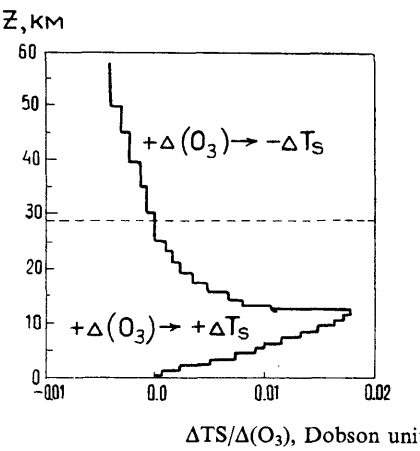


Figure 2. "Radiation" change in the temperature at the Earth's surface when the total content of ozone changes by 3% on account of the local change in ozone content at different altitudes[1] (D. U. = Dobson units).

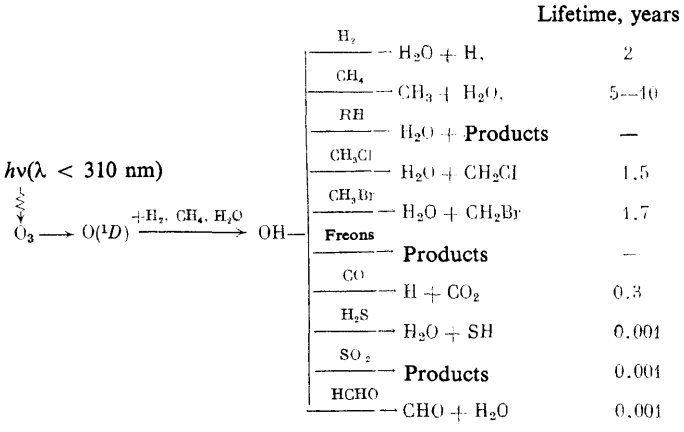
It is known that the greenhouse effect reaches a maximum at the maximal temperature contrast between absorbed and emitted radiation and that the temperature reaches the lowest values in the tropopause region.

"Cooling" as a result of the increase in content of ozone at altitudes greater than 30 km is associated with the absorption of solar radiation.

The possible change (according to data issued by the World Meteorological Organisation) in temperature of the Earth's surface within 50 years as a result of a change in the composition of microcontaminants in the atmosphere including ozone during expansion of industrial and agricultural production is shown in Fig. 3. It is apparent from assessment models that the ozone content will increase in troposphere and decrease in the stratosphere. This leads to effects acting in one direction and being additive. In this regard one should emphasise that these evaluations are not highly accurate, since it is difficult to take into account all feedbacks which arise in the system. The temperature change range for the various microcontaminants corresponds to the potential range of changes of their content within fifty years. It is evident that the maximum possible climatic effect of ozone may be even greater than that of carbon dioxide.

III. Atmospheric ozone as a factor in the chemical degradation of contaminants entering the atmosphere

It has been mentioned above that chemically active solar radiation with a wavelength shorter than 300 nm does not penetrate the troposphere and in the photochemical sense one might say that eternal night reigns. However various chemical processes occur in this short-wave "darkness" which are caused by the absorption of longer wavelength ultraviolet radiation by ozone. The mode of action of ozone towards anthropogenic and natural atmospheric components in the troposphere is presented below. The lifetimes of the atmospheric components governed by their reactions with the hydroxyl radical are also presented below. The basis of this mechanism is that photolysis



of ozone by light with a wavelength of 300—310 nm leads to the creation of metastable excited oxygen atoms in state ^1D with an energy of 1.97 eV and a radiative lifetime of 110 sec (i.e. very great in comparison with the time between collisions under tropospheric conditions). By reacting with water vapour, hydrogen and methane the $O(^1D)$ radicals form the hydroxyl radical, which in turn interacts with many anthropogenic and natural contaminants, thereby determining their lifetime in the atmosphere.

The mechanism described is an important component of the overall mechanism for the removal of contaminants from the troposphere and, as can be seen below, its actual existence may lead to the protection of the ozonosphere from certain Freons.

One should mention that similar processes also occur in the stratsophere, although in this case short-wave radiation is the main factor acting upon the Freons, and furthermore from the ecological standpoint these processes are not of such key importance as in the troposphere.

The ecological importance of the ozone layer and therefore the reason why it is essential to conserve this layer unchanged has already been mentioned.

