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Key Points:

- *D*-layer ion chemistry enhances production of mesospheric nitric acid through ion cluster recombination with a seasonal maximum in winter
- Medium-to-high energy electrons precipitating into the mesosphere in April–May 2010 further enhance the formation of nitric acid
- Occurring at a time of year with low background abundance, the enhancement brought nitric acid abundance close to its annual cycle maximum

Correspondence to:
Y. J. Orsolini,
yvan.orsolini@nilu.no

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Mesospheric Nitric Acid Enhancements During Energetic Electron Precipitation Events Simulated by WACCM-D

Yvan J. Orsolini[1,2], Christine Smith-Johnsen[3,2], Daniel R. Marsh[4], Frode Stordal[3], Craig J. Rodger[5], Pekka T. Verronen[6], and Mark A. Clilverd[7]

[1]NILU–Norwegian Institute for Air Research, Kjeller, Norway, [2]Birkeland Centre for Space Science, University of Bergen, Bergen, Norway, [3]Department of Geosciences, University of Oslo, Oslo, Norway, [4]NCAR, Boulder, CO, USA, [5]Department of Physics, University of Otago, Dunedin, New Zealand, [6]Space and Earth Observation Centre, Finnish Meteorological Institute, Helsinki, Finland, [7]British Antarctic Survey, Cambridge, UK

Abstract While observed mesospheric polar nitric acid enhancements have been attributed to energetic particle precipitation through ion cluster chemistry in the past, this phenomenon is not reproduced in current whole-atmosphere chemistry-climate models. We investigate such nitric acid enhancements resulting from energetic electron precipitation events using a recently developed variant of the Whole Atmosphere Community Climate Model (WACCM) that includes a sophisticated ion chemistry tailored for the *D*-layer of the ionosphere (50–90 km), namely, WACCM-D. Using the specified dynamics mode, that is, nudging dynamics in the troposphere and stratosphere to meteorological reanalyses, we perform a 1-year-long simulation (July 2009–June 2010) and contrast WACCM-D with the standard WACCM. Both WACCM and WACCM-D simulations are performed with and without forcing from medium-to-high energy electron precipitation, allowing a better representation of the energetic electrons penetrating into the mesosphere. We demonstrate the effects of the strong particle precipitation events which occurred during April and May 2010 on nitric acid and on key ion cluster species, as well as other relevant species of the nitrogen family. The 1-year-long simulation allows the event-related changes in neutral and ionic species to be placed in the context of their annual cycle. We especially highlight the role played by medium-to-high energy electrons in triggering ion cluster chemistry and ion-ion recombinations in the mesosphere and lower thermosphere during the precipitation event, leading to enhanced production of nitric acid and raising its abundance by 2 orders of magnitude from 10^{-4} to a few 10^{-2} ppb.

1. Introduction

Nitric acid (HNO_3) is an important minor species in the middle atmosphere. Over the last decades, its distribution has been characterized by means of ground-based, aircraft and satellite observations at infrared and millimeter wavelengths (e.g., Damiani et al., 2009, 2016; de Zafra & Smyshlyaev, 2001; Kinnison et al., 2008; López-Puertas et al., 2005; Orsolini et al., 2005, 2009; Santee et al., 2004; Stiller et al., 2005; Urban et al., 2009; Verronen et al., 2008, 2011). HNO_3 is most abundant in the polar lower stratosphere in winter, where its long lifetime during the dark conditions makes it a key reservoir of reactive nitrogen ($NO_x = NO + NO_2$), which drives the main ozone-depleting cycle in the middle and upper stratosphere. Yet satellite observations have revealed descent of HNO_3 from above the upper stratosphere, leading to the formation of a secondary maximum, well above the main lower stratospheric layer. These recurrent enhancements are observed in the polar regions of both hemispheres with a large degree of interannual variability, and they have been linked to energetic particle precipitation (EPP), the main source of NO_x in the mesosphere-lower thermosphere (MLT). Satellite and ground-based observations are often limited to the stratosphere due to retrieval constraints, but occasional mesospheric HNO_3 enhancements have been documented during solar proton events (SPEs; Verronen et al., 2011), when larger abundances expand vertically the validity range of the retrievals.

Both SPEs and energetic electron precipitation (EEP) lead first to the formation of primary ions such as O^+, O_2^+, N_2^+, and N^+ through dissociation and dissociative ionization. These ions are then involved in fast ion-chemistry reactions, ultimately producing NO_x and hydrogen oxides (HO_x; e.g., see Sinnhuber et al., 2012 for a review). The chemistry of ion clusters plays a key role in the production of the neutral nitrogen species. Ion clusters are groups of m molecules tied to a positive or negative ion. For example, m water molecules can form the hydrated water cluster $H^+(H_2O)_m$, or else other water clusters like $NO_3^-(H_2O)_m$ or $NO^+(H_2O)_m$. The

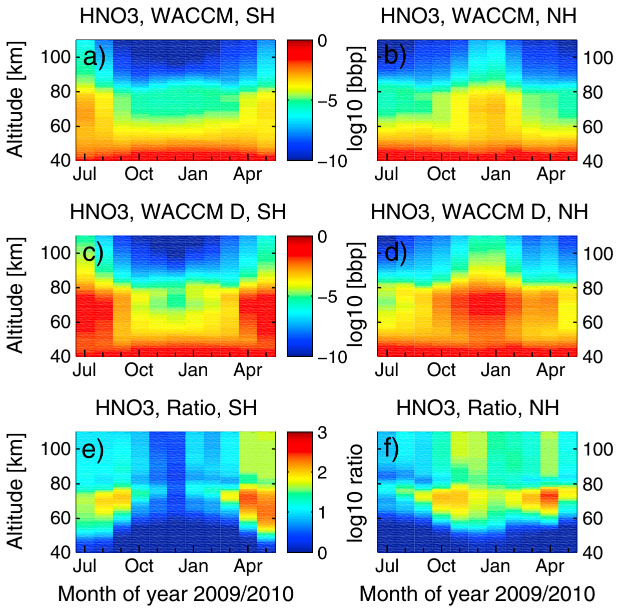

Figure 1. Monthly mean polar cap average of HNO_3 (in ppb, log10 scale). Period is from July 2009 until June 2010, for both the southern hemisphere (over latitudes poleward of 50°S) and northern hemisphere (over latitudes poleward of 50°N), from 40 to 110 km. (a and b) Standard Whole Atmosphere Community Climate Model (WACCM), (c and d) WACCM-D, and (e and f) the ratio (WACCM-D/WACCM), also in log scale. All simulations are with medium-to-high energy electron included.

number *m*, the order of the cluster, indicates the attachment of *m* molecules. Another important ion cluster group for the production of HNO_3 which was identified in previous studies (Andersson et al., 2016; Verronen et al., 2011) is the HNO_3 cluster $NO_3^-(HNO_3)_m$, that is, *m* HNO_3 molecules attached to the negative NO_3^- ion.

With only a few exceptions, the EPP-related upper stratospheric/mesospheric source of HNO_3 is not accounted for in middle atmosphere global models, as they do not incorporate the relevant ion chemistry. Reddmann et al. (2010) included a parametrization of HNO_3 hydrolysis in a chemistry transport model, focusing on the aftermath of the SPE of October 2003. Kvissel et al. (2012) used the same approach, along with an idealized background distribution of hydrated water clusters, in simulations using the free-running Whole Atmosphere Community Climate Model (WACCM). In addition to producing wintertime enhancements of HNO_3, the latter study showed complex chemical-dynamical feedbacks, which extended the effect of the EPP-induced winter increase of NO_x into the warm season by weakening the polar vortex and enhancing the poleward transport of NO_x from lower latitudes. The vortex weakening (when the parameterized ion chemistry reaction was included) arose from strengthened planetary waves due to zonal asymmetries in ozone induced by enhanced NO_x anomalies.

