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Key Points:

- Evaluation of the EPP-induced O₃ variability on long time scales
- EPP causes an average upper stratospheric O₃ depletion of about 10–15% on a monthly basis
- Discrimination between EPP and solar irradiance effects on ozone

Supporting Information:

- Supporting Information S1

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Energetic particle precipitation: A major driver of the ozone budget in the Antarctic upper stratosphere

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Abstract Geomagnetic activity is thought to affect ozone and, possibly, climate in polar regions via energetic particle precipitation (EPP) but observational evidence of its importance in the seasonal stratospheric ozone variation on *long time scales* is still lacking. Here we fill this gap by showing that at high southern latitudes, late winter ozone series, covering the 1979–2014 period, exhibit an average stratospheric depletion of about 10–15% on a monthly basis caused by EPP. Daily observations indicate that every austral winter EPP-induced low ozone concentrations appear at about 45 km in late June and descend later to 30 km, before disappearing by September. Such stratospheric variations are coupled with mesospheric ozone changes also driven by EPP. No significant correlation between these ozone variations and solar ultraviolet irradiance has been found. This suggests the need of including the EPP forcing in both ozone model simulations and trend analysis.

1. Introduction

In the 1980s the discovery of the so-called ozone hole [Farman *et al.*, 1985] in Antarctica underlined the effects of human activity on the environment and global change. Soon after, an international agreement to preserve the ozone (O₃) layer was signed, and the international community started accurate monitoring of atmospheric gases in order to evaluate the effectiveness of precautions taken. Nevertheless, since natural factors also influence O₃, they must be fully understood in order to assess the expected future O₃ recovery.

Among these natural factors, solar activity is known to affect the abundance of O₃ in the middle atmosphere in several ways. The wavelength dependence of the solar irradiance variation over both the 11 year and 27 day cycles can induce O₃ changes in phase with solar activity [Hood *et al.*, 2015]. The analysis of various long-term O₃ data sets has shown that the solar cycle (SC) amplitude of stratospheric O₃ is of a few percent. However, since these measurements are mainly based on solar occultation and backscatter instruments, they do not cover the dark winter high latitudes.

Limb sounders aboard polar-orbiting spacecraft can probe the winter night polar regions although these data sets usually extend to less than one SC. The energetic particle precipitation (EPP), which is directly or indirectly influenced by solar activity, has its major impact in the winter polar night. Thus, the limb sounders have a great advantage for understanding the influence of EPP on atmospheric composition, and O₃ in particular. EPP routinely impacts the polar regions, ionizes the atmosphere, and affects the neutral molecules by enhancing the concentration of odd nitrogen (NO_x) and odd hydrogen (HO_x) species. Thus, O₃ can be depleted by efficient HO_x and/or NO_x-catalytic cycles [Crutzen *et al.*, 1975; Solomon *et al.*, 1981] during sporadic solar proton events (SPE) [Jackman *et al.*, 2001; Funke *et al.*, 2011; López-Puertas *et al.*, 2005] as well as during the occurrence of energetic electron precipitation (EEP) [Verronen *et al.*, 2011a] and by low-energy particles [Randall *et al.*, 2007; Sinnhuber *et al.*, 2014]. In particular, while SPE and EEP can directly affect the mesosphere (EPP-DE, direct effect), the (almost) continuous flux of lower energy precipitating electrons related to geomagnetic activity produces high NO_x amounts in the upper mesosphere/thermosphere. Since NO_x is chemically long lived in the absence of solar radiation, it can be transported downward during winter NO_x inside the polar vortex by the residual circulation and thus influence stratospheric O₃ [Callis *et al.*, 1998; Randall *et al.*, 2005]. This so-called EPP-IE (indirect effect) is more important in the Antarctic than in the Arctic because the larger stability of the Antarctic vortex allows NO_x to be transported deeper in the stratosphere [Randall *et al.*, 2007; Funke *et al.*, 2014; Baumgaertner *et al.*, 2009].

Previous simulations of the EPP-induced stratospheric O₃ depletion for the Antarctic showed decreases of up to about 20–40% under extreme geomagnetic conditions [Baumgaertner *et al.*, 2009; Peck *et al.*, 2015] and up to about 10% on average [Semeniuk *et al.*, 2011; Rozanov *et al.*, 2012]. Nevertheless, although this mechanism is thought to be a significant process in governing the O₃ budget and, potentially, the regional climate, observational evidence is still limited [Callis *et al.*, 1998; Fytterer *et al.*, 2015].

