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The Effect of Galactic Cosmic Rays on the Chemical Composition of the Atmosphere, Greenhouse Effect and Ozone Layer of the Earth

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Abstract—Estimations of the effects of galactic cosmic rays (GCR) on chemical composition of the troposphere and stratosphere in view of known mechanisms of formation of NO and OH under impact of GCR have been made. It has been shown that GCR may significantly change a chemical composition of the upper troposphere and the stratosphere. However, GCR do not influence on an abundance of H-containing greenhouse gases (such as methane and ozone–harmless freons) but can noticeably reduce the concentration of atmospheric ozone. Those estimations have shown a necessity to take into account the influence of GCR on the composition of the atmosphere at the analysis of ozone related processes and, in particular, at forcasting recovery of the ozone layer.
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INTRODUCTION

Currently, the main impact of galactic cosmic rays (GCR) on the properties of the atmosphere is associated with the formation of clouds as a result of appearance of charged particles in the atmosphere that serve as condensation nuclei of atmospheric humidity [1–5]. However, apart from this indirect effect, there is a direct effect of the chemical composition of galactic cosmic rays on the atmosphere relating to the formation of an additional amount of nitrogen oxides and hydroxyl radicals. OH radicals are the main oxidants of troposphere, providing a runoff of most H-containing components including methane and ozone–harmless substitutes for freons, which have greenhouse properties. In addition, OH radicals and nitric oxide are involved in the chain processes of ozone destruction. In this regard, the presented study estimates the impact of galactic cosmic rays on chemical composition of the atmosphere, the greenhouse effect and ozone layer.

Energy, which is brought to the Earth by the flux of galactic cosmic rays (GCR) is only 0.007 Erg cm^2 s^{-1}, which is eight orders smaller than the flux of radiant energy of the sun, and roughly corresponds to the energy flow received by the Earth from all the stars in our galaxy [6]. However, in contrast to the radiant energy of the sun, most of which pass through the Earth's atmosphere, the energy of the GCR is completely absorbed in the atmosphere, and the maximum absorption occurs in the lower stratosphere and upper troposphere. This area of heights is characterized by a marked weakening of the flow of chemically active solar ultraviolet radiation, so the role of galactic cosmic rays as a source of active chemical particles is worthy of note.

The main products of the interaction between galactic cosmic rays and atmospheric air is oxygen, nitric oxide and (in the presence of humidity), hydroxyl radicals OH. At present, it is assumed that the atoms of oxygen and nitric oxide are formed in the air as a result of these processes [7, 8]:

$$N_2 + \vec{e} \rightarrow + 2e,$$

$$N_2 + \vec{e} \rightarrow N^+ + N + 2e,$$

$$N^+ + O_2 \rightarrow N + O_2^+,$$

$$N + O_2 \rightarrow NO + O,$$

where $\vec{e}$ — fast secondary electrons produced in the pri-

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mary events of air ionization by protons and α-particles of galactic cosmic rays.

The mechanism of formatiton of hydroxyl radicals as a result of ion–molecule reactions involving the primary ions includes the following reactions:

$$N_2^+ + O_2 \rightarrow \ + N_2,$$

$$O_2^+ + O_2 + M \rightarrow \cdot O_2 + M,$$

$$O_2^+ \cdot O_2 + H_2O \rightarrow \cdot H_2O + O_2,$$

$$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ + OH + O_2,$$

$$H_3O^+ + H_2O + M \rightarrow H_3O^+ \cdot H_2O + M,$$

$$H_3O^+ \cdot (H_2O)_{n-1} + H_2O + M \rightarrow H_3O^+ \cdot (H_2O)_n + M$$

This reaction scheme was proposed in [9] to explain the ionic composition of the D-region of ionosphere, and in [10] it was first used to analyze the possible influence of galactic cosmic rays on the ozone layer.

