Ozone as a mediator of galactic cosmic rays’ influence on climate

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Abstract. This paper provides information about the important role played by galactic cosmic rays (GCRs) in the lowermost stratosphere ozone budget. We show that the electron impact ionisation of molecular oxygen O2, followed by the production of O4+ and its consecutive dissociation to: 1.) O3++O or 2.) O2++O2 creates an autocatalytic cycle for continuous production of ozone in the lowermost stratosphere. The amount of so produced O3 has the same order of magnitude as the mid-latitude steady-state peak ozone density. This is an indication that the lowermost ozone profile could be substantially distorted by the galactic cosmic rays and sporadically by particles of solar origin. This result is a complementary to previous studies reporting for enhanced climate sensitivity to the variations of the lower stratospheric ozone. We show that the ozone variations near the tropopause act as a commutator – increasing or decreasing the water vapour density in the upper troposphere/lower stratosphere – through changes in the temperature of the layer. These small humidity fluctuations have a tremendous impact on the Earth’s radiation balance, as is shown by other authors. This new mechanism for influence on the surface temperature could change seriously our understanding for the factors driving climate variability, as well as our expectations for the future evolution of the Earth climate

Keywords: galactic cosmic rays, ozone, upper tropospheric humidity, climate variations

Introduction

The scepticism, regarding the leading role of CO2 in the contemporary global warming, increases progressively. The currently observed rise of the global mean surface temperature does not match that predicted by climate models, which indicates either an inaccurate assessment of climate sensitivity to CO2 concentration, or existence of other processes not included in current models [1]. Exaggerated climate sensitivity to CO2 density is pointed out also in [2], whose authors have analysed the top-of-atmosphere outgoing radiation, comparing the data from ERBE (1985-1999) and CERES (2000-2008) instruments with models’ calculations. These and some more similar examples, as well as the experimental evidences for a current levelling of the global mean surface temperature, require a re-assessment of our understanding related to the factors controlling climate variability and the tendency of its change.

In our previous study [3, 4] we have found that Northern Hemisphere land air temperature (LandT) highly anti-correlates with the density of the columnar ozone (see Fig.1). We have created a nonlinear regression model (driven by multi-decadal and interannual variations of Arosa total ozone) and show that it describes 75% of the LandT total variability – slightly more than those explained by CO2 enhancement.

This result raises two more questions: (i) which are factors controlling the variations of the lower stratospheric O3; (ii) what is the mechanism of such a strong influence. In [4] we show that the main driving factor of the lower stratospheric O3 density is galactic cosmic rays (GCR). In this paper we put the accent on the answer of the second question: What is the mechanism of GCR influence on the ozone?

Data and methods of analysis

Data

In this analysis we have used the annual values of Northern Hemisphere land air temperature anomalies (CRUTEM3v time series), Sunspot numbers for the period 1900-2010 and the longest time series of the total ozone from Arosa, Switzerland - for the period 1926-2010.

Fig.1 Time series of Northern Hemisphere land air temperature compared with Arosa total ozone
Methods for estimation of Chemical Reactions’ Efficiency

The ionization efficiency of the atmospheric constituents by the secondary electrons and ions (produced by GCR) is calculated using the Maxwell-Boltzmann distribution (a well established approach in quantum statistics):

\[
\frac{N_i^+}{N} = \frac{g_i e^{-\Delta E_i / kT}}{\sum_{j=1}^{N} g_j e^{-\Delta E_j / kT}} \tag{M1}
\]

where \(N_i^+\) and \(N\) are the number density of ionized molecules of type \(i\) and the total neutral density; \(\Delta E_i\) is the ionization potential of the \(i\)-th molecule; \(T\) is the mean temperature of secondary electrons converted to their mean energy \(E_e=35\) eV by the formula: \(kT=2/3E_e\); \(g_i\) are the weighting factors accounting for the fractional ratio of each constituents to the total atmospheric number density, i.e. \(g_{N_2}=0.77\), \(g_{O_2}=0.2299\) and \(g_{O_3}=0.0001\). The sum in the denominator is called partition function.