In order to fill this gap, this paper focuses on the analysis of the O₃ variability within the southern polar regions in response to solar/geomagnetic activity during the 1979–2014 period by combining satellite O₃ observations from Solar Backscatter Ultraviolet Radiometer (SBUV and SBUV/2) and Microwave Limb Sounder (MLS). In particular, we analyze the correlation of the O₃ variability with the geomagnetic conditions and with solar irradiance in an attempt to distinguish between the two effects and to quantify the O₃ variations caused by EPP on long time scales.

2. Data and Methods

We used version 3.3 (v.3.3) level 2 data of O₃ and HNO₃ from 2005 to 2014 from the NASA EOS (Earth Observing System) MLS aboard the Aura satellite [Froidevaux *et al.*, 2008; Santee *et al.*, 2007; Livesey *et al.*, 2013]. The vertical resolution of MLS O₃ data between the upper stratosphere and the lower mesosphere is about 2.5–4 km, while the precision of the individual O₃ profiles ranges from 0.1 to 0.5 ppmv, and the accuracy is about 5–20%. The vertical resolution of MLS HNO₃ data is about 3–5 km, the precision is 0.7–1.2 ppbv, and the accuracy ranges between 0.5 and 2 ppbv.

We also analyzed O₃ data measured by SBUV/2 instruments for the 1979–2014 period. Recently, the data have been reprocessed based on the v8.6 retrieval algorithm with several improvements [Bhartia *et al.*, 2013; Kramarova *et al.*, 2013]. Here we used two different SBUV time series, based on different intersatellite calibration approaches (i.e., the SBUV MOD data set and the SBUV merged cohesive data set).

A multiple linear regression (MLR) analysis has been applied to MLS, SBUV MOD, and SBUV merged cohesive data. In addition to the usual predictors, the regression includes also a geomagnetic/EPP term. For the MLR of the MLS data we employed a monthly quasi-biennial oscillation term (i.e., zonal winds over Singapore at 10 and 30 hPa), an ENSO term (multivariate ENSO index), a solar term ($F_{10.7}$ index), a geomagnetic term (A_p or AE index), and a linear term as predictors. In order to account for the observed time lag introduced by vertical transport, below 0.5 hPa the geomagnetic index was weighted with the contribution of the preceding months (up to 3 months) as in a recent work [Funke *et al.*, 2014], while no lag was used for the upper altitudes. Note that the specific weight is slightly different for the early and late winter months and reflects the different descent rates and the altitude of the bulk of EPP-NO_x. Overall, this results in a stronger weight applied to both the current and the closest (farthest) preceding month for the early (late) winter period.

The MLR applied to SBUV data slightly differs in using the equivalent effective stratospheric chlorine instead of the linear term and in the additional inclusion of a volcanic term. Results are presented in percent per 13 A_p (204 AE) index units (which corresponds to the average of the investigated period) and 100 $F_{10.7}$ units. The autocorrelation of residuals of the various MLR analyses is corrected as in Tiao *et al.* [1990].

3. Results

Figure 1a shows the temporal evolution of the solar and geomagnetic activity during the 1979–2014 period. We employed the widely used $F_{10.7}$ index as a proxy of the solar irradiance variation and the A_p and AE indices as proxies of the geomagnetic/EPP activity. Both solar irradiance and geomagnetic activity are affected by the 11 year component of the solar activity [Echer *et al.*, 2004]. In particular, the peak of the geomagnetic activity typically follows the peak in the solar irradiance with a lag of about 1–2 years [Echer *et al.*, 2004; Du, 2011].

Figure 1b shows the temporal evolution of the recently developed A_p -based parameterization of the EPP-related NO_y (total reactive nitrogen) amounts below 0.02 hPa within the southern polar vortex [Funke *et al.*, 2014] (EPP-NO_y) from April to September for the 1979–2014 period. Although EPP-NO_y amounts peak in 1982, 1991, 2000, and 2003, with values reaching about 2.3 gigamole during the latter winter, we also note significant amounts of EPP-NO_y in 2005, very low amounts particularly in 2008–2010, and then slightly higher values mostly for 2012 and 2013.