Then positively charged ion clusters of water recombine with the negative ion clusters, which can be $HSO_4^- \cdot (H_2SO_4)_3$, $HSO_4^- \cdot (HNO_3)_3$, $NO_3^- \cdot (HNO_3)_2$ и $HSO_4^- \cdot (H_2SO_4)_2$ [11, 12]. As a neutral molecule H_3O does not exist, in any case, the recombination of positive and negative ion clusters the positively charged core of the ion cluster H_3O dissociates with the formation of H atom, for example, as follows:

$$H_3O^+ \cdot (H_2O)_n + X^- \rightarrow H + \text{products},$$

where X^- is one of the possible negatively charged ion clusters mentioned above. Followed by a fairly quick chain reaction, leading to the birth of the radicals OH and HO_2:

$$H + O_2 + M \rightarrow HO_2 + M,$$

$$HO_2 + O_3 \rightarrow OH + 2O_2,$$

$$H + O_3 \rightarrow OH + O_2$$

Thus, it can be assumed that the formation of one ion pair in the lower stratosphere and upper troposphere leads to the birth of one NO molecule and two OH radicals, which is agreement to the data published in [13]. It is known that nitrogen oxides and hydroxyl radicals are involved in the chain destruction of stratospheric ozone, and this GCR effect, as well as the effect of solar proton flares, ionizing the upper stratosphere and mesosphere, has been debated in the studies [14–16]. At the same time, the effect of hydroxyl radicals formed by GCR on the maintenance of the greenhouse gas components, which runoff is due to their reaction with OH radicals, has been discussed only once [17], and, apparently, the influence of galactic cosmic rays on the components of the families O_x, NO_x, Cl_x, Br_x, HO_x, has never been discussed before.

EVALUATION OF THE INFLUENCE OF GCR ON CHEMICAL COMPOSITION OF TROPOSPHERE AND STRATOSPHERE

Calculations are performed using one-dimensional photochemical model of the atmosphere, as described in [19], for latitude 55° N and at daytime conditions. Vertical profiles of the component families O_x = O(3P), O(^{1}D), O_3; Cl_x = Cl, ClO, HOCl, HCl, $ClONO_2$; NO_x = N, NO, NO_2, NO_3, HNO_2, HNO_3, HNO_4; Br_x = Br, BrO, HOBr, $BrONO_2$; HO_x = H, OH, HO were calculated. Altitude profile of ionization is taken from [20] and corresponded to a minimum solar activity and the rigidity of galactic cosmic rays, equal to 1.5 GeV. It should be mentioned that the GCR rigidity is interpreted as the minimum energy at which the galactic rays penetrate the Earth's atmosphere at a given geomagnetic latitude, and the closer geomagnetic latitude is to the poles, the smaller the rigidity is (rigidity 1.5 GeV corresponds to the geomagnetic latitude of 55°). The dependence of the GCR flux from solar activity is explained by the influence of the solar magnetic field, blown to the Earth by solar wind. Just as the intensity of the solar wind increases with solar activity, so GCR flux decreases with its growth.

Obtained data on the impact of galactic cosmic rays on atmospheric components, are shown in Fig. 1. Different components have different in sign effects of GCR, as well as the scale effect reaches several tens of percent. It is also evident that the effect of galactic cosmic rays for all the components increases with the high–side and becomes significant above 15 km, which is explained by the dependence of the ionization rate on height.

Fig. 2 shows the effect of GCR on families HO_x, O_x and NO_x. It can be seen that the families HO_x and NO_x change in the opposite way, which is explained by the interaction of the components of these families, which leads to the transformation of the radicals OH and HO_2 in HNO_2 and HNO_3. The odd–electron oxygen also changes, which is discussed hereafter. Effect of GCR on the families of Cl_x and Br_x was not studied.

The above mentioned data indicate considerable impact of galactic cosmic rays on the composition of small components in the upper troposphere and lower stratosphere.