It is apparent that ion chemistry needs to be taken into account to correctly represent the observed distribution of HNO_3 and also that this chemistry could exert a potential feedback on ozone and dynamics. Hence, a more comprehensive ion chemistry is needed to account for the effect of EPP *on neutral species* in models. Previous studies with comprehensive ion chemistry were limited to one-dimensional (1-D) models, which at best only crudely represent transport. For example, Verronen et al. (2011) investigated the chemistry involved in the HNO_3 enhancements during the SPEs of January 2005 and December 2006. They compared the results from the comprehensive 1-D Sodankylä Ion and Neutral Chemistry (SIC) model with satellite observations from the Microwave Limb Sounder (MLS) instrument at the highest sampled latitudes, where horizontal mixing was assumed to be small. The same model was used to analyze the chemical impact of EPP during pulsating auroras (Turunen et al., 2016).

Very recently, an extended ion chemistry based on a subset of reactions and species from the comprehensive SIC model has been incorporated into the global chemistry-climate model WACCM. This variant of WACCM called WACCM-D, where *D* stands for the *D*-layer of the ionosphere (below the mesopause), is described in detail by Verronen et al. (2016). Andersson et al. (2016) investigated the chemical effects of the SPE of 2005, in particular on HNO_3, and showed that the production of HNO_3 increased by 2 orders of magnitude between 40 and 70 km, bringing WACCM-D closer to the MLS satellite observations.

The aim of this paper is to investigate, through a case study, the effect of EEP events on the distribution of HNO_3 and relevant ion clusters in the new WACCM-D model in comparison to the standard WACCM, in the presence of medium-to-high energy electron (MEE) forcing. We analyze a series of events which took place in April and May 2010, the first in a series of moderate geomagnetic storms that perturbed the upper atmosphere from April to July 2010 (Kirkwood et al., 2015). Our focus is on the high-latitude mesosphere and lower thermosphere. Hence, our study differs from the above-mentioned studies with WACCM-D in that we investigate EEP events rather than a SPE. Our simulation also covers an entire year rather than the weeks around the precipitation event, allowing us to examine the EEP events in the context of the seasonal variations of neutral and ionic species.

2. The WACCM-D Simulations and Ancillary Data

We use the WACCM-D model jointly developed by researchers from the National Center for Atmospheric Research (NCAR) and the Finnish Meteorological Institute (Andersson et al., 2016; Verronen et al., 2016).

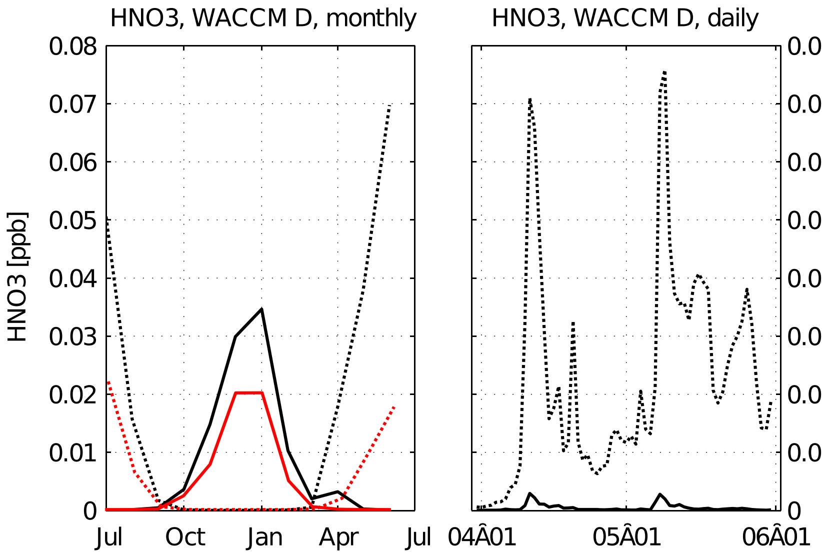

Figure 2. Time evolution of HNO_3 (in ppb). (left) Monthly mean annual (July 2009–June 2010) evolution of HNO_3 in Whole Atmosphere Community Climate Model *D*-layer with medium-to-high energy electron (MEE) included, for the southern hemisphere (black dashed line, over latitudes poleward of 50°S) and the northern hemisphere (black solid line, over latitudes poleward of 50°N) averaged over the 70–75 km layer. Corresponding results from simulations without MEEs are also shown (red lines). (right) Same but showing daily evolution in April and May 2010 for simulations with MEEs included.

WACCM-D is a recent development of WACCM (version 4), a global circulation model with fully coupled chemistry and dynamics, which extends from the surface to ~145 km (with 88 pressure levels in total). The ion chemistry in WACCM-D, with 20 positive ions, 21 negative ions, and 307 reactions, includes a selected subset of ionic species and reactions based on the analysis of Verronen and Lehmann (2013), and it has

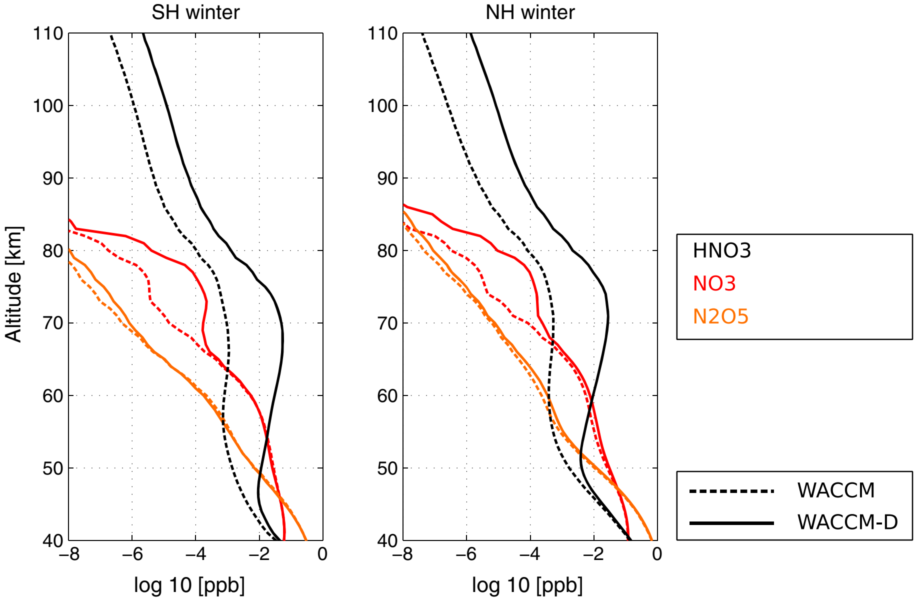

Figure 3. Winter-averaged vertical profiles of the three neutral species (in ppb, log10 scale). Shown are the three neutral species HNO_3, NO_3, and N_2O_5 in Whole Atmosphere Community Climate Model (WACCM; dashed lines) and WACCM-D (solid lines) in (left column) June-July-August for the southern hemisphere (latitudes poleward of 50°S) and in (right column) December-January-February for the northern hemisphere (latitudes poleward of 50°N). All simulations are with medium-to-high energy electron included.

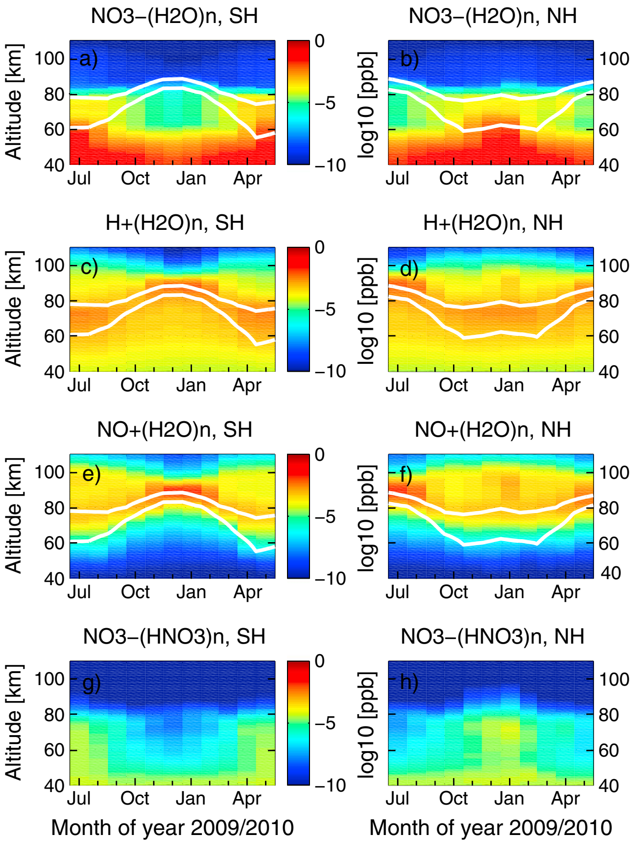

Figure 4. Monthly mean polar cap average of key ion clusters (in ppb, log10 scale). (a and b) NO_3^- $(H_2O)_n$, (c and d) $H^+(H_2O)_n$, (e and f) $NO^+(H_2O)_n$, and (g and h) $NO_3^-(HNO_3)_n$ from July 2009 until June 2010, for both the southern hemisphere (a, c, e, and g; over latitudes poleward of 50°S) and northern hemisphere (b, d, f, and h; over latitudes poleward of 50°N) in Whole Atmosphere Community Climate Model *D*-layer. The two white lines are the contours of 2 and 5 ppm of H_2O (upper and lower contours, respectively). All simulations are with medium-to-high energy electron included.