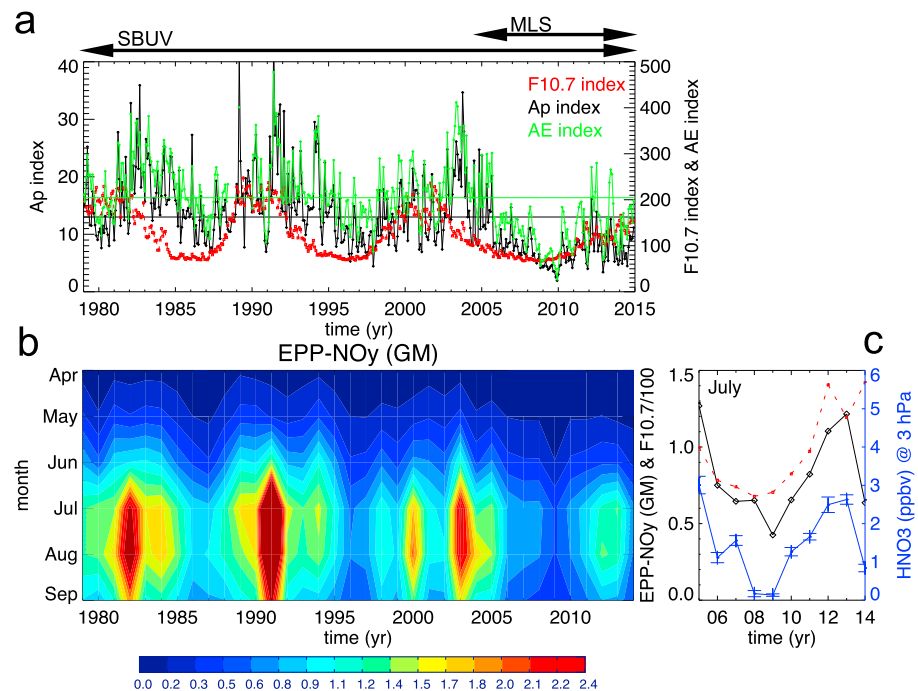
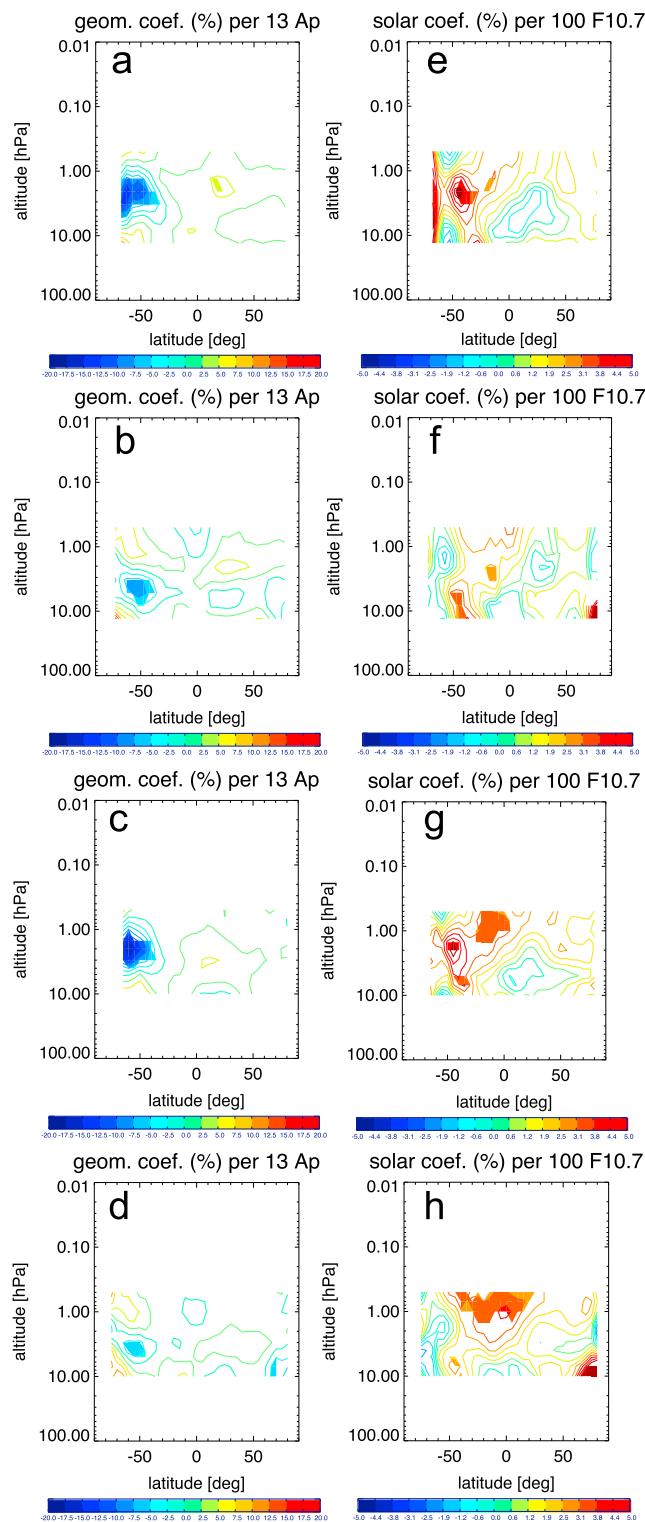