Of all the anthropogenic factors which are potentially damaging to the ozone layer the present authors are only focussing on those Freons, which are generally considered to present the greatest hazard to the ozonosphere. This conclusion is based on results obtained by many authors over the past fifteen years from numerical modelling and from laboratory data and full-scale measurements.

An example of a model prediction of the change in content of ozone in the presence of Freons and other anthropogenic and natural contaminants is presented in Fig. 4. It is apparent from these data that the ozone content may significantly decrease with increase in the production of Freons (one has in mind mainly Freons 11 and 12).

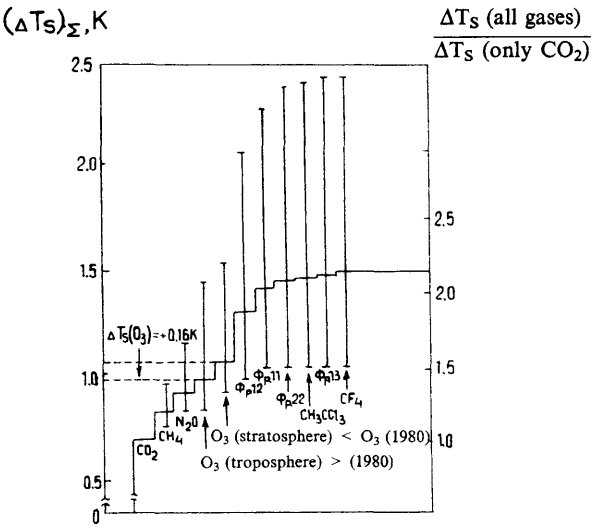


Figure 3. Change in temperature of the Earth's surface within fifty years as a result of the increase in various minor components in the atmosphere.

As regards the experimentally determined ozone trend, according to data obtained with the aid of the American satellite Nimbus-7 between 1978 and 1985 there was a 2.6 to 10% decrease in the ozone content in different latitudinal zones and an increase in the content of chlorine, and the anthropogenic proportion of the latter is nowadays one third of the total number of chlorine particles in the atmosphere.

Finally the observation in 1985 of the so-called Antarctic ozone "hole", which is characterised by a decrease of tens percent of the total content of ozone in this region in spring, supports the argument that the Freons pose a real threat to the ozonosphere.

These findings have led to the adoption of international agreements on refrigeration and the subsequent phaseout of the production of ozone-destroying Freons, which are the main source of supply of anthropogenic chloride to the stratosphere. One has in mind the Vienna convention on the protection of the ozone layer (23 May 1988) and the Montreal Protocol of the convention adopted in September 1987 and ratified by the Soviet Union in September 1988. Essentially the question concerns the prospects of renouncing the production of ozone-destroying Freons and replacing them by ozone-friendly compounds, ideally by Freons which possess the same physicochemical and biological properties but which do not destroy the ozone layer.

As a result the need arose to compare the extent of the hazard which different Freons presented to the ozonosphere and to select the less active so-called alternative compounds.

In order to meet this objective it was at first necessary to answer the question why are certain Freons harmful while others present no

hazards for the ozonosphere. In order to answer this question it was necessary to understand the mode of action of the Freons on stratosphere ozone. The mode of action is relatively well understood and in general terms all Freons, which enter the stratosphere, undergo photodissociation in the presence of solar ultraviolet radiation with emission of chlorine atoms or atoms of other halogens which destroy ozone in the following chain of reactions:

$$Cl + O_3 \rightarrow ClO + O_2,$$
$$ClO + O \rightarrow Cl + O_2.$$

In each pair of reactions of this type two particles of so-called odd oxygen, O and O_3, disappear while the chlorine atom is conserved, thereby enabling one chlorine atom to enter the stratosphere to destroy up to 100 000 ozone molecules. This "chemical amplification" is the reason for the potential hazard of Freons for the ozone layer.