been shown to produce a representation of the *D* region ionosphere very similar to the more comprehensive but 1-D SIC model (Verronen et al., 2016). The selected additional ionic species were added to five preexisting ones in the standard WACCM (O^+, NO^+, O_2^+, N_2^+, and N^+).

The EPP-related production of HO_x and NO_x which is parameterized in WACCM is, importantly, replaced by the ionic chemical reactions. The reader is referred to the two above-mentioned papers for an exhaustive description of WACCM-D and to Marsh et al. (2007) for the MLT representation in the standard WACCM. Our simulations with WACCM-D or the standard WACCM are mostly intercompared in terms of the *ratio* (WACCM-D divided by WACCM) in key minor constituents. Only in section 3.3 will the absolute differences be used. All simulations have been performed with enhanced eddy diffusion, using a Prandtl number of 2 (Garcia et al., 2014). Galactic cosmic rays are also accounted for in these simulations.

Note also that all the simulations described in the current study are in specified dynamics (SD-WACCM) mode (e.g., Marsh, 2011), that is, nudged up to about 0.79 hPa toward the Modern-Era Retrospective Analysis for Research and Application reanalysis of NASA's Global Modeling and Assimilation Office (Rienecker et al., 2011). Above this level (i.e., in the region where the ion chemistry is particularly active), SD-WACCM transitions linearly to a free running model. For brevity, we omit the "SD" prefix and refer simply to WACCM and WACCM-D, although we use the specified dynamics mode throughout this paper. Our simulations were made at a horizontal resolution of 1.9° × 2.5° (latitude × longitude), cover the period July 2009 to June 2010, and were initialized from existing WACCM initial states. We particularly examine the period spanning April to May 2010 using daily mean data, although the annual cycle from July 2009 to June 2010 will also be shown using monthly mean data.

The parameterization of auroral electron precipitation in WACCM has been supplemented by the inclusion of additional ionization due to MEEs. The details on the derivation of the MEE fluxes and the calculation of the associated ionization rates are given in Appendix A. Having twin simulations with and without MEEs allows us to separate the contributions to the HNO_3 enhancement from the *D* region ion chemistry to that from the MEE forcing. We focus on high latitudes where EEP is concentrated and thus undertake polar averaging over all latitudes poleward of 50° to include the full meridional extension of the auroral ovals. In total, we carried out four simulations, that is, with and without ion chemistry (WACCM-D or WACCM), and with and without the MEE forcing.

We examine the distribution of HNO_3 and of the following four key ion cluster groups: the water clusters $H^+(H_2O)_n$ (with $n = 1.5$), NO^+ $(H_2O)_n$ (with $n = 1.3$), NO_3^- $(H_2O)_n$ (with $n = 1.2$), and the HNO_3 ion cluster NO_3^- $(HNO_3)_n$ (with $n = 1.2$). Our model output is for an ion cluster group, that is, for all n and not for individual cluster orders. The individual ion clusters are treated as prognostic species only in WACCM-D and are not included in the standard WACCM. Although individual ion clusters are short-lived, their abundances adjust to the transport and chemical production or loss of their longer-lived source species. In the thermosphere, the abundances of ion clusters become very low, and it is expected that the ion chemistry is driven by the five primary ions already included in WACCM.

The geomagnetic storm period of April 2010 was driven by a combination of both co-rotating interaction regions associated with high-speed solar wind streams and of coronal mass ejections associated with dense transient solar wind flows. This period is also described in more detail in Smith-Johnsen et al. (2017). We use the Disturbance Storm Time (*Dst*) index to characterize the storm onset and evolution. The minimum of −81 nT (nanoTesla) on 5 April classifies it as a moderate geomagnetic storm. The recovery period is

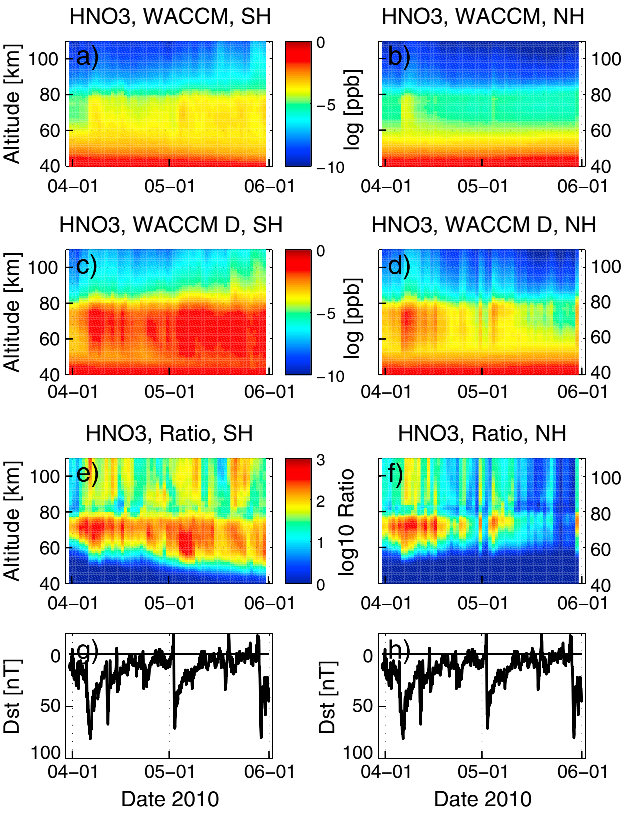

Figure 5. Daily mean polar cap average of HNO_3 (in ppb, log10 scale). The period is April–May 2010, for both the southern hemisphere (over latitudes poleward of 50°S) and northern hemisphere (over latitudes poleward of 50°N) from 40 to 110 km. (a and b) Standard Whole Atmosphere Community Climate Model (WACCM), (c and d) WACCM-D, and (e and f) the ratio (WACCM-D/WACCM), also in log scale. (g and h) The *Dst* index for the same period to highlight the timing of geomagnetic activity. All simulations are with medium-to-high energy electron included.

interrupted by a second moderate geomagnetic storm (with *Dst* of -67 nT) on 12 April. Further storms of similar magnitudes, in terms of *Dst* deflections, occurred in early May and June of that year. There were no large SPEs during the simulated year.

3. Results

3.1. Annual Evolution

3.1.1. Monthly Mean Polar-Averaged HNO_3 Distributions

The monthly mean, polar-averaged (zonally and over latitudes poleward of 50°) evolution of HNO_3 throughout the modeled year (July 2009 to June 2010) from 40 to 110-km altitude is shown in Figure 1 for standard WACCM and for WACCM-D, as well as their ratio (WACCM-D divided by WACCM), for both hemispheres. In both WACCM and WACCM-D, there is a seasonal march in the HNO_3 abundance, which culminates in the winter months (e.g., June–July in the SH, in this case July 2009 and June 2010, and December–January in the NH, in this case December 2009 and January 2010). Inspection of the ratio shown in the lowest panels reveals that the abundance of HNO_3 is increased by over 2 orders of magnitude in WACCM-D in the altitude range 55–75 km, pointing to the important role of ion chemistry in producing mesospheric HNO_3. The ratio is most strongly amplified in April–May 2010 in both hemispheres, raising abundances from 10^{-4} to a few 10^{-2} ppb and suggesting that the EEP events may play a role then. Above 90 km, the background abundance of HNO_3 is very low in both models, but the increase in the ratio in April–May 2010 remains substantial throughout the lower thermosphere (over a factor 10) in both hemispheres, although weaker than for the altitudes below. We will return to this influence of the precipitation events in section 3.2. We further note that, in the upper stratosphere, there is no large increase even though the ion chemistry could have been, in principle, active in the cold winter conditions.