Figure 1. (a) Monthly temporal evolution of the A_p (black line), AE (green line), and $F_{10.7}$ (red line) indices during the 1979–2014 period. Horizontal lines show the average value for the investigated period. Horizontal lines with arrows show the time coverage of MLS and SBUV observations. (b) Temporal evolution of the parameterized monthly $EPP-NO_y$ amounts within the southern polar vortex from April to September for the 1979–2014 period. (c) Year-to-year variability of the $EPP-NO_y$ amounts (black line), the zonal mean at 3 hPa of MLS HNO_3 averaged over latitudes poleward of $70^\circ S$ (blue line; for a meaningful visualization values have been reduced by 2 ppbv) and the $F_{10.7}$ index (red dashed line) in July for the 2005–2014 period.

While in the mesosphere NO_x almost coincides with the total NO_y , in the upper stratosphere the conversion from NO_x to other reservoirs must be taken into account. There, NO_x is mainly converted to N_2O_5 , $ClONO_2$, and HNO_3 . Indeed, various studies reported winter stratospheric HNO_3 enhancements within the polar regions depending on the geomagnetic activity [de Zafra and Smyshlyayev, 2001; Stiller et al., 2005; Verronen et al., 2011b; Orsolini et al., 2009]. Those authors pointed out that HNO_3 formation in the polar upper stratosphere requires a sufficient amount of NO_x and is produced by heterogeneous chemistry on sulfate aerosols and/or by ion cluster chemistry via different paths. The latter, together with the presence of a significant amount of $EPP-NO_x$, is perhaps the most important factor for the investigated altitudes. Moreover, Stiller et al. [2005] proved that EPP -induced HNO_3 depends on the formation of N_2O_5 as an interim step and that nighttime conditions are essential for its production. Since the widely used Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) NO_y observations [Funke et al., 2014] ends in early 2012, we also use MLS HNO_3 which is a good proxy for the odd nitrogen species. In Figure 1c we compare the parameterized $EPP-NO_y$ with the measured zonal mean HNO_3 at 3 hPa for latitudes poleward of $70^\circ S$ in July for the period of MLS HNO_3 measurements (i.e., 2005–2014 years). Despite some minor discrepancies, the interannual variability of the $EPP-NO_y$ is generally close to the observed HNO_3 variability. As a further result we find that the $EPP-NO_y$ parameterization also gives a good prediction for the 2012–2014 winters when MIPAS NO_y observations (on which the parameterization is based) are no longer available.

Since there are evident changes in $EPP-NO_y$ amounts during the austral winters of the 1979–2014 period (Figure 1b), it is reasonable to expect a corresponding modulation of O_3 . Thus, we have applied a MLR analysis to the O_3 profiles retrieved from both SBUV and MLS instruments. As the intersatellite calibration is an important issue when dealing with SBUV data [Tummon et al., 2015], two independent merged data sets, i.e., the SBUV MOD and SBUV merged cohesive data, have been considered. Moreover, since SBUV observations are available only for daytime conditions, we limited the analysis to August–September (Figure 2). The EPP signal is similar in both SBUV data sets and shows a significant and homogeneous O_3 reduction of about



10–15% (Figures 2a and 2c) and 5–10% (Figures 2b and 2d) at latitudes poleward of about 50°S in August and September, respectively. In late winter, the upper stratospheric edge of the Southern polar vortex is usually located around 50–55°S [Peck *et al.*, 2015]. Therefore, the altitude of the peak of the O₃ response (2–3 hPa in August and 4–5 hPa in September) is consistent with the expected descent of the mesospheric NO_x-rich air down to the stratosphere. Moreover, Figures 2a and 2c suggest that even larger O₃ reduction could occur at latitudes poleward of about 70°S where the bulk of NO_x is likely located.