The efficiency of the ion-molecular or ion-atomic reactions of the type:

\[
A^+ + B \rightarrow C^+ + D
\]

has been calculated by using the Saha equation:

\[
\frac{[A^+][B]}{[C^+][D]} = \left[ \frac{2\pi m(A^+) m(B)}{m(C^+) m(D)} \right] \frac{kT}{h^2} Z(A^+) Z(B) Z(C^+) Z(D) \tag{M3}
\]

where \(m[i]\) denotes the mass of the reactant or product; \(k\) is the Boltzmann const.; \(T\) – the temperature of the reaction; \(h\) – the Plank const.; \(Z[i]\) – the partition function of the corresponding reactant or product. The right side of eq. M3 is also known as the equilibrium rate of reaction (M2).

Ion-chemistry model of the lower stratosphere

Since the famous work of Chapman [8] the stratospheric ozone has been thought to be produced by the UV band of solar radiation, which dissociates the molecular oxygen \(O_2\) in two oxygen atoms \(O\), thus forcing a three-body reaction of ozone formation: \(O_2+O+M\rightarrow O_3+M\). The lower stratosphere, however, is less affected by the solar UV radiation, because the latter is strongly absorbed by the ozone aloft. Nevertheless, the maximal \(O_3\) concentration is observed not in the upper but in the lower stratosphere (at ~20 km). In attempt to resolve this paradox, and because the peak of the GCR adsorption in the atmosphere is very close to the maximum of the ozone layer, we have decided to estimate the amount of ozone produced by the ion-molecular reactions driven by GCR.

Model of the positive ion chemistry in the lower stratosphere

At this first stage of our investigation of the lower stratospheric ion chemistry, we have focused our attention on the primary atmospheric constituents. Our chemical model includes the following reactions

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^+ + 2e^- + 12.07 \text{ eV} \quad (1) \\
O_2 + e^- & \rightarrow O_2^+ + O + 2e^- + 18.69 \text{ eV} \quad (2) \\
N_2 + e^- & \rightarrow N_2^+ + e^- + 15.58 \text{ eV} \quad (3) \\
O_3 + e^- & \rightarrow O_3^+ + 2e^- + 12.75 \text{ eV} \quad (4) \\
O_3 + e^- & \rightarrow O_3^+ + O + 2e^- + 13.125 \text{ eV} \quad (5) \\
O_3 + e^- & \rightarrow O_3^+ + O + 2e^- + 15.2 \text{ eV} \quad (6) \\
O_3 + e^- & \rightarrow O_3^+ + O + e^- + 3.773 \text{ eV} \quad (7) \\
O_3^+ + e^- & \rightarrow O_3^{++} + O + e^- + 0.64 \text{ eV} \quad (8) \\
O_3^+ + e^- & \rightarrow O_3^{++} + O_2 + e^- + 2.19 \text{ eV} \quad (9) \\
O_3^+ + M & \rightarrow O + O + O + \sim 0 \text{ eV} \quad (10) \\
O_2^+ + O_2 + M & \rightarrow O_2^{++} + M + 3.5 \text{ eV} \quad (11) \\
O_2^+ + e^- & \rightarrow O + O + 5.12 \text{ eV} \quad (12) \\
O_4^+ + O & \rightarrow O_2^{++} + O_2 + 5.6 \text{ eV} \quad (13) \\
O_4^+ & \rightarrow O_3^+ + O + 0.82 \text{ eV} \quad (14) \\
O_4^+ & \rightarrow O_4^+ + O_2 + 1.26 \text{ eV} \quad (15) \\
N_2^+ + O_2 & \rightarrow O_2^{++} + N_2 + 3.5 \text{ eV} \quad (16) \\
N_2^+ + O_2 & \rightarrow NO + NO^+ + 4.45 \text{ eV} \quad (17) \\
O_2^+ + O_2 & \rightarrow O_2^{++} + O + 1.5 \text{ eV} \quad (18) \\
N^+ + O_2 & \rightarrow O_2^+ + N + 2.49 \text{ eV} \quad (19) \\
N^+ + O_2 & \rightarrow O + NO^+ + 6.67 \text{ eV} \quad (20)
\end{align*}
\]