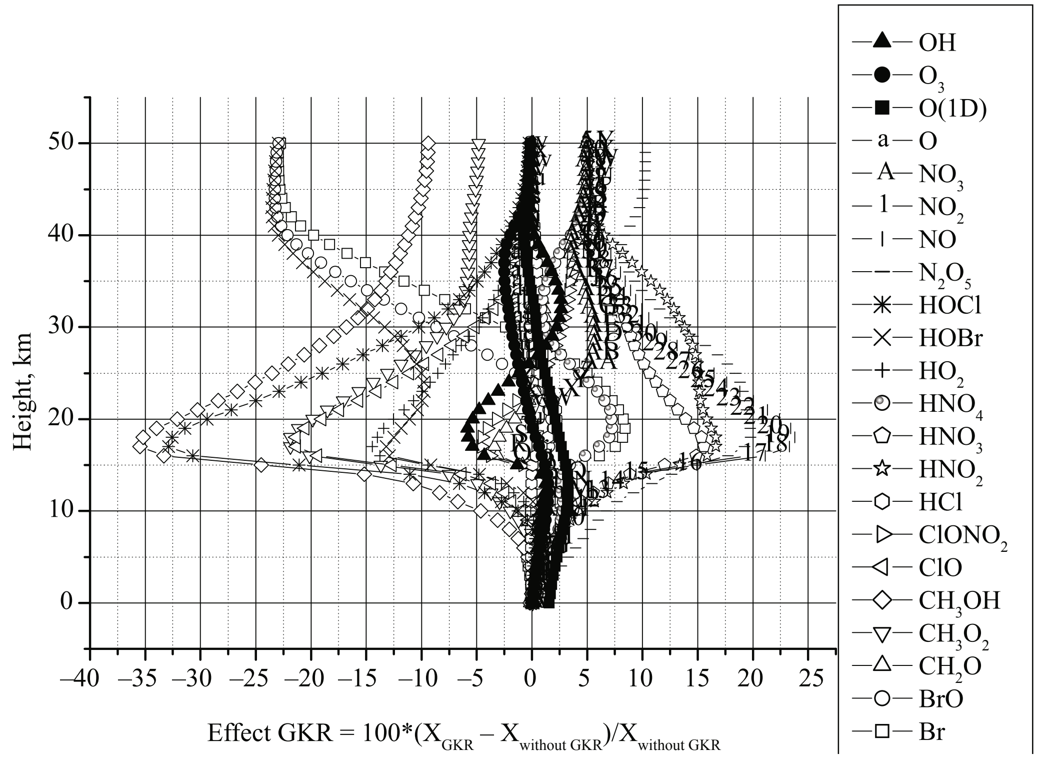

Fig. 1. Relative (%) effect of galactic cosmic rays on atmospheric components at the altitude range of 0 – 50 km.

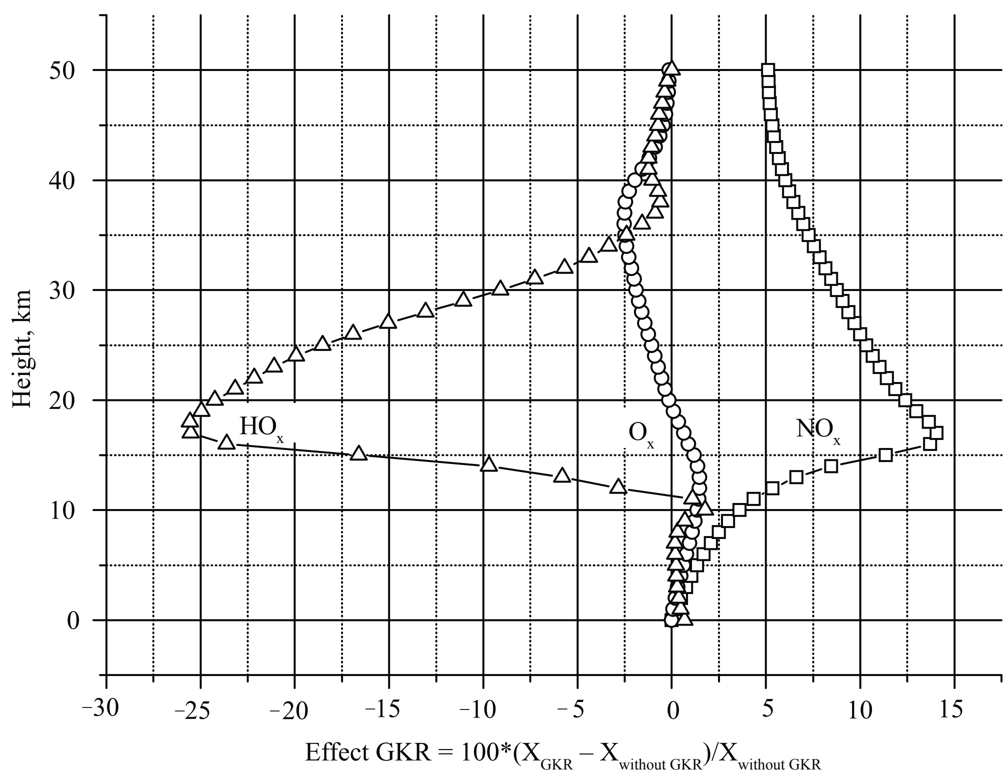

Fig. 2. Relative (%) effect of galactic cosmic rays on the families HO_x, O_x and NO_x.