On the other hand, the largest response of the solar UV coefficient appears at middle to low latitudes of the winter hemisphere (Figures 2e–2h) and suggests that photochemical processes as well as dynamical variability could play a role in determining such patterns [Hood *et al.*, 2015]. Indeed, we can expect the strongest solar response at low latitudes and in the summer hemisphere where the ozone is roughly in steady state, but both SBUV data sets show an overall stronger response at the middle latitudes of the winter hemisphere. One possible explanation of this apparent incongruence could be that solar UV variation can modulate also dynamical changes in the stratosphere [Kodera and Kuroda, 2002] although this hypothesis is still under discussion.

Figure 2. (a, b) Geographic distribution of the geomagnetic coefficient (per 13 Ap units, in percent) between 0.01 and 100 hPa as obtained by a multiple linear regression (MLR) based on SBUV MOD O₃ data in August (Figures 2a) and September (Figure 2b) for the 1979–2014 period (see text for details); (c, d) same as Figures 2a and 2b except using SBUV Merged Cohesive O₃ data as predictor; (e–h) same as Figures 2a–2d except showing the solar coefficient (per 100 F_{10.7} units, in percent). Filled contours indicate statistical significance at the 2 sigma level. Note that because of the limited vertical resolution in the lower stratosphere/troposphere, data below about 10 hPa have not been used.

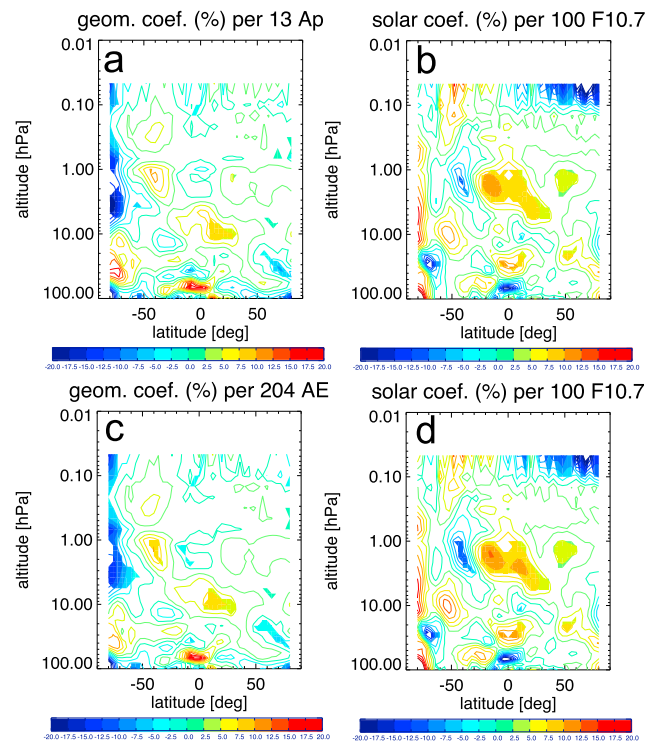


Figure 3. (a) Geographic distribution of the A_p -based geomagnetic coefficient (per 13 A_p units, in percent) between 0.01 and 100 hPa as obtained by a multiple linear regression based on MLS O_3 in May–September for the 2005–2014 period (see text for details); (b) same as Figure 3a except showing the solar coefficient (per 100 $F_{10.7}$ units, in percent); (c and d) same as Figures 3a and 3b except using an AE -based geomagnetic coefficient (shown in Figure 3c per 204 AE units, in percent) in the multiple linear regression. Filled contours indicate statistical significance at the 2 sigma level.

Figure 3a shows the geographic distribution of the geomagnetic coefficient between 0.01 and 100 hPa. Analogously to recent model results including the EPP forcing [Rozanov *et al.*, 2012], O_3 decrease (up to about 15 %) is evident in both the upper stratosphere and the mesosphere at latitudes poleward of 60–70°S, suggesting an EPP-induced effect there. While the mesospheric O_3 depletion is related to EPP-DE via HO_x -catalytic cycles, upper stratospheric changes are likely related to EPP-IE via descent of high NO_x amounts produced at upper altitudes. Note that the larger equatorward extension of the region affected by EPP of Figure 2 in comparison to that showed in Figure 3 is mainly due to the different months included in the regression (i.e., only August or September for SBUV while May to September for MLS).

Moreover, it is interesting to note that similar results are obtained when the MLR includes the AE index, instead of the A_p index, as geomagnetic term (Figure 3c). In the latter case the amplitude of the response is somewhat smaller (larger) in the stratosphere (mesosphere) and slightly more statistically significant above 0.5 hPa.

