Does Cosmic-Ray-Induced Heterogeneous Chemistry Influence Stratospheric Polar Ozone Loss?

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Cosmic-ray (CR) -induced heterogeneous reactions of halogenated species have been suggested to play the dominant role in causing the Antarctic ozone hole. However, measurements of total ozone in Antarctica do not show a compact and significant correlation with CR activity. Further, a substantial CR-induced heterogeneous loss of chlorofluorocarbons is incompatible with multiyear satellite observations of N_2O and CFC-12. Thus, CR-induced heterogeneous reactions cannot be considered as an alternative mechanism causing the Antarctic ozone hole.

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The discovery of the Antarctic ozone hole in 1985 [1] came as a great surprise (e.g., [2,3]) because, at that time, none of the major physicochemical mechanisms responsible for its occurrence, were known. Today, it is well established [2,4] that the precipitous loss of O_3 in Antarctic spring is caused by a chain of events starting in autumn with cooling of the polar stratosphere and the formation of a strong wind jet that, to a great extent, isolates the polar air-mass from midlatitudes. This isolated, rotating air mass is referred to as the polar vortex. In winter, when stratospheric temperatures are low enough, polar stratospheric clouds (PSC) form providing surfaces which allow heterogeneous reactions to occur. These reactions convert chlorine from so-called reservoir species (mostly HCl and $ClONO_2$), to an active, O_3-destroying form [2,5]. The O_3 destruction occurs in catalytic cycles, in the Antarctic stratosphere mainly through a cycle involving chlorine peroxide (ClOOCl) [2,6]. The O_3 destruction stops either when extremely low mixing ratios of O_3 are reached [7,8] or when temperatures rise above the PSC existence threshold, so that the chlorine reservoir species are reformed at the cost of active chlorine, a process which causes O_3 depletion to halt. Uncertainties still exist; for example, the exact mechanism of heterogeneous chlorine activation is being debated (e.g., [9]) and chemical rate constants that strongly impact the speed at which O_3 loss proceeds in the polar stratosphere are not yet satisfactorily known [6,10,11].

Recently, Lu [12] put forward the idea that cosmic rays (CR) lead to the presence of trapped electrons in PSC particles followed by dissociative electron attachment to both chlorine reservoir species (HCl and $ClONO_2$) and chlorofluorocarbons (CFC). This issue has been debated before [13–18]. Lu [12] reports "reliable satellite data in the period of 1980–2007 covering two full 11-yr cosmic-ray (CR) cycles, clearly showing the correlation between CRs and ozone depletion, especially the polar ozone loss (hole) over Antarctica." Here we revisit the issue showing that, first, in the Antarctic there is no strong and significant correlation between CR activity and polar O_3 loss, second, that the 11-year modulation in tropical and midlatitude O_3 is both well known and unrelated to polar processes, and, third, that CR-driven reactions can only be a possible *addition* to the set of processes known to cause the O_3 hole and not an alternative mechanism.

Lu [12] presents correlations between CR intensity and different spatial and temporal averages of total column O_3 measurements, namely, annual mean total O_3 in the latitude band 0°–60° S, October mean total column O_3 poleward of 60° S, and annual mean total O_3 at two Antarctic stations (Halley and Vernadsky). He states that the "...appearance of the polar O_3 hole is known to have a consequent effect on annual total O_3 in the polar area and globally." While this statement is somewhat misleading (the Antarctic O_3 hole is not known to have an effect on the tropics [4]), it is important to note that the proposed CR effect is a polar winter and spring effect as it is coupled to the occurrence of PSC. Therefore, its signal (and the correlation with CR intensity) should be strongest in the Antarctic in spring. In the annual average of polar total O_3 [[12], Fig. 3], the signal of the PSC-driven CR effect will be damped by other unrelated processes, for example, the strong nitrogen-oxide-driven chemical polar O_3 loss in summer [19]. Further, even in austral spring, the Vernadsky station is located at the edge of the O_3 hole region so that these measurements are influenced by both polar and midlatitude processes.

It is well known [4,20] that the solar cycle has an impact on total O_3 outside the polar regions, in the tropics and in midlatitudes [[12], Fig. 1]. The solar-cycle variation of tropical O_3 is also detected in vertical profile measurements of upper stratospheric O_3 [21]. Further, the solar-cycle variation of tropical and midlatitude total O_3 was observed in ground-based data sets covering the years 1960–1980, when no substantial Antarctic O_3 loss was observed [22].