The energy on the right side is the activation energy of the reactions in electron-volts (eV).
The main derivatives from a direct ionization and ion-molecular reactions producing ozone in our ion chemistry model are \( O_2^+, O_3^+, O_4^+ \) and \( O^+ \). Atomic oxygen rapidly reacts with \( O_2 \) creating ozone, i.e.: \( O+O_{2+}M\rightarrow O_3 \). The charge exchange of \( O^+ \) with \( O_2 \) forms \( O_3^+ \) and \( O^+ \), while the \( O_3^+ \) is the main source of tetraoxygen cation \( O_4^+ \) (see reaction 11). After the work [9] it becomes clear that the latter dissociates very quickly in two different channels. One of them produces \( O_2^+ \) and \( O \) (react. 14) and according to [10] may be a source of ozone in the atmosphere, while the other restores the \( O_2^+ \) (react. 15). The \( O_3^+ \) cation is weakly bound and easily dissociates by photon absorption, collision or recombination. According to [11] the \( O_3^+ \) undergoes also efficient charge exchange with molecular oxygen \( O_2 \) to yield neutral \( O_2 \). However, the dissociative recombination of ozone cation, with the free electrons (reaction 10), according to [14] is less energy demanding.

Thus reactions (11, 14, 15 and 10) form an autocatalytic cycle for continuous production of \( O_3 \) in the lower stratosphere, having a maximum at the level of strongest absorption of GCR.

What concern the quenching of \( N_2^+ \), Banks and Kockarts [13] pointed out that production of nitric oxide \( NO \) by means of reaction (17) is not competitive to the charge exchange between \( N_2^+ \) and \( O_2 \) (react. 16) since the former requires a double bond breakage. Therefore we exclude (17) from our further estimations. Moreover, the dissociative ionization of \( N_2 \) and the production of \( N^+ \) cation is much less probable than the simple ionization of molecular nitrogen, due to the higher ionization potential of the former reaction \(( E=24.34 \text{ eV}) \). For this reason the production of \( O \) and \( O_2^+ \) from reactions (19) and (20) is not included in the following estimations.

The efficiency of the direct ionization of \( N_2, O_2 \) and \( O_3 \) – calculated by the Maxwell-Boltzmann distribution (eq. M1) – are given in Table 1. It can be seen that despite the lower ionization potential of \( O_2 \) (compare reactions 1 and 3), the efficiency of the \( N_2 \) ionization is 2.88 times greater because of its higher number density \(( N_{N_2}/N_{O_2}=3.71) \).

### Table 1. Efficiency of electron impact fractional ionization of \( N_2, O_2 \) and \( O_3 \); numbers in brackets indicate the number of chemical reaction.

<table>
<thead>
<tr>
<th>Products</th>
<th>( O_3 )</th>
<th>( O_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 )</td>
<td>( O_2^+ )</td>
<td>( O^+ )</td>
</tr>
<tr>
<td>( O_3^+ )</td>
<td>( O^+ )</td>
<td>( O_2^+ )</td>
</tr>
<tr>
<td>( O_4^+ )</td>
<td>( O_3^+ )</td>
<td>( O^+ )</td>
</tr>
</tbody>
</table>

\[
\text{Efficiency} = 0.206, 0.154, 0.594, 0.009, 0.009, 0.008, 0.014
\]

Comparison with the corresponding values of [14] shows almost identical values for the efficiency of the electron impact ionization of \( N_2 \). The efficiencies of \( O_2^+ \) and \( O^+ \) appearance (calculated by us) are slightly higher: 0.206 against 0.176 for \( O_2^+ \) and 0.154 against 0.076 for \( O^+ \). It is worth to note, however, that in our model the partitioning between all reactions (1 to 7) is assessed simultaneously, while in [16] only the partitioning between (1) and (2) is estimated. For the mesospheric levels they separate production of \( N_2^+ \) from the dissociative-ionization of \( N_2 \) (i.e. \( N_2+e^-\rightarrow N^++N+24.34 \text{ eV} \)), which has not bee taken in consideration in our lower stratospheric model because the appearance of \( N^+ \) cations is practically not possible by the electrons with energies below 30 eV [15]. Having in mind that the mean energy of the secondary electrons produced by GCR is \(-35 \text{ eV} \), the appearance of \( N^+ \) cations in the lower stratosphere is highly improbable. Moreover, the amount of \( NO \) at these levels is very small [16], which make the possibility for ionisation of the products of the reaction: \( \text{NO} + e^- \rightarrow \text{N}^+ + \text{O} \) very unlikely.