Figures 3b and 3d are analogous to Figure 3a except for showing the solar coefficient. While at low/middle latitudes a UV-induced O_3 enhancement is evident, no statistically significant changes are present at very high southern latitudes. Moreover, the strong negative O_3 response in the summer mesosphere is mainly related to increased water vapor photolysis and consequent HO_x production during high solar irradiance periods.

In order to give a more solid ground to these correlations, we examined in detail the temporal evolution of the EPP-induced O_3 and HNO_3 variability as well as their correlations for the 2005–2014 period.

Because of its large temporal extension and the dense sampling at high latitudes, the SBUV data set is probably the best data set to investigate the seasonality of the ozone response; nevertheless, drift issues in the data sets could also potentially affect the reliability of this response [Lean, 2014]. The significant solar UV response at high southern latitudes (60–70°S) in the SBUV MOD data set (Figure 2e) is not present in the SBUV Merged Cohesive O_3 data set (Figure 2h). It is then not clear if it is a realistic feature or an artifact introduced in the merging of the data. This should be further investigated.

In order to take advantage of the MLS nighttime observations and due to the shortness of the data set, MLR has been applied to monthly O_3 data in May–September (Figure 3). Moreover, since MLS probes not only the stratosphere, where the NO_x -catalytic cycles dominate the O_3 loss, but also the mesosphere, where O_3 loss is controlled by the HO_x -catalytic cycles; in the following regression analysis we employed the weighted A_p index below 0.5 hPa (as in the previous analysis) while the actual A_p index for higher altitudes. In this way, we account for the direct impact of EPP (i.e., EPP-DE) and for the time needed to transport the air from the upper to the lower atmosphere (i.e., EPP-IE).

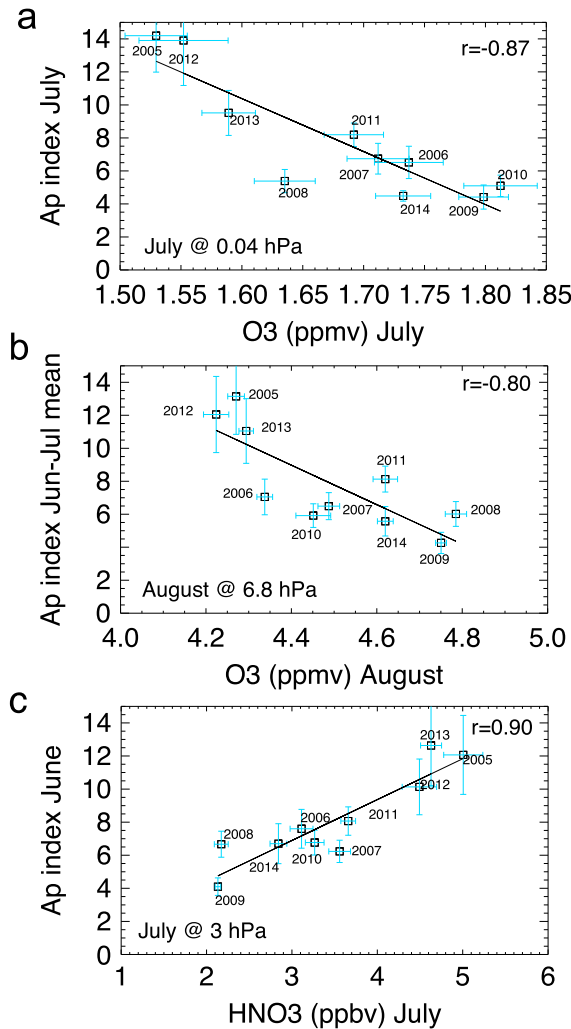


Figure 4. (a) Scatterplots between O₃ at 0.04 hPa and the Ap index for July, (b) O₃ at 6.8 hPa in August and the Ap index averaged over June and July, and (c) HNO₃ at 3 hPa in July and Ap index in June during the 2005–2014 period. O₃ and HNO₃ zonal means have been computed over latitudes poleward of 70°S (see text for details).