EVALUATION OF THE IMPACT OF GCR ON THE GREENHOUSE EFFECT

Effect of GCR on the greenhouse effect has been estimated by the example of methane, as well as some ozon–harmless substitutes of freon (HCFC-22 ($CHClF_2$), HCFC-123 ($CHCl_2CF_3$), HCFC-124 ($CHClFCF_3$) and HFC-134a (CH_2FCF_3). The runoff of these components in the atmosphere and, consequently, their atmospheric lifetimes are determined mainly by reactions with OH radicals, and partly from metastable excited oxygen atoms $O(^1D)$, which additional amount arises as a result of photodissociation of formed by GCR ozone and chlorine atoms, an additional amount of which results from the reactions of OH radicals with HCl formed by GCR:

$$OH + HCl \rightarrow H_2O + Cl$$

Thus, a possible chemical mechanism of the impact of galactic cosmic rays on the greenhouse effect may be caused by the following processes:

$$XH + O(^1D) \rightarrow OH + \text{poducts},$$

$$XH + OH \rightarrow H_2O + \text{poducts},$$

$$XH + Cl \rightarrow HCl + \text{poducts},$$

where XH is H–containing component with greenhouse properties. The rate constants of corresponding reactions are given in [18].

Despite the fact that the components of $O(^1D)$, OH and Cl significantly change under the influence of galactic cosmic rays (Fig. 3), yet their influence on the content of methane and ozone–harmless substitutes for freons is insignificant. It is explained by the altitude dependence on the concentration of methane, shown in Fig. 4. As it follows from this Fig., the majority of methane (92.5%) is concentrated below 15 km, where the change of OH and Cl, as follows from the data in Fig. 3, does not exceed 2% (and even then only above 10 km). As for $O(^1D)$, though its relative change under the influence of GCR is slightly higher, its absolute value is too small to affect the concentration of methane. The same result with the same reasons has been received for ozone–harmless substitutes of freon.

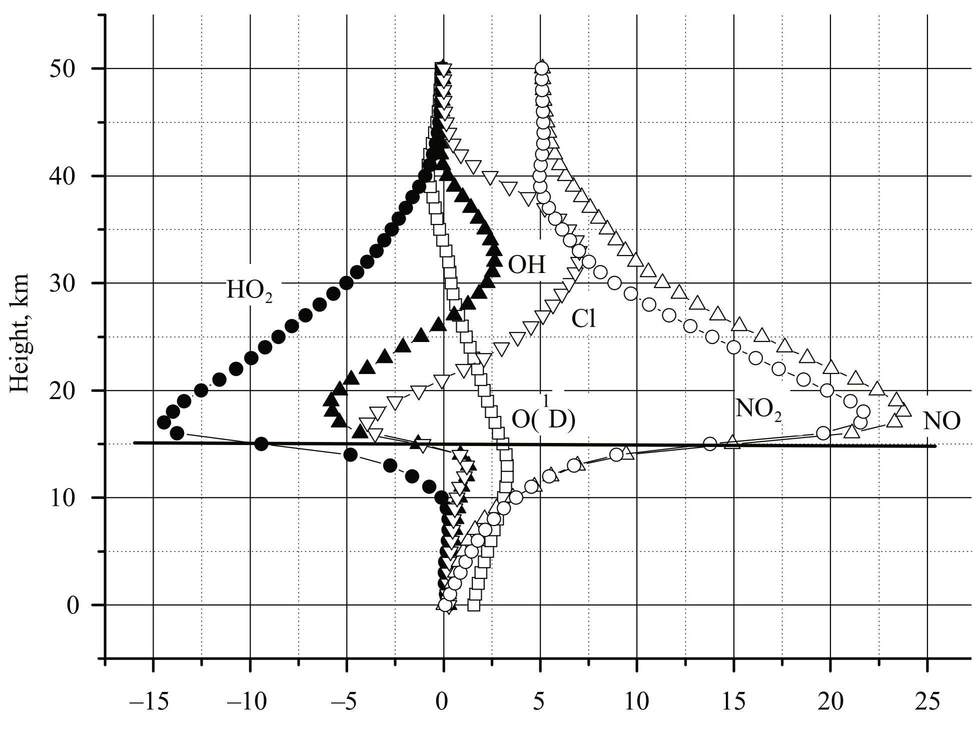

Fig. 3. Relative (%) change of altitude profiles of the components possible to affect the H- containing greenhouse gases and ozone.