For recent decades, the detection of the solar-cycle signal has been complicated by the fact that the eruptions of El Chichón (1982) and Mt. Pinatubo (1991) occurred near the declining phases of the solar cycle in 1982–1984 and 1992–1994, so that there is the possibility of aliasing

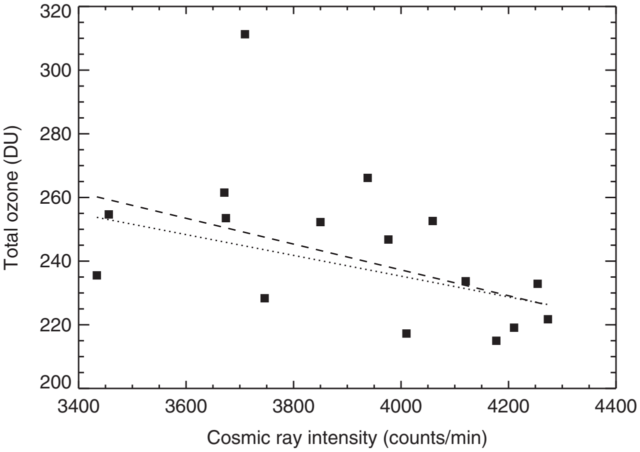

FIG. 1. Relation between cosmic-ray intensity (from Ref. [17]) and mean total column O_3 for October poleward of 60° S for 1990–2005 (from Refs. [27,28]). Dashed line shows the linear fit to all data points, dotted line shows the linear fit to the data points excluding 2002 (column O_3 311 DU). We assume an upper limit of the uncertainty of the mean total O_3 of 5%.

volcanic and solar-cycle related effects on column O_3 [23]. Moreover, a periodic fluctuation of global total O_3 is caused by the quasi-biennial oscillation in tropical stratospheric winds [4,24], which has to be taken into account when analyzing the 11-year solar-cycle signal in column O_3 [25]. Thus, the 11-year variation of total column O_3 in the extra-polar region of the southern hemisphere (0°–60° S) is highly unlikely to be related to polar processes.

Therefore, in the following, we focus on the comparison of the percentage variation of CR intensity and October mean total O_3 poleward of 60° S during the period 1990–2007 [[12], Fig. 2]. In the discussion of this figure, it is tacitly assumed that the October mean total O_3 poleward of 60° S constitutes a suitable measure of chemical O_3 loss. While this quantity is certainly strongly influenced by chemical loss in the O_3 hole, there are also other factors unrelated to chemistry that influence this quantity, in particular, the size and the shape of the polar vortex. Sophisticated measures of chemical polar O_3 loss have been developed [26] including additional information to disentangle the impact of transport and chemistry on O_3, which should be employed whenever possible. But even when only total O_3 measurements are available, a better measure of chemical O_3 loss than October mean total O_3 poleward of 60° S is available [27], namely, the minimum of daily average total O_3 poleward of 63° equivalent latitude. A time series of this quantity over the years 1979–2005 shows no correlation with solar intensity or CR activity [17]. The data set used in Ref. [17] has been criticized as "noisy", considering the entire temporal variability in the time series of about 20% as "noisy level" [18]. However, the data set used in Ref. [17] and in the present work is essentially the same as the TOMS-OMI data set analyzed by Lu [12], the TOMS-OMI data are solely corrected for consistency between the different series of instruments and, when TOMS-OMI data are not available, data gaps are filled using other instruments [27,28]. This allows the years 1993 and 1995 to be included in the analysis which are omitted in Ref. [12]. The corrections applied to the total O_3 data set are small [28] and are not relevant for the large interannual variability which is of interest here.

In Fig. 1 we show the relation between CR-intensity and the mean total column O_3 for October poleward of 60° S for the time period 1990–2005. There is only a moderate variation of polar O_3 with CR intensity over this time period (Fig. 1, dashed line) which only extends over less than two solar cycles. The variation is even weaker when the year 2002 is excluded from the fit (Fig. 1, dotted line), a year which shows an extremely unusual dynamics of the polar vortex [4,29]. The (linear Pearson) correlation coefficient between CR intensity and the mean total column Antarctic O_3 for October (for the data in Fig. 1) for the entire time series (1979–2005) is $r = -0.37$, for the time period 1990–2005, $r = -0.49$, and for the time period 1990–2005 excluding the year 2002, $r = -0.52$. The reduced χ^2 goodness of fit parameter for the fit for 1990–2005 is 2.7 and, if 2002 is excluded it is 1.6. The probability of such a poor χ^2 value occurring by chance is 6.4×10^{-4} and 8.7×10^{-2}, respectively. We assumed an upper limit of the uncertainty of the monthly mean total column Antarctic O_3 of 5%. The correlation coefficient for the data shown in Fig. 2 of Ref. [12] is $r = -0.37$. Thus, there is no solid statistical foundation for a linear correlation between CR intensity and the mean total column Antarctic O_3 in October for the years since 1990.