Under high geomagnetic activity conditions, polar O₃ can be depleted as a consequence of both medium- and low-energy precipitating electrons, which impact the middle/high mesosphere (above approximately 70 km) and the lower thermosphere, respectively. Therefore, we expect a prompt response of mesospheric O₃, which is directly influenced by EPP, but a delayed response of stratospheric O₃ due to the time required for the NO_x-rich air to descend from upper to lower altitudes. Figure 4 depicts the relationship between the geomagnetic Ap index and O₃ and HNO₃ zonal means averaged over latitudes poleward of 70°S (i.e., in the region not probed by SBUV observations) for July and August of the 2005–2014 period. Figure 4a presents a clear negative correlation ($r \sim 0.9$) between the Ap index and mesospheric O₃ (at 0.04 hPa, i.e., around the so-called tertiary ozone peak) in July. The years characterized by stronger geomagnetic activity (i.e., 2005, 2012, and 2013) show a reduced abundance of O₃, while increasing levels of O₃ along with decreasing levels of geomagnetic activity characterize the other years. Nighttime mesospheric O₃ depletion in polar regions under high geomagnetic activity has been reported before and ascribed to both sporadic SPEs [Seppälä *et al.*, 2006] and strong EEP events which can affect the composition of the mesosphere [Andersson *et al.*, 2014]. Both phenomena cause an additional ionization of the atmosphere, the production of high HO_x mixing ratios and a consequent transient O₃ depletion [Damiani *et al.*, 2008]. Various SPEs able to affect these altitudes occurred mostly in July 2005 [Damiani *et al.*, 2010] while strong EEP events occurred in both 2005 and 2012 [Andersson *et al.*, 2014].

It is interesting to compare the mesospheric O₃ variability with the stratospheric O₃ changes caused by downward transport of upper mesospheric/thermospheric NO_x. Thus, Figure 4b shows the correlation between the O₃ zonal means at 6.8 hPa in August and the Ap index averaged over June and July (we take this averaged index to account for the time needed to transport the air from the lower thermosphere/mesosphere, where the EPP occur, to the stratosphere). As in Figure 4a, we note an intense O₃ depletion in 2005, 2012, and 2013, when the geomagnetic activity and EPP-NO_y amounts are higher. On the other hand, record-high O₃ levels occur during 2008 and 2009, possibly because of the very low EPP-NO_y amounts.

Because of the increasing solar illumination toward the end of the Antarctic winter, the EPP-induced enhancement in HNO₃ is mostly confined to July and the first half of August. Then, the vortex exposition to sunlight leads to fast photolysis of HNO₃ [Stiller *et al.*, 2005] and prevents its use as a proxy of EPP-induced odd nitrogen species. Therefore, Figure 4c shows the regression between the HNO₃ zonal mean at 3 hPa in July and the Ap index in June. The picture shows a positive correlation ($r = 0.9$) and is coherent with the expected high (low) EPP-NO_y amounts during years with high (low) geomagnetic activity.

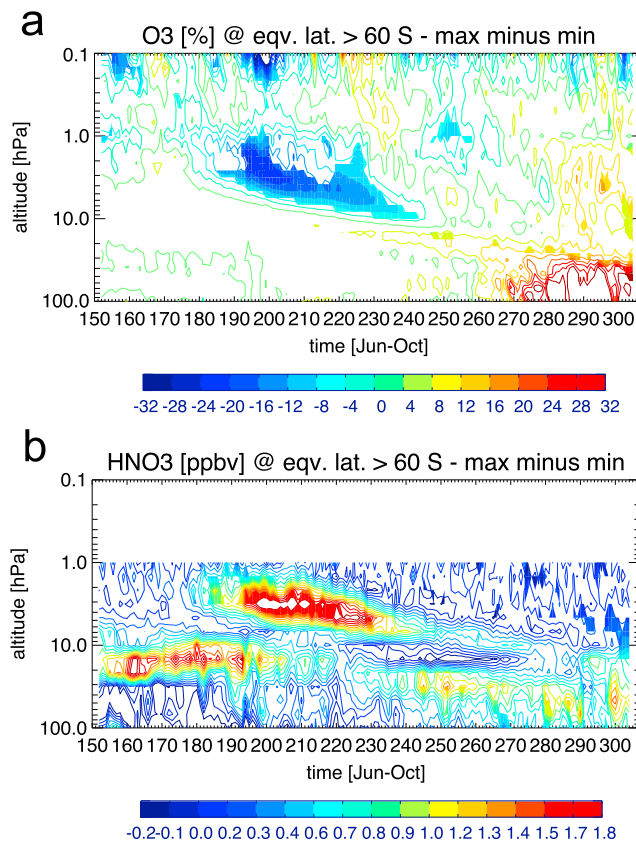


Figure 5. Differences in MLS (a) O₃ and (b) HNO₃ between the composite built by averaging the years characterized by high EPP-NO_y (2005, 2012, 2013; maximum composite) and another one based on the remaining years (minimum composite) during the 2005–2014 period. Results are presented on a daily basis by computing the difference within the equivalent latitude of 60°S. Filled contours indicate statistical significance at the 2 sigma level.

also in the mesosphere (Figure S1 in the supporting information; note the increased HNO₃ between 1 and 0.1 hPa, likely caused by low-energy precipitating electrons, and the strong O₃ depletion above 0.1 hPa).