The efficiencies of \( O_3^+ \) and \( O_2^+ \) dissociation, and the formation of \( O_4^+ \) are given in Table 2.

### Table 2. Efficiencies of electron impact dissociation of \( O_3^+ \) and \( O_2^+ \), and formation of \( O_4^+ \); numbers in brackets indicate the number of chemical reaction.

<table>
<thead>
<tr>
<th>Products</th>
<th>( O_3^+ )</th>
<th>( O_2^+ )</th>
<th>( O_4^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effeciency</td>
<td>0.0032</td>
<td>0.003</td>
<td>0.0033</td>
</tr>
<tr>
<td></td>
<td>0.009</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

The statistically derived efficiency of \( O^+ \) dissociation gives almost equal probability for occurrence of reactions (8, 9 and 10). The experimental measurements [12] show, however, that for ground state ozone cations and low energetic electrons, reaction (10) occurs in 94% of all cases. This means that the dissociation of one ozone cation is a source for production of three new ozone molecules.

### Density Estimation of the \( O_3 \) producing substances (\( O_2^+, O^+, O_4^+ \))

Sources of \( O^+ \) are reactions (2), (6) and (9). Using the efficiency for the occurrence of each reaction, listed in Tables 1 and 2, the production term of \( O^+ \) is equal to:

\[
P(O^+) = (0.154 + 0.008 + 0.003)Q = 0.166Q \quad (21)
\]

where \( Q \) denotes the density of electron/ion pairs [cm\(^{-3}\)] produced by GCR.

Examination of reactions (1 ÷ 20) shows that the \( O_2^+ \) production term includes reactions (1, 5, 8 and 18). The restoration of \( O_2^+ \) – through dissociation of \( O_2^+ \) (react. 15) – is not included in the balance equation because the density of a short-lived \( O_2^+ \) is unknown (we will calculate it from the estimated concentrations of \( O_2^+ \) produced in our model). The fast process of charge exchange between \( O^+ \) and \( O_2 \) allow us to define the amount of \( O_2^+ \) – formed through reaction (18) – as \( P(O^+) \). Moreover, the \( N_2^+ \) – produced via reaction (16) – is almost immediately converted in \( O_2^+ \) through a charge exchange (e.g. [13], [16] and references therein). So the quantity of \( O_2^+ \) – produced through reaction (16) – has been included in the \( P(O_2^+) \) term as \( P(N_2^+) \). Thus:

\[
P(O_2^+) = (0.206 + 0.009 + 0.0032 + 0.166 + 0.594)Q \quad (22)
\]

= 0.978Q
Similarly, the production term of atomic oxygen is calculated using reactions (2, 5, 7, 8, and 10). 

$$P(O) = (0.154 + 0.009 + 0.014 + 0.0032 + 3 + 0.0033)Q = 0.190Q$$

(23)

The calculated profiles of O$_{2}^{+}$, O$^{+}$ and O are given in Fig.2. Comparison with mid-latitude O$_{3}$ profile by the US standard atmosphere shows that the maximum of O$_{2}^{+}$, O$^{+}$ and O profiles actually coincides with the maximum of ozone variability. It is obvious however, that the calculated amount of the products of the direct ionization by GCR is orders of magnitude less than O$_{3}$ density and could not be responsible for distortion of its profile. For this reason we attempt to estimate the concentration of O$_{3}$ molecules produced by the O$_{3}$ autocatalytic cycle.