Figure 2 (left) shows the monthly mean seasonal cycle of HNO_3 averaged in the polar caps (poleward of 50° latitude) in both hemispheres and averaged over an altitude range of 70–75 km. It reveals a peak-to-peak variation in the seasonal cycle that is twice as large in the SH as in the NH and a maximum abundance in winter (0.07 ppb in the SH and 0.035 ppb in the NH).

3.1.2. Chemical Pathways for HNO_3 Production

Up to now, we have not yet discussed which pathways of ion or neutral chemistry described in Verronen and Lehmann (2013) are the most important for the production of HNO_3 in WACCM or WACCM-D. In the standard WACCM, there is some weak HNO_3 production (Figure 1) arising from the neutral reaction

$$NO_2 + OH + M \rightarrow M + HNO_3$$

Whole Atmosphere Community Climate Model *D*-layer, however, includes the key ion-ion recombination reactions between water ion clusters and the HNO_3 ion clusters, which produce HNO_3:

$$\begin{gathered}(\text{reaction pathway R1}: \text{ion-ion recombination reactions forming } HNO_3)\\ H^+(H_2O)_n + NO_3^-(HNO_3)_m \rightarrow (m+1)\ HNO_3 + n\ H_2O\\ NO^+(H_2O)_n + NO_3^-(HNO_3)_m \rightarrow NO + NO_3 + m\ HNO_3 + n\ H_2O\end{gathered}$$

Another set of ionic reactions involved in the production of HNO_3 in the stratosphere is the conversion of N_2O_5 into HNO_3 through a hydrolysis reaction involving hydrated water clusters (Kawa et al., 1995; Kvissel et al., 2012 and references therein):

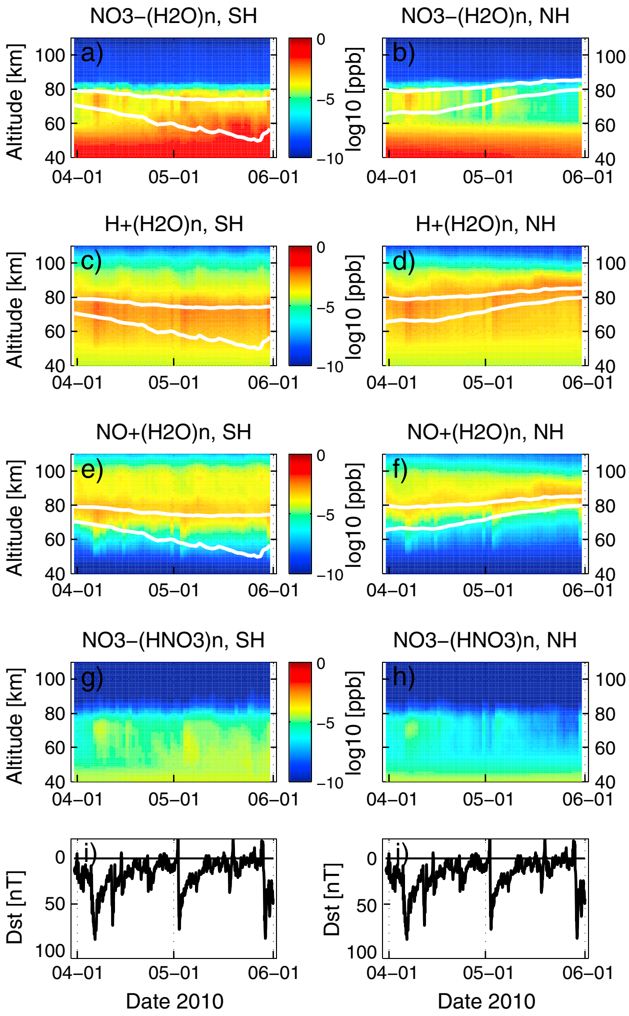

Figure 6. Daily-mean polar cap average of key ion clusters (in ppb, log10 scale). (a and b) $NO_3^-(H_2O)_n$, (c and d) $H^+(H_2O)_n$, (e and f) $NO^+(H_2O)_n$, and (g and h) $NO_3^-(HNO_3)_n$ for April–May 2010, for both the southern hemisphere (a, c, e, and g; over latitudes poleward of 50°S) and northern hemisphere (b, d, f, and h; over latitudes poleward of 50°N) in WACCM-D. (i and j) The *Dst* index for the same period to highlight the timing of geomagnetic activity. The two white lines are the contours of 2 and 5 ppm of H_2O. All simulations are with medium-to-high energy electron included.

$$\text{(reaction pathway R2 : hydrolysis of } N_2O_5)$$

$$H^+(H_2O)_n + N_2O_5 \rightarrow H^+(H_2O)_{n-1}(HNO_3) + HNO_3$$
$$H^+(H_2O)_{n-1}(HNO_3) + H_2O \rightarrow H^+(H_2O)_n + HNO_3$$

This reaction pathway (R2) sequesters NO_x from the N_2O_5 reservoir into the longer-lived HNO_3 reservoir and mostly plays a role in the stratosphere, since the abundance of N_2O_5 falls rapidly with height in the upper stratosphere and mesosphere.

Figure 3 compares the winter-mean vertical profiles of several (neutral) nitrogen species between WACCM and WACCM-D, in each hemisphere. We first remark that the winter increase in WACCM-D is found not only in HNO_3 but also in NO_3 and to a much smaller extent in N_2O_5. HNO_3 is enhanced above 40-km altitude. The NO_3 production is not very efficient in the mesosphere, and its background level is very low. As seen on Figure 3, NO_3 is only very weakly enhanced below 65 km and strongly enhanced between 70 and 85 km. Ion-ion recombination reactions involving the several types of water ion clusters can explain—through ion chemistry—the increase in NO_3 by up to 2 orders of magnitude (from 10^{-6} to 10^{-4} ppb) in WACCM-D compared to WACCM. Such reactions include

$$H^+(H_2O)_n + NO_3^-(H_2O)_m \rightarrow H + NO_3 + (n+m)\, H_2O$$
$$NO^+(H_2O)_n + NO_3^-(H_2O)_m \rightarrow NO + NO_3 + (n+m)\, H_2O$$
$$NO^+ + NO_3^-(H_2O)_n \rightarrow NO + NO_3 + n\, H_2O$$

Ion chemistry also enhances the NO_x production compared to the parameterization used in standard WACCM (Andersson et al., 2016), which is another factor relevant to the increased NO_3 through neutral chemistry. N_2O_5 also increases only very weakly below 65 km; the increase is larger above 70 km, though still smaller than that for NO_3. The increase in this case is consistent with the neutral reaction

$$NO_2 + NO_3 + M \rightarrow M + N_2O_5$$

and the N_2O_5 increase is limited to the layer where NO_3 is produced by the ion-ion recombination in WACCM-D. In short, the hydrolysis of N_2O_5, pathway R2, is unimportant for the seasonal production of HNO_3 due to the small abundance of N_2O_5 in the mesosphere, itself tied to NO_3 (Figure 3).

3.1.3. Monthly Mean Polar-Averaged Distributions of Ion Clusters

The corresponding seasonal evolution of the four ion cluster species is shown in Figure 4. The abundances vary with season and height. The $H^+(H_2O)_n$ and $NO^+(H_2O)_n$ water clusters have a maximum abundance in summer. This seasonal-dependence and its height variation follow the seasonal march of water vapor abundance as indicated by two white contours on Figure 4, corresponding to 2 and 5 ppmv, with the summer-to-winter pole meridional circulation in the mesosphere bringing up air enriched in water vapor at high latitudes in summer and bringing down dry air in winter. The $NO_3^-(H_2O)_n$ water cluster and the HNO_3 cluster $NO_3^-(HNO_3)_n$ tend to maximize in winter, indicating that the abundance of NO_3^- is, in this case, the limiting factor. A higher abundance of NO_x has been previously reported in the winter high latitudes due to the descent from the MLT (e.g., Randall et al., 2007). This coincidence in time between higher abundance of precursory NO_x and the secondary winter maximum in $H^+(H_2O)_n$, weaker than the summer one and occurring when abundance of water vapor is low, is suggestive of a role for conversion of $NO^+(H_2O)_n$ to $H^+(H_2O)_n$ (Verronen & Lehmann, 2013).