4. Discussion

Since EPP forcing is potentially able to affect polar climate, mostly via O₃ depletion [Baumgaertner et al., 2009; Semeniuk et al., 2011; Rozanov et al., 2012; Andersson et al., 2014], work is ongoing to include it within multi-model initiatives like Coupled Model Intercomparison Project Phase 6. Nevertheless, although some case studies have been reported [Randall et al., 2005], definitive observational evidences on the importance of the EPP-NO_x as an efficient modulator of O₃ over longer time scales are still lacking, and currently, the majority of CCMs still do not include this mechanism.

Here we showed that both MLS and SBUV observations at high southern latitudes present a clear response of stratospheric O₃ to EPP activity over solar cycle time scales. Overall, at high southern latitudes, the resulting O₃ depletion has been quantified at about 10–15 % on average. Nevertheless, the actual effects will depend also on the polar vortex dynamics which further can contribute to modulate the amount of NO_y reaching the stratosphere.

On the other hand, the expected positive correlation between stratospheric O₃ and solar UV irradiance maximizes at middle latitudes possibly because solar UV modulates also dynamical changes [Kodera and Kuroda, 2002].

In order to further examine the seasonal evolution of the EPP-induced effects on MLS O₃ and HNO₃, we build two composites by averaging the years characterized by high EPP-NO_y (i.e., 2005, 2012, and 2013; maximum composite) and another based on the remaining years (minimum composite). To provide a vortex-centered view, Figure 5 shows the seasonal evolution of the O₃ and HNO₃ maximum-minimum differences in the zonal means computed within 60°S equivalent latitude [Butchart and Remsburg, 1986; Manney et al., 2007] for the June–October period on a daily basis. In the stratosphere the amplitude of the daily differences peaks in July with changes up to about 20% and 2 ppbv in O₃ and HNO₃, respectively. O₃ changes start in June and then propagate to lower altitudes in July and August. No significant variations below 10 hPa occur in September. Similarly, enhancements in HNO₃ propagate from the upper to the middle stratosphere during the June–August period, after which incoming sunlight prevents that NO_y descent in the form of HNO₃ in September.

Furthermore, although not shown here, a clear EPP signature in both O₃ and HNO₃ monthly data can be discerned

Detailed analysis based on MLS observations carried out on a daily basis shows negative (positive) O₃ (HNO₃) differences between years characterized by high and low geomagnetic activity and changes propagating from about 1 to 10 hPa during the June–September period. In particular, the winters of 2005, 2012, and 2013, which were characterized by stronger geomagnetic activity, showed the lower O₃ levels not only in the stratosphere, as expected due to EPP-NO_x effects, but also in the mesosphere, where a direct impact of EPP has been recently reported to occur [Andersson *et al.*, 2014], and this clearly points to a common geomagnetic origin of such changes.

In winter a negative latitudinal gradient in O₃ occurs because of the decrease with increasing latitude of the solar UV-induced O₃ production rate. Although the peaks of the solar and geomagnetic activity are somewhat lagged each other, on average the geomagnetic activity is higher around the solar maximum than around the solar minimum. Therefore, the latter, through the influence of the EPP-NO_y, would tend to further strengthen the O₃ gradient at high latitudes during solar maximum conditions. Additional modeling studies are necessary to assess to what degree these EPP-induced O₃ changes are actually able to influence the polar climate via temperature and wind perturbations.

Because O₃ variability in the upper polar stratosphere is mainly driven by chemistry, this region is commonly used for the detection of ozone hole recovery [Miyagawa *et al.*, 2014]. The results of this study suggest that EPP-induced O₃ variations on a decadal time scale might be of importance in the analysis of upper stratospheric O₃ trends.

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Erratum

In the originally published version of this article, coauthor M. López Puertas (Instituto de Astrofísica de Andalucía, CSIC, Granada, Spain), was omitted from the author list. The omission has since been corrected, and this version may be considered the authoritative version of record.