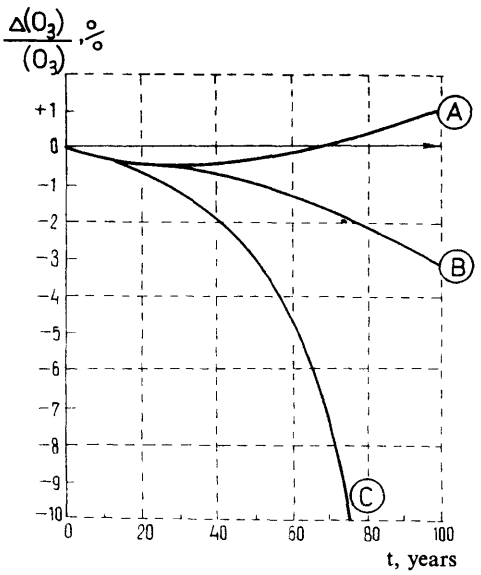


Figure 4. Change in the total content of ozone for different scenarios of increase in anthropogenic contaminants in the atmosphere[1]: A, an increase in content of CH_4 by 1% per annum; N_2O, a 0.25% increase per annum; CO_2, a 0.5% increase per annum in comparison with the level of 1980 (without any increase in content of Freons); B is A + a 1.5% increase in the content of Freons per annum in comparison with 1980; C is A + a 3% increase in the content of Freons per annum in comparison with 1980.

Thus if Freons undergo photodissociation or by some other route supply halogen atoms to the stratosphere, the ozone will be destroyed.

If the Freons underwent photodissociation or were destroyed in the troposphere, ozone-destroying particles would not appear in the stratosphere, since they may normally be rapidly washed on to the Earth's surface.

Thus a search for compounds which present no hazard for ozone would involve the identification of compounds which are destroyed in the troposphere.

It can be demonstrated that of all possible processes for the destruction of Freons in the troposphere the most important are those reactions with a hydroxyl radical and reactions involving photodissociation in the presence of light with a wavelength of more than 300 nm entering the troposphere.

The relative hazard of chlorine-containing Freons may be quantified according to the following formula:

$$\xi = W_{str}/(W_{str} + W_{trop}),$$

where W_{str} and W_{trop} is the rate of destruction of the Freon in the stratosphere and troposphere respectively. According to this formula the hazard rating of Freons 11 ($CFCl_3$) and 12 (CF_2Cl_2), which are extensively used nowadays and which are not destroyed in the troposphere, is equal to unity, while for the required ideal Freons, which undergo total degradation in the troposphere, a hazard value of zero will be obtained.

Knowing the concentration of hydroxyl radicals in the troposphere it is possible to find the minimal value of the rate constant for the reaction between the Freon and OH so that this process could have competed with the photodissociation process of Freons 11 and 12 in the stratosphere giving a lifetime of 100 years, a value typical of ozone-destroying Freons. Setting the characteristic reaction time of the Freons with OH to 100 years it is found that the required value of the rate constant should be equal to or in excess of the value of 3×10^{-16} cm^3 s^{-1}.

In fact there is a larger group of Freons with a rate constant value for the reaction with OH significantly higher than this minimal value, and the lifetime is less than 100 years. These compounds include Freons containing hydrogen atoms which can be detached by the hydroxyl radical. Freons which contain no hydrogen atoms, do not react with OH, and hence they are not degraded via this route in the troposphere. This group of compounds includes Freons 11 ($CFCl_3$), 12 (CF_2Cl_2), 113 ($C_2F_3Cl_3$), 114 ($C_2F_4Cl_2$), and 115 (C_2F_5Cl) which are extensively used in refrigeration technology and other branches of the economy and which are considered to be ozone-destroying compounds. It also follows that it could have been possible to find a substitute for these ozone-destroying compounds. However, this is not such a simple objective, because in a decomposition in which a hydrogen atom is detached from the molecule while the remaining radical can still travel around the troposphere the halogen (chlorine or bromine) remains a hazard for the ozonosphere. This reduces the problem to the chemical (with respect to the subsequent collision of the radical) or photochemical "troposphere" fate of this radical, a problem which still requires investigation.

For this reason the prediction of the extent of the hazard for ozone based on the photo-detachment of the dangerous halogen by troposphere ultraviolet radiation would be a more realistic approach.

Of those Freons which are being developed in the MGO Tekhnokhim in Leningrad as alternative compounds, three Freons are currently under investigation in the Institute of Energy Problems of Chemical Physics, Academy of Sciences of the USSR, i.e. Freons 123 ($C_2HCl_2F_3$), 134 ($C_2H_2F_4$) and 114B2 ($C_2F_4Br_2$). It has been found that with all of these compounds the rate constants of the reactions with free hydroxyl are such that for at least two of them (if these reactions would be adequate) degradation would primarily occur in the troposphere. Unfortunately the extent of

photodissociation of these two compounds by troposphere ultraviolet radiation was found to be extremely low.