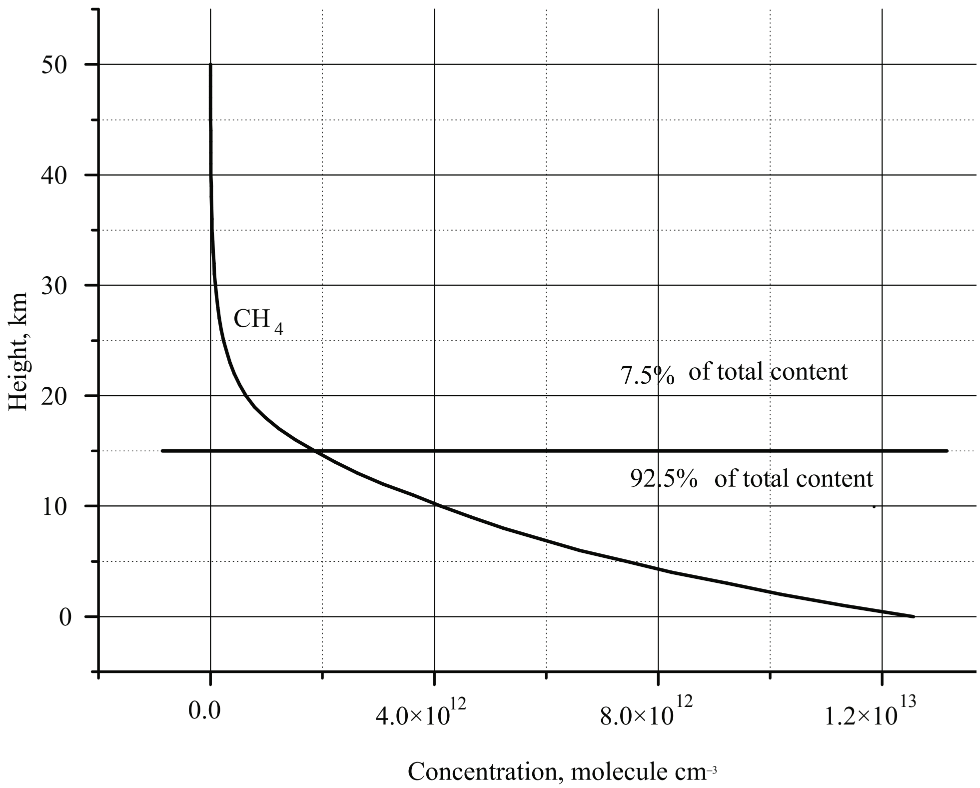

Fig. 4. Altitude profile of methane and its total relative abundance above and below 15 km.

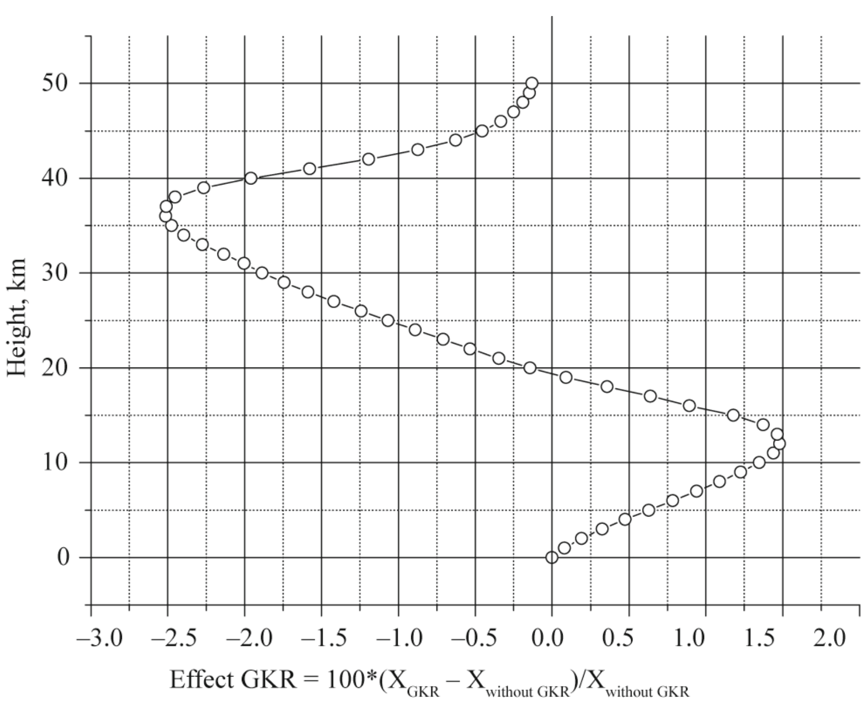

Fig. 5. Relative (%) change in vertical profile of ozone under the influence of galactic cosmic rays.