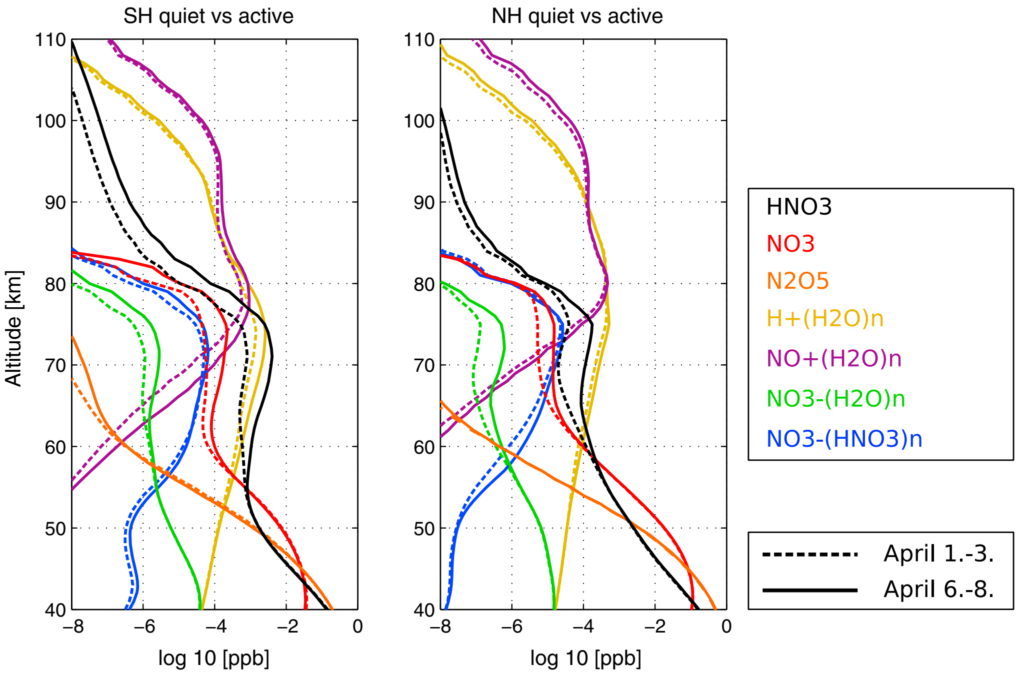

Figure 7. Vertical profiles of abundance of ion clusters and neutral species (in ppb, log10 scale). Three-day averages in quiet conditions (1–3 April, dashed lines) and active conditions (6–8 April, solid lines; southern hemisphere in left column, latitudes poleward of 50°S, and northern hemisphere in right column, latitudes poleward of 50°N) of the vertical profiles of abundance of the four key ion clusters and the neutral species HNO_3, NO_3, and N_2O_5 in Whole Atmosphere Community Climate Model *D*-layer. All simulations are with medium-to-high energy electron included.

3.2. Changes Around the April and May Geomagnetic Storms

3.2.1. Daily Polar-Averaged HNO_3 Distributions

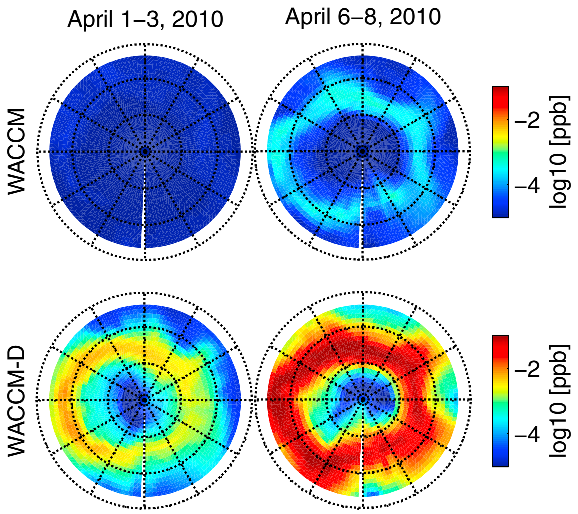

Figure 8. Geographic maps of HNO_3 (in ppb, log10 scale) over the northern hemisphere. Maps correspond to 3-day averages at 70 km, in (left column) quiet (for 1–3 April) and (middle column) active (6–8 April) conditions. (top row) Whole Atmosphere Community Climate Model (WACCM) and (bottom row) WACCM-D. In this figure and all following figures with maps, latitude circles are at 45°, 60°, and 75°, and zero degree longitude is at the bottom. All simulations are with medium-to-high energy electron included.

The period of April and May 2010 is characterized by large enhancements in mesospheric and lower thermospheric HNO_3 in WACCM-D, following the *Dst* negative excursions that mark the occurrences of the storms. The daily-averaged, polar-averaged abundances in WACCM-D (Figure 5) are higher than in WACCM by over 2 orders of magnitude. Close inspection of the ratio indicates that the short-lived relative enhancements clearly appear in bursts. These bursts are tied to the *Dst* fluctuations, but also, in the mesospheric layer at 50–70 km in particular, the daily-varying increases related to the geomagnetic storms are superimposed on a seasonal cycle variation. In the SH, the daily-varying enhancements also occur when the HNO_3 abundance is increasing as the winter approaches, while it is decreasing in the NH (see Figure 1).

Returning to Figure 2 (right), we note that the HNO_3 increase due to the April 2010 EEP event in WACCM-D is much smaller than the corresponding increase after the January 2005 SPE, discussed by Andersson et al. (2016). They found an increase in HNO_3 of 0.5–1.0 ppb near 70–75 km during the SPE (their Figure 9, top) in the NH. By contrast, Figure 2 (right) shows that, in the SH, the increase during the EEP events has a maximum value of 0.075 ppb near 70–75 km in WACCM-D, at the peak of the events. It is hence a factor 5 to 10 smaller than for the SPE. In the NH, the HNO_3 increase is only about 0.005 ppb, that is, 20 times smaller than in the SH. It is important to note that SPEs are comparatively rare events, while MEE electron precipitation is considerably more common. The EEP event occurred at a time of year (April) when background abundances of HNO_3

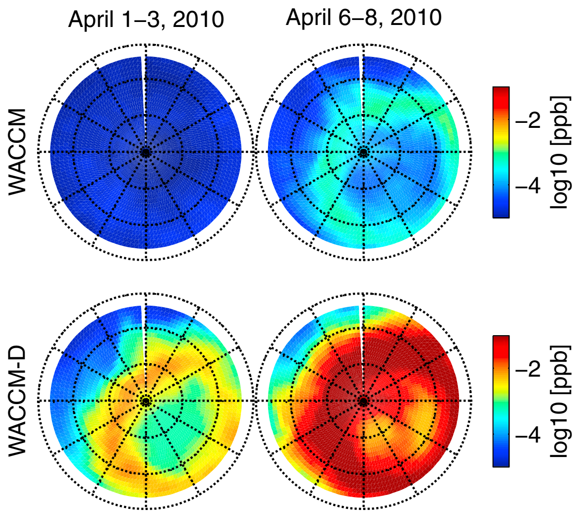

Figure 9. Geographic maps of HNO_3 (in ppb, log10 scale) over the southern hemisphere. (as in Figure 8).

are low in both hemispheres (Figure 2, left), but the abrupt increase in the austral polar cap during the EEP event brings HNO_3 close to its seasonal maximum.