![Fig.2 Comparison of the vertical profiles of O$_{2}^{+}$, N$_{2}^{+}$, O$^{+}$ and O in [cm$^{-3}$] (produced by our ion chemistry model) with the variability of the standard mid-latitude O$_{3}$ profile (US Standard Atmosphere).](image)

The ozone production within the autocatalytic cycle is constrained by the amount of the existing O$_{2}^{+}$. In order to estimate the efficiency of reaction (11) – producing O$_{2}^{+}$, we have assumed that after a collision with energetic electron or ion, O$_{2}^{+}$ receives at least 20% of the energetic particle’s energy. The mean energy of the secondary electron/ion pair (formed in the atmosphere by GCR) is estimated to be ~35 eV (19). Therefore the estimated reactants temperature in reaction (11) is ~7 eV.

Applying the Saha equation (eq. M3) we have calculated the amount of O$_{2}^{+}$ produced from reaction (11), for GCR with energy E=1.5 GeV. The resulted profile is shown in Fig. 3. Note that the maximum of calculated O$_{2}^{+}$ profile is comparable to the maximum ozone density, which naturally raises the question: If the density of tetraoxygen is so high, why has it not been measured till now? The answer could be found in the works [9, 10 and 18]. These authors have shown that due to the very short life span of O$_{2}^{+}$ complex, there is continuous cycling between O$_{2}^{+}$, O$_{3}^{+}$ and O$_{2}^{+}$ cations. Moreover, in the upper and middle stratosphere the accumulation of O$_{2}^{+}$ is prevented by the pressure dependence of the intensity of O$_{2}^{+}$ formation (decreasing with a pressure decrease) [10]. Moreover, the higher affinity of H$_{2}$O vapour to O$_{2}^{+}$ [18], leads to a formation of the water clusters in the upper stratosphere. The maximum of O$_{2}^{+}$ calculated by our model appears near the tropopause, and one reason for this could be the fact that it is the driest place in the lower and middle atmosphere.

**Ozone production**

By the use of the Saha eq. we have calculated the value of branching ratio between reactions (14) and (15) to be 0.505/0.495. The efficiency of reaction (13) – also producing ozone – is very low (due to its higher activation energy) and practically has no impact in variations of O$_{3}$ profile. Taking into account that the reaction (10) is not energy demanding and occurs in the 94% of observed cases [14], we have calculated the amount of ozone – produced through the autocatalytic cycle – by the formula:

$$O_{3} \text{prod} = (0.505 \cdot O_{4}^{+}) \cdot 4$$

(24)

where the multiplication by the factor of 4 reflects the number of O$_{3}$ molecules produced by reactions (14) and (10). The resulting O$_{3}$ profile from our ion chemistry model is also shown in Fig.3. Comparison with the ozone profile from the US Standard Atmosphere shows that the lower stratospheric ozone could be strongly influenced by the ion chemistry initiated by GCR.

**Mechanism of O$_{3}$ Influence on Climate**

The above calculations reveal an existence of alternative (to solar UV radiation) source of O$_{3}$, which could effectively control the variability of the lowermost stratospheric ozone density. This result is a complementary to the previous modelling studies, which have noticed the high climate sensitivity to the O$_{3}$ concentration in the lower stratosphere [19-24], but could not point out the factor(s) capable of influencing the ozone. Here we show that GCR are able to control effectively the lower stratospheric O$_{3}$ through a chain of ion-molecular reactions.

Not less intriguing, however, is the mechanism of O$_{3}$ influence on climate, having in mind that the radiative forcing of O$_{3}$ is quite small compared to that of CO$_{2}$ or H$_{2}$O. First, we have to remind that due to the higher ability of the O$_{3}$ to absorb electromagnetic radiation in different bands of its spectrum, ozone variations could influence locally the atmospheric temperature. Experimental evidences for sun an influence are given in [25, 4].