Moreover, the enhancement of the stratospheric aerosol loading caused by the eruption of Mt. Pinatubo in 1991 had a strong impact on polar stratospheric O_3 [7,30,31]; in particular, the low Antarctic O_3 values in the 1990s (during an ascending phase of CR intensity) have been associated with the Mt. Pinatubo eruption [7,30]. Thus, the coincidence of a strongly enhanced stratospheric aerosol layer and increasing CR intensity in the 1990s could lead to a spurious correlation via an aliasing effect. Furthermore, Lu [12] assumes that "from 1992 up to now [...] the total halogen amount of the stratosphere [...] is nearly constant ...". This is not correct; the Antarctic stratospheric halogen burden for 1990 is ~20% below the peak value in ~2001 and in 2020 is predicted to be ~10% below the peak value [32,33].

Lu [12] also puts forward a linear relation between CR intensity and total O_3 variation as a method of predicting the future development of the O_3 hole. This relation is deduced by first reducing the variability of the October polar data (1990–2007) by a factor of 5, the annual polar data (1990–2007) by a factor of 2.5, then combining the two data sets with the (1980–2007) 0–60° total O_3 data into one single data set. A linear fit to the combined data set (Ref. [12], red line in Fig. 4) is then scaled up again by a factor of 5 to obtain a prediction of October polar O_3 levels. This procedure is questionable insofar as three very differ-

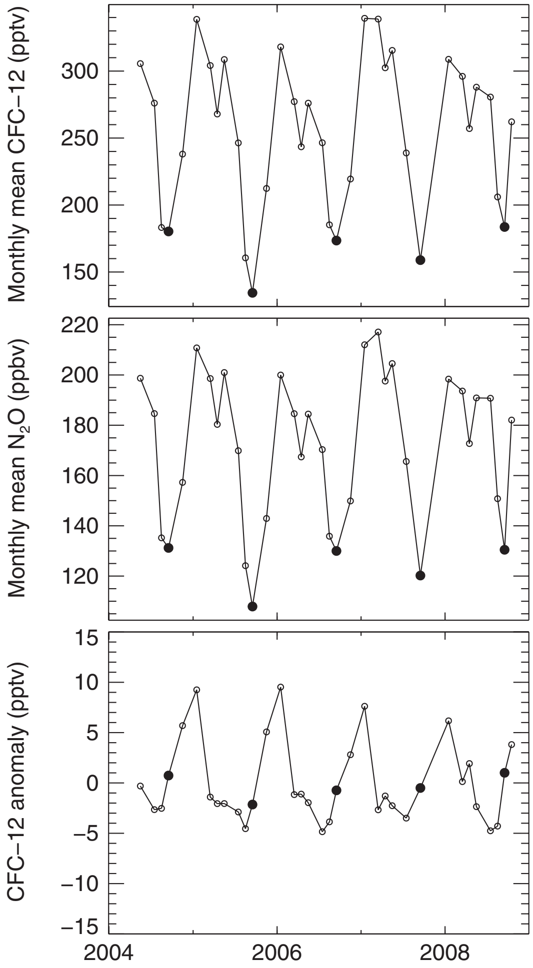

FIG. 2. Time series of ACE-FTS satellite measurements of CFC-12 (top) and N_2O (middle) as well as the CFC-12 anomaly relative to N_2O (bottom) at 18.5 km, monthly averaged poleward of 60° S. September data are marked by filled circles. The CFC-12 anomaly is deduced by first calculating from ACE-FTS data poleward of 60° S between 10 and 25 km an empirical relation: $\mu_{\text{CFC-12}} = 4.77 + 0.558\mu_{\text{N}_2\text{O}} + 0.00741(\mu_{\text{N}_2\text{O}})^2 - 1.31 \times 10^{-5} \times (\mu_{\text{N}_2\text{O}})^3$, where $\mu_{\text{N}_2\text{O}}$ and $\mu_{\text{CFC-12}}$ are volume mixing ratios in parts per billion (ppbv) and parts per trillion (pptv), respectively. Then, the CFC-12 anomaly is calculated for each data point as the difference of the observed CFC-12 and CFC-12 derived from the correlation using the observed N_2O. The latitude of the ACE-FTS observations in September is 74° ± 6° S due to the satellite's viewing geometry.

ent data sets are combined into one single fit, so that the properties of one data set influence the prediction of the other. In particular, the known 11-year solar cycle signal of extrapolar O_3 may influence the prediction of October Antarctic O_3. Also, the TOMS-OMI total column O_3 averages reported by Lu [12] are incorrect. The reported average O_3 column for October 1992 between 60° S and 90° S is 219 Dobson units (DU), while the correct value for this quantity obtained from Nimbus-7 TOMS Version 8 data is 254 DU, when first averaged over time and then, area weighted, over area.