3.2.2. Daily Polar-Averaged Distributions of Ion Clusters

The corresponding day-to-day evolution of the abundance of the four ion cluster species (Figure 6) is marked by an abrupt increase in most of the clusters following the *Dst* negative excursions indicating storm onsets. While Figure 4 had shown that the $H^+(H_2O)_n$ abundance followed the seasonal H_2O cycle, it is clear from Figure 6 that the rapid enhancements during the EEP events occur in the declining phase of water vapor abundance in the SH or in its slowly increasing phase in the NH (see the white contours). Enhancements of hydrated water cluster ions during the EEP event are due to higher ionization and higher abundances of ions, including precursory $NO^+(H_2O)_n$ ion clusters or also oxygen ion clusters $O_2^+(H_2O)_n$, followed by the conversion to $H^+(H_2O)_n$ (Verronen & Lehmann, 2013).

In Figure 7, we also compare the changes in WACCM-D during the EEP event, that is, contrasting the quiet and active periods (1–3 April and 6–8 April, respectively), for the aforementioned three neutral species and the four key ion clusters. Starting with the neutral species, the changes during the event are qualitatively similar to those seen during the seasonal cycle. The layer where HNO_3 increases is somewhat narrower for the EEP-related changes than for the changes due to the seasonal cycle, since the latter are also influenced by transport, due to the longer time scales involved. Since the event took place in April, the abundance of N_2O_5, which is easily photo-dissociated, is smaller in the NH, which is more sunlit in boreal spring conditions. Again, the N_2O_5 change is constrained by the increase in NO_3 produced by the ion cluster chemistry during the EEP event. Turning now to the ion clusters and their changes between the quiet and active period, we again notice how their respective abundances decrease sharply with increasing altitude, reflecting the decreasing availability of H_2O or HNO_3, as seen earlier (Figure 4). Above 90 km, the $NO^+(H_2O)_n$ ion cluster becomes the most abundant, reflecting the primary importance of the NO^+ ion in the thermosphere. It is apparent that the additional production of HNO_3 and NO_3 between the quiet and active period is tied to the enhanced abundances of the various ion clusters in WACCM-D, which recombine in ion-ion reactions. For example, NO_3 is decreasing sharply above 80 km along with the two ion clusters tied to the negative ion NO_3^-. Also, the lower boundary of the HNO_3 increase near 55 km is tightly constrained by the altitude where the abundance of hydrated ion water clusters starts to increase due to the influence of energetic electrons (this will be even clearer in Figure 12). In short, these figures are consistent with ion cluster recombinations (R1) playing the dominant role in the formation of HNO_3 during the EEP event.

3.2.3. Geographical Maps of Nitric Acid and Ion Cluster Abundances

We focus hereafter on the changes in the geographical distribution of HNO_3 at 70 km between the prestorm quiet period (a 3-day period, 1–3 April) and the active storm period (a 3-day period, 6–8 April). These are shown as geographic maps in Figures 8 and 9 for the NH and the SH, respectively. We chose the early April storm since it is easier to contrast to the quiet prestorm conditions, but the same changes are seen in the simulations for the May event (not shown). It is apparent that there is already some enhancement in WACCM-D compared to WACCM within most of the whole polar cap even during the quiet period, related to the seasonal cycle enhancement in WACCM-D, albeit at much lower levels than during the time of the storm. The changes between the active and quiet periods are already present in WACCM (see Figure 5), but the amplification is stronger and much more widespread in WACCM-D, up to 10^{-2} rather than to 10^{-3} ppb. In the active period, HNO_3 increases considerably along the oval regions, that is, in the region symmetric in geomagnetic coordinates which experiences enhanced ionization (see Appendix A). The equatorward expansion of the ovals at the initiation of the storm can be noticed in the enhancements on the equator side of the prestorm oval edges (Figures 8 and 9). The increase is stronger in the SH, as had been shown earlier in Figure 2.

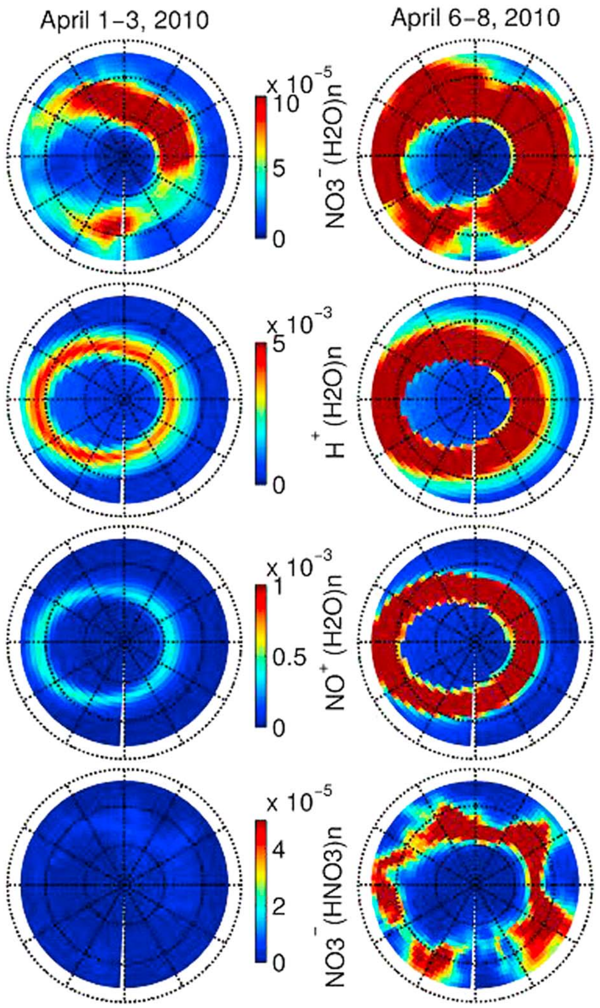

Figure 10. Geographic maps of key ion clusters (in ppb) over the northern hemisphere. Shown are NO_3^- $(H_2O)_n$, $H^+(H_2O)_n$, $NO^+(H_2O)_n$ and $NO_3^-(HNO_3)_n$ from Whole Atmosphere Community Climate Model *D*-layer at 70 km, in (left column) quiet (1–3 April) and (right column) active (6–8 April) conditions. All simulations are with medium-to-high energy electron included.

The geographical distributions of the four ion cluster species at 70 km (Figures 10 and 11) readily illustrate the enhancements of the ion cluster distributions along the ovals during the EEP event. That is, the chemical effect of EEP is not limited to NO_y species and the enhancements in ion clusters play an important role as outlined in section 3.1.2. The distribution of the ion cluster containing the NO_3^- ion is more complex than the water ion clusters. The ion clusters are short-lived, but their distributions reflect the changing distributions of precursory neutral species, like NO_x in the case of the NO_3^- ion clusters. It is also apparent from Figures 8–11 that, while HNO_3 and ion clusters remain close to their production around the auroral oval in the NH, they are more readily redistributed within the polar cap in the SH. The interhemispheric differences, namely, that the changes are confined to a narrow latitude band characteristic of the auroral oval in the NH but spread into the polar cap in the SH, can be explained by the larger oval offset (i.e., difference in the zonal direction between the magnetic and geographic coordinate systems) in the SH. Hence, in the SH, there is a tendency for the zonal winds to rapidly redistribute species with isopleths along magnetic coordinates. Also, the NH is more sunlit at this time of the year and NO and HNO_3 are more readily photolysed. The transport by the mean meridional circulation is stronger in April–May in the SH (during austral fall) than in the NH (during boreal spring; e.g., Smith et al., 2015). The interhemispheric differences during the EEP event, with

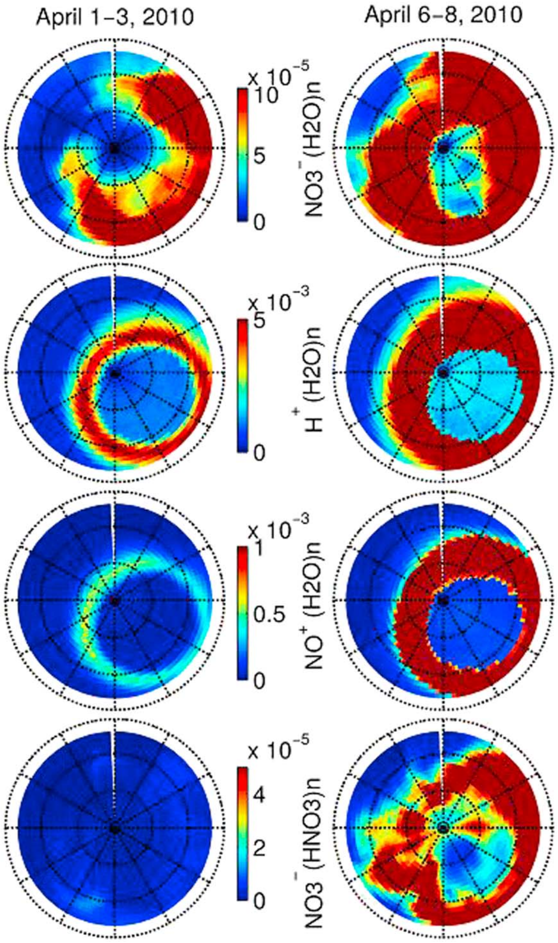

Figure 11. Geographic maps of key ion clusters (in ppb) over the southern hemisphere (as in Figure 10).

stronger polar cap-averaged abundances of HNO_3 or ion clusters in the SH, can also be seen in the profiles shown in Figure 7.