Second, the temperature dependence of atmosphere humidity is well recognised. So having in mind the interrelation between saturated lapse rate, specific humidity and temperature (see eq. 24) we have conducted some numerical experiments to test the sensitivity of this relation. We use the formula for
saturated adiabatic lapse rate recommended by the American meteorological society (eq. 24):

$$\Gamma_w = g \cdot \frac{1 + \frac{H_v \cdot SpH}{R_{sd} \cdot T}}{c_{pd} + \frac{H_v^2 \cdot \varepsilon \cdot SpH}{R_{sd} \cdot T^2}}$$  \hspace{1cm} (24)$$

The experimental T profile from Terra Nova (Antarctica) [26] has been distorted by ±10℃ and the specific humidity profile fixed to the measured one by the same authors. We have calculate the $\Gamma_w$ by the use of (24). Results from calculations are given in Fig.4. Then, using the so calculated $\Gamma_w$ profiles, we determine the specific humidity as a function of temperature and $\Gamma_w$ – again for uniformly decreased (increased) by ±10℃ T profile from Terra Nova. Calculated specific humidity profiles are also given in Fig.3. Note that uniform warming of the atmosphere actually reduces the water vapour density due to the increased $\Gamma_w$ (compare red profiles). Oppositely, the cooling of UTLS increases humidity there, due to the reduced lapse rate, allowing more vapour to propagate upward (compare blue profiles).

Third, in 1997 Spencer and Braswell [27] have shown that outgoing long-wave Earth radiation (OLR) is the most sensitive to the humidity fluctuations in the driest free atmosphere. They show that a small enhancement of the humidity near the tropopause leads to a nonlinear decrease of the OLR and consequently – to a greenhouse warming of the Earth surface [27]. Consequently, the above experiment shows that humidity variations, related to the temperature induced variations in the moist adiabatic lapse rate, could efficiently influence the Earth radiation balance.

Actually the greatest impact of the water vapour in the global warming is also pointed out in the IPCC reports. However, the recent enhancement of the upper tropospheric water vapour is interpreted by the IPCC as a feedback of the climate system response to the CO$_2$ warming. In this study we show that it can be attributed to the depletion of the lowermost stratospheric ozone → decrease temperature near the tropopause → decreased moist adiabatic lapse rate → moistening of UTLS region and increased greenhouse warming of the planet. This new concept could change seriously our understanding of the factors driving climate variability, as well as our expectations for the future evolution of the Earth climate. Thus instead of the continuous warming, projected by IPCC, a flattening or a weak cooling of the climate may be expected, depending on the intensity of the heliomagnetic and Earth magnetic fields, controlling the intensity of GCR and correspondingly the lower stratospheric O$_3$ density [4].

**Fig.3** Vertical profiles of O$_3^+$ calculated by the use of the Saha equation and O$_3$ produced through react. (14) and (10). The standard mid-latitude O$_3$ profile is also given for comparison; densities are in [cm$^{-3}$].

The conclusions of this study are that...

**Conclusions:**

In this paper we have put a stress on the O$_3$ positive ion chemistry in the lower stratosphere not only because little is known about it [18 and references therein] but also because the peak of the mid-latitude ozone layer is very close to the level of maximal attenuation of galactic cosmic rays (GCRs) in the atmosphere – known as Pfotzer maximum. The influence of the highly energetic charged particles on...
the lower atmospheric aeronomy has been ignored for a long time, because of their lower density (~10^3). However, having in mind that the most of charged and excited neutral particles in the Pflotzer maximum are not in a thermal equilibrium (due to the continuous impact of GCR and because the collisional frequencies are not enough to ensure thermalisation of the quantum state distribution) we have shown that these highly reactive molecules are very effective in O_3 formation at this level, despite their small concentration.

We show that the electron impact ionization of molecular oxygen O_2 and formation of tetraoxoxygen cation O_4^+ (reaction 11), followed by the two channels of its dissociation (reactions 14 and 15) together with reaction (10), forms an autocatalytic cycle for ozone production in the lowestmost stratosphere. The quantity of O_3 produced by the positive ion chemistry has the same order of magnitude as the mid-latitude steady-state ozone profile. This is an indication that the lowestmost ozone could be substantially distorted by the highly energetic particles.

In addition we offer a non-conventional point of view on the causal relations between climate, its main external forcing agents and water vapour feedback. Unlike the broadly accepted assumptions that H_2O vapour appears a response of the Earth climate to the recent global warming, we bring the readers’ attention to the fact that humidity near the tropopause can be substantially influenced by the galactic cosmic rays and sporadically by the solar protons. The mediator of this control is ozone density near the tropopause, influencing the thermodynamical regime near the boundary where the radiative forcing is determined (i.e. the tropopause).

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