An important assertion made by Lu [12] is that his results "cannot be explained by the photochemical model" and that one is forced "to conclude that the CR-driven electron-induced reaction is the dominant mechanism for causing the polar O_3 hole." This gives the impression that two independent and competing mechanisms exist that may explain polar stratospheric O_3 depletion. However, the effect of the proposed CR-driven heterogeneous chemistry can only be a destruction of CFC or chlorine reservoir species on PSC surfaces and, therefore, only an enhanced activation of chlorine. Ozone destruction, also in the CR mechanism, can only occur through the action of the activated chlorine on O_3 in catalytic loss cycles. Therefore, clearly, the CR mechanism proposed by Lu [12] cannot resolve the discrepancy between the simulated and observed O_3 loss that was raised by recent measurements of the ClOOCl cross sections [6,10]. This issue is more likely to be resolved by new laboratory work [34].

A fundamental problem with the CR mechanism is that a direct, linear relation between CR activity and polar O_3 loss is assumed [[12], Fig. 4]. However, for "the regulating effect of CRs on O_3 loss" [12] to become manifest, it needed to be demonstrated, first, that there is a regulating effect of CRs on low-energy electrons in PSC, and, second, that the density of low-energy electrons in PSC is rate limiting for the heterogeneous CR-induced destruction of CFC, HCl, or $ClONO_2$. There is some support from laboratory experiments for the latter step, but none of these experiments have been conducted under stratospheric conditions [35].

If one nonetheless assumes that heterogeneous chlorine activation is regulated by CR activity, this in no way implies that also polar O_3 loss depends linearly on chlorine activation. For example, in the 1990s, Antarctic O_3 loss was frequently *saturated* in the sense that O_3 was essentially zero in extended regions of the O_3 hole [4,7,8]; under such conditions, no chemical effect, whether a greater stratospheric chlorine burden, a more rapid chlorine activation, or more efficient catalytic O_3 loss cycles, can lead to enhanced O_3 destruction.

If CFC were destroyed by CR-induced heterogeneous chemistry, the effect should be visible in measurements of CFC. Figure 2 shows a time series of CFC-12 (top) and N_2O mixing ratios (middle) at 18.5 km from more than four years of measurements from the Atmospheric Chemistry Experiment (ACE-FTS) on SCISAT-1 [36]. All data poleward of 60° S are monthly averages. An annual cycle is clearly visible with the lowest observations in September (filled circles) with very similar behavior for N_2O and CFC-12. The September air masses spent the longest time in the stratosphere, so that about two thirds of the CFC-12 originating from the troposphere has been photolytically dissociated. Because of interannual variability, both of atmospheric dynamics and latitude coverage of the satellite observations, the September CFC-12 values vary as do the N_2O values. Therefore, we deduced the CFC-12 anomaly relative to N_2O (bottom panel of

Fig. 2). If the proposed CR-mechanism caused significant additional dissociation of CFC-12 in the polar stratosphere, a decrease of the CFC-12 anomaly with time should be seen for the September values (when PSCs occur) with increasing CR intensity. However, between 2004 and 2008, when the CR intensity increased significantly, no corresponding decrease in the CFC-12 anomaly is observed.

Further, Lu [12] states that "…the solar-cycle effect [that is the "photochemical model"] should also predict that the higher solar intensity would lead to more destruction of CFCs and thus produce more active Cl to destroy O_3" [12]. This argument is flawed because the air in the polar regions has spent about five to six years in the stratosphere [32] so that the photochemical degradation of CFC is not controlled by the solar activity in a particular year. Moreover, the fact that the CR-induced ionization rate peaks in the same region where temperatures are low enough for PSC to exist [12,13,18] does not provide any support for the CR mechanism [15,33]. Finally, Lu [12] misinterprets model projections of the future development of polar O_3 [4]. The models neither predict a monotonic recovery of polar total O_3 since 2000, nor are the predictions of total O_3 over 60° S to 60° N and Antarctic springtime O_3 inconsistent with observed data (see also Ref. [33]).

In summary, we have demonstrated here that the 11-year modulation in tropical and midlatitude O_3 is both well known and unrelated to polar processes. It is rather driven by the 11-year cycle in solar radiation. Further, we have shown that in the Antarctic a compact and significant correlation does not exist between CR activity and chemical O_3 loss in spring (i.e., the O_3 hole). Moreover, a significant CR-induced heterogeneous loss of CFCs is incompatible with recent, multiyear satellite observations of CFC-12. However, CR activity may possibly impact the heterogeneous activation of the chlorine reservoir species HCl and $ClONO_2$ [16,37], a possibility that should be further explored in laboratory studies under stratospheric conditions. In any case, CR-driven heterogeneous reactions can only be considered as a possible addition to the set of processes known to cause the Antarctic O_3 hole and not as an alternative mechanism.

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