3.3. Role of the MEE Ionization

Since the aim of this paper was to examine an EEP event, it appears sensible to include the forcing by MEEs. The previous figures hence showed results from WACCM or WACCM-D simulations with the MEEs included. In this section, we nevertheless compare those simulations with simulations where the MEE forcing is removed, leaving only auroral electron precipitation, in order to delineate more specifically the effect of this MEE precipitation.

Covering the period around the EEP event, Figure 12 shows the April mean zonally averaged meridional-height cross sections of HNO_3 from both WACCM and WACCM-D, with and without the inclusion of MEEs, as well as their absolute differences. Hence, the differences between the plots along a row (i.e., (b)-(a) or (e)-(d)) indicate the change due to the introduction of the MEEs in WACCM or WACCM-D, while the differences along a column (i.e., (d)-(a) or (e)-(b)) indicate the changes due to the introduction of the *D* region ion chemistry. From Figure 12c, it is clear that, in the standard WACCM, the MEEs produce little change in HNO_3 in the upper stratosphere or MLT region. It is only with the inclusion of the ion chemistry in WACCM-D that the EEP-induced production of HNO_3 is amplified (Figure 12f). Although there is already a mesospheric and thermospheric HNO_3 increase in WACCM-D without the MEEs, it is further increased by the inclusion of that precipitation. This is an indication that energetic electrons, which penetrate deeper into the mesosphere region, further trigger the ionic reactions which produce HNO_3. Figure 12i contrasts the

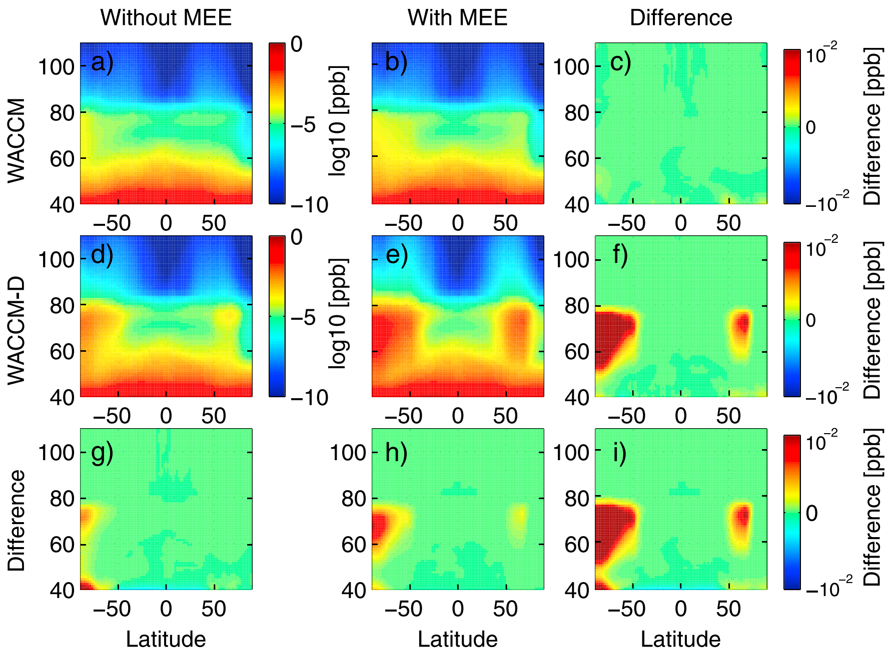

Figure 12. April-mean latitude/height zonal-mean cross sections of HNO_3 (in ppb, log10 scale) for all simulations. (a–c) Standard Whole Atmosphere Community Climate Model (WACCM) without and with medium-to-high energy electron (MEE) and their absolute difference (the later minus the former), respectively. (d–f) Standard WACCM without and with MEE and their absolute difference (the later minus the former), respectively. (g and h) Absolute difference between WACCM-D and WACCM without and with MEE. (i) Absolute difference between WACCM-D with MEE and WACCM without MEE. Difference is expressed in ppb.

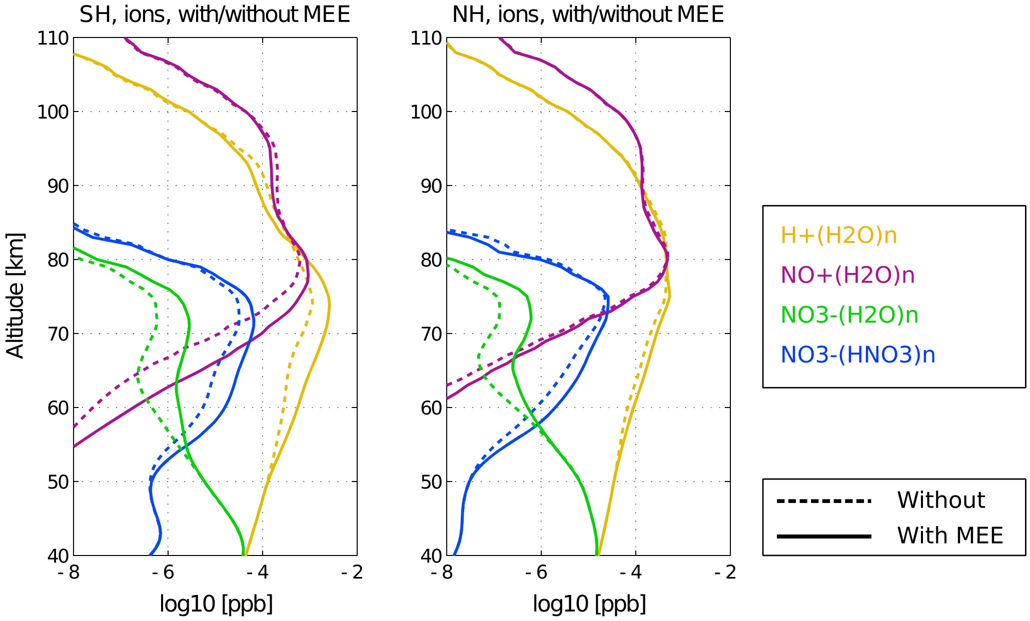

Figure 13. Vertical profiles of abundance of ion clusters (in ppb, log10 scale) in simulations with and without medium-to-high energy electrons (MEEs). Profiles of the four key ion clusters in Whole Atmosphere Community Climate Model *D*-layer correspond to 3-day averages during the active period (6–8 April) for (left) southern hemisphere (latitudes poleward of 50°S) and (right) northern hemisphere (latitudes poleward of 50°N), with MEEs included (solid lines) and without (dashed lines). The color coding for the ion clusters is the same as in Figure 7.

simplest and the most elaborate model, that is, the standard WACCM without MEE and WACCM-D with MEE. Figure 12 hence stresses the important role played by MEEs during the event: In the absence of MEEs, the HNO_3 enhancements in WACCM-D are much weaker. To further stress the important triggering role played by particle precipitation and by MEE in particular on the HNO_3 production during the event, Figure 13 compares the two versions of WACCM-D, with and without MEE, at the peak of the EEP event (6–8 April). Importantly, the abundances of the four key ion clusters clearly increase in the mesosphere with the inclusion of the MEEs above 55 km, which is consistent with the strong increase of the HNO_3 production by MEE demonstrated in Figure 12.