The prediction in relation to the third compound, $C_2F_4Br_2$, is more realistic. The extent of light absorption in the 300 nm region was found to be low (10^{-22} cm^2) but adequate, so that $C_2F_4Br_2$ underwent photodissociation primarily in the troposphere. Nevertheless on account of the significantly greater efficiency of bromine particles in comparison with chorine particles the hazard of $C_2F_4Br_2$ was found to be greater than that of for example Freons 11 and 12.

Thus the problem of the assessment of the hazard of alternative compounds can be considered to be correctly set up but further studies are necessary in order to resolve this problem.

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Mathematical modelling of the distribution of atmospheric contaminants taking account of chemical transformations

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The troposphere is the layer of the atmosphere adjacent to the surface of the Earth. Although the altitude of this layer is small, no more than 11 km, it plays a dominant role in the chemical processes which take place in the atmosphere. Various chemical impurities enter the troposphere, originating both from the Earth's surface as a result of natural geological, biological, chemical and physical processes, and from the upper layers of the atmosphere. In recent years, a considerable proportion of substances entering the troposphere have stemmed from anthropogenic influences, their strength being in some instances comparable to that of natural sources. A very important outcome of the anthropogenic influences is the emission into the atmosphere of substances which either do not occur in the natural state, or have until now been present in very small concentrations as, for example, freons. This may have completely unexpected and hardly foreseeable consequences.

On entering the atmosphere, the impurities become immediately involved in processes of two types:
(a) physical dilution and transport caused by different processes of diffusion and motion of air masses;
(b) chemical transformations.

The aim of the present work is to describe secondary mechanisms of atmospheric pollution, associated with the chemical transformation of impurities in the troposphere, and modelling of these mechanisms combined with hydrometeorological processes.

1. Chemical transformation of substances in the troposphere

Let us consider the possible ways of chemical transformation of substances in the troposphere. The following can be regarded as the main impurities in the troposphere: O_3, CO_2, CO, NO, NO_2, NH_3, CH_4, H_2, SO_2, CH_2O, H_2S, etc.[1] Under typical conditions (at a temperature of 25 °C) all these substances are stable enough. With few exceptions, they do not react with each other or with the main components of the atmosphere. A typical exception is apparently nitric oxide, capable of entering the reaction

$$2NO + O_2 \rightarrow 2NO_2,$$

However, the rate of this reaction, too, is insignificant as long as the NO concentration is low. Nevertheless, chemical transformations in the atmosphere do occur.

The main reason for these chemical reactions is the effect of solar radiation on constituents of the atmosphere.[2] The spectrum of solar radiation measured at the Earth's surface and in the stratosphere, is shown in Fig. 1. It is clear from it that only photons with wavelengths in excess of 300 nm reach the surface of the Earth. Thus in the troposphere photochemical dissociation of oxygen, and even to a greater extent that of nitrogen, into atoms is impossible, although some impurities may undergo photolysis. Table 1 presents some information on these components.[3]

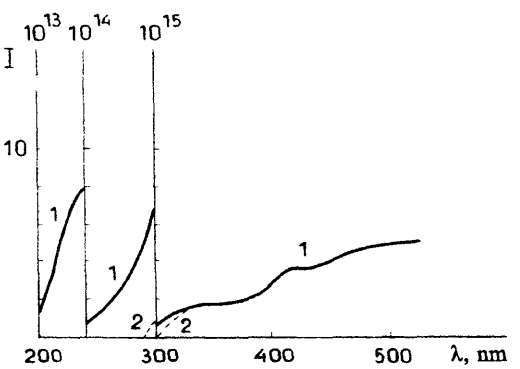


Figure 1. Spectrum of solar radiation.[3] *I* is the number of photons per second reaching an area normal to their propagation: *1*, in the stratosphere; *2*, at the Earth's surface.

It can be seen from the table that the number of substances undergoing photochemical dissociation in the atmosphere is small. Yet some of these substances, for example, HNO_2, H_2CO, NO_2, and O_3, may exhibit very high dissociation rates, their lifetimes in the troposphere being as short as a few hours. However, not all these processes play an important part in the elimination and transformation of tropospheric substances, since the path a particular substance has entered the atmosphere is also important. For example, the photolysis of nitrous acid HONO, which proceeds at a high rate, leads to the formation of OH and NO radicals, but then nitrous acid itself is formed in the atmosphere (if one excludes its anthropogenic origin) as a result of the reaction between OH and NO particles:

$$OH + NO \rightarrow HONO.$$