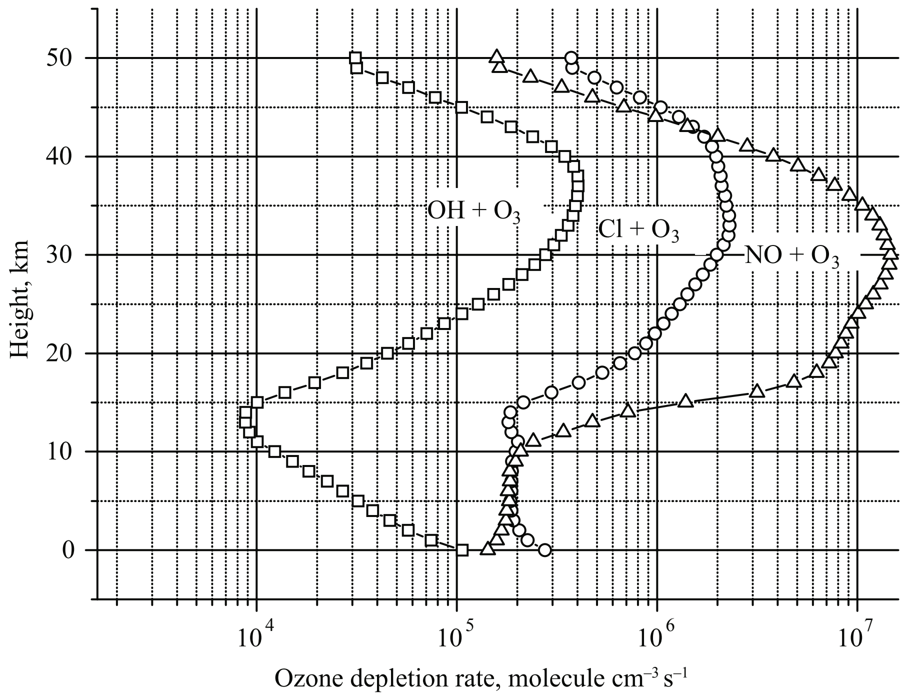

Fig. 6. Altitude profiles of ozone depletion rates with the participation of NO, Cl and OH.

This suggests the influence of galactic cosmic rays on the greenhouse effect to be neglected.

EVALUATION OF THE INFLUENCE OF GCR ON THE OZONE LAYER

The impact of galactic cosmic rays on the ozone layer is much larger than on the climate, as it is evident from the data for the variation of the vertical profile of ozone in Fig. 5. At heights up to 20 km the impact of GCR leads to some increase of ozone due to reaction of OH + CH_4, leading to the formation of O_3, while at altitudes of 20–50 km ozone decreases, because of chain processes of ozone destruction in nitric oxide, chlorine and hydrogen cycles involving NO, Cl and OH. Evaluated to the full content of ozone in a column the GCR effect equals to minus 0.8%. Fig. 6 shows the vertical profiles of ozone depletion rates with NO, Cl and OH. At all altitudes ozone depletion involving NO plays a dominant role.

It should be taken into account that the given data characterize the maximum impact of GCR on atmospheric ozone at the latitude of 550 N, which takes place at the minimum of solar activity. When the latitude is lower, this impact also decreases, while the latitude is gigher, the impact increases. In addition, periodic changes in the effects associated with the 11–year cycle of solar activity [21] take place.

Finally, according to [22], the mid–latitude total ozone content in the period of 2002–2005 was 3% less than up to 1980. This means that the impact of galactic cosmic rays on the ozone layer may take up to one third of the loss of ozone at the end of the last century.

CONCLUSIONS

1. GCR lead to the significant change in content of small atmospheric constituents in the troposphere and stratosphere that should be taken into account in atmospheric models.

2. The impact of galactic cosmic rays on climate is negligible.

3. The maximum effect of galactic cosmic rays on the ozone layer at mid–latitudes may take up to one third of the ozone loss (that happened at the end of the last century) and should be taken in account, while calculating the recovery of the ozone layer.

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