Finally, returning to Figure 2 (left, red lines), we can see that the forcing by MEEs is strengthening the seasonal cycle in both hemispheres outside of the period of large negative *Dst* fluctuations in April and May 2010.

4. Summary

In summary, EPP induces the formation of ion clusters, and the ion-ion recombinations (reaction pathway R1) between these clusters lead to the production of HNO_3. Our study of an EEP event indicates that the effect is 5 to 10 times smaller than during a SPE event. The event occurred at a time of year when the seasonally varying background of HNO_3 is low, but it brought its abundance close to its annual cycle maximum. Our study also confirms the importance of the ion-ion recombination pathway (R1) over the hydrolysis of N_2O_5 (R2), as shown by Verronen et al. (2011) during SPEs. NO_3 is also produced by similar ion-ion recombinations. There is a seasonal component of this HNO_3 production, independent of the EEP event, which is stronger in WACCM-D compared to WACCM due to the background presence of ion clusters, and which is stronger in WACCM-D with the inclusion of MEE. Superposed on this seasonal cycle, the EEP event considerably augments the production of HNO_3, raising its abundance by two orders of magnitude from 10^{-4} to a few 10^{-2} ppb. This effect is enhanced by the inclusion of the MEE, allowing more production of the necessary ion clusters down to 55 km in the latitude bands characteristic of the auroral ovals.

Three-dimensional middle atmospheric modeling with ion chemistry models such as WACCM-D is in its infancy and only the aforementioned handful of studies have been published in the last year. Such model simulations with WACCM-D open new possibilities to study the connection between the neutral middle-atmosphere and the *D*-region ionosphere. It has been already shown by Andersson et al. (2016) that the ion chemistry in WACCM-D leads to a better agreement with satellite observations of HNO_3, HO_x, and NO_x during SPEs. Further studies of the short- and long-term variability in mesospheric HNO_3 using satellite observations (e.g., from MLS, Michelson Interferometer for Passive Atmospheric Sounding, Atmospheric Chemistry Experiment-Fourier Transform Spectrometer, or other instruments) would be warranted in order to support the conclusions of this model study. This would, however, require that satellite retrievals are improved and validated in the mesosphere. It should be also noted that WACCM-D ion chemistry can provide a realistic electron density also in the lower ionosphere (Verronen et al., 2016), so that comparison against ionospheric observations such as ground-based radars can be used to study, for example, the quality of the simulated EPP forcing. Further work with WACCM-D can be made to test our overall understanding of important ions and their reactions, both in the MLT and the stratosphere.

Appendix A: Producing the MEE forcing

The EEP forcing applied in the current study was developed as part of an effort to include EEP in climate models, such as WACCM. The approach used here is based on direct satellite measurements. By contrast, recent efforts undertaken to produce the EEP forcing as part of the solar forcing data set recommended for CMIP6, as described in van de Kamp et al. (2016) or Matthes et al. (2017), rely on a proxy-based parametrization in order to extend the series back in time, prior to the satellite era.

The EEP flux was determined from the experimental measurements made from 1998 to 2012 by the Space Environment Monitor 2 (SEM-2) instrument packages onboard the constellation of Polar Orbiting Environment Satellites (POES). The POES are a long-lived series of spacecraft in Sun-synchronous high-inclination orbits at roughly 800–850 km altitude. Included in the POES SEM-2 instrument is the Medium Energy Proton and Electron Detector (MEPED) and the Total Energy Detector that together monitor electron fluxes over the nominal energy range from 50 eV to 2.5 MeV (Evans & Greer, 2004; Rodger, Carson, et al., 2010). Here we focus on the electron fluxes observed by the 0^0 MEPED telescope, as this principally measures electrons with pitch angles inside the Bounce Loss Cone (Rodger, Clilverd, et al., 2010), which will be lost locally on short time scales (i.e., on the order of seconds). Observations from this telescope can provide an indication of the EEP input into the atmosphere at a location joined by the geomagnetic field line to the satellite in question. During the period studied here, up to six distinct SEM-2 carrying satellites were operational simultaneously (see Table 2 of Neal et al., 2013 for a list with summary information), each of which had orbital periods of ~100 min.

The MEPED electron observations are of integral electron counts for the nominal energy ranges >30 keV (e1), >100 keV (e2), and >300 keV (e3). Previous studies have identified significant contamination in the electron channels by protons with energies of hundreds of keV (Yando et al., 2011). Unfortunately, such protons can reach considerable levels during geomagnetic storms, which is also when EEP is likely to be most active. We correct for this proton contamination by applying a NOAA-developed algorithm (Lam et al., 2010), validated by Whittaker et al. (2014). In addition, SPEs and the high-energy protons in the South Atlantic Magnetic Anomaly are known to swamp the electron detectors, leading to no meaningful electron measurements. Hence, all SPE periods, as well as observations from inside and around the South Atlantic Magnetic Anomaly, are excluded. We note that for the period studied in this paper, there were no data excluded due to SPEs.

The original MEPED electron observations have 2-s resolution. In order to produce long-term EEP fluxes, the electron observations from each integral channel were combined from all operational POES instruments by zonally averaging the measurements in geomagnetic coordinates with 3-hr time resolution and 0.5 L resolution (where L is the McIlwain L-parameter; McIlwain, 1961). We restrict ourselves to the L range from 2.25 to 9.75, which encompasses the outer radiation belt. It has previously been shown that power laws are an accurate representation of the EEP flux spectrum, that is, through a comparison of high energy resolution DEMETER electron flux observations with POES MEPED measurements (Whittaker et al., 2013). Hence, we fit a power law spectrum to the three 0° electron telescopes (e1, e2, and e3) to obtain the energy spectral gradient (k) for the precipitating electrons.

Unfortunately, the small angular size of the MEPED/POES telescope results in low sensitivity at lower flux magnitudes (Yando et al., 2011), which causes the MEPED electron observations to have a comparatively high minimum detectable flux (~10^2 el cm^{-2} s^{-1} sr^{-1} in each integral channel). Due to experimental noise, periods with lower EEP fluxes may appear to have near constant EEP at this minimum detectable level, although they have been shown to be inconsistent with other experimental data sets (e.g., Neal et al., 2015). So as not to bias the fluxes during the relatively common situation of geomagnetic quiet times (when EEP levels are likely near-zero), we set all EEP flux magnitudes <250 cm^{-2} s^{-1} sr^{-1} to zero. The near noise-level fluxes can also produce artificially hard power law spectra; we therefore limit $k < -1$ and set any periods with $k \geq -1$ to $k = -1$. Finally, we follow Rodger et al. (2013) and remove all electron observations when the MEPED P7 omnidirectional detector reports >36 MeV protons, that is, set them to zero. This should suppress the impact of SPE contamination. However, is important to note that this means that the EEP flux representation provided here will not be fully accurate during SPEs, where no meaningful experimental measurements of EEP are available from POES.

The combination of these processes should ensure that unrealistically high levels of EEP are excluded during quiet times or during SPEs, an issue that has been identified in other EEP products derived from POES electron observations (e.g., Neal et al., 2015).

The power law fitted EEP parameters were then used to determine ionization rates, assuming the EEP had a differential power law flux spectrum covering the energy range from 50 keV to 2 MeV using 78 logarithmically spaced bins. The power law assumption for the spectrum is the same as the one described by van van de Kamp et al. (2016, section 2.1). The ionization rate calculation is based on a continuously slowing-down approximation and a normalized energy dissipation distribution function for electrons; this method is described in detail by Rees (1989). A prior WACCM simulation was used to provide daily, zonal mean neutral background data for the ionization rate calculation, specifically the concentrations of the main atmospheric constituents N_2 and O_2 and O. The ionization rates were calculated in 3-hr time resolution for each of the L shell bins (latitudes), after the differential electron fluxes were integrated over pitch angles 0–80° and azimuth angles 0–360°, assuming an isotropic angular distribution. The ionization rates were calculated for the WACCM altitude (km) grid which changes slightly from day to day but corresponds to a fixed pressure level grid. The L

shell-dependent ionization rates were then converted to magnetic latitude and, with the assumption of uniformity on magnetic longitude, projected onto the WACCM geographic (latitude-longitude) grid.

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