

## RESEARCH ARTICLE

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## WACCM-D—Improved modeling of nitric acid and active chlorine during energetic particle precipitation

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## Key Points:

- WACCM-D, including *D* region chemistry, can reproduce atmospheric effects of the January 2005 SPE
- Results show significant improvement in modeling of polar HNO<sub>3</sub>, HCl, ClO, OH, and NO<sub>x</sub>
- Order-of-magnitude enhancements in HNO<sub>3</sub> above 45 km are in agreement with satellite data

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**Abstract** Observations have shown that a number of neutral minor species are affected by energetic particle precipitation (EPP) and ion chemistry (IC) in the polar regions. However, to date the complexity of the ion chemistry below the mesopause (i.e., in the *D* region ionosphere) has restricted global models to simplified EPP/IC parameterizations which are unable to reproduce some important effects, e.g., the increase of mesospheric nitric acid (HNO<sub>3</sub>). Here we use WACCM-D, a variant of the Whole Atmosphere Community Climate Model which includes a selected set of *D* region ion chemistry designed to produce the observed effects of EPP/IC. We evaluate the performance of EPP/IC modeling by comparing WACCM-D results for the January 2005 solar proton event (SPE) to those from the standard WACCM and Aura/Microwave Limb Sounder (MLS) and SCISAT/Atmospheric Chemistry Experiment-Fourier Transform Spectrometer (ACE-FTS) observations. The results indicate that WACCM-D improves the modeling of HNO<sub>3</sub>, HCl, ClO, OH, and NO<sub>x</sub> during the SPE. Northern Hemispheric HNO<sub>3</sub> from WACCM-D shows an increase by 2 orders of magnitude at 40–70 km compared to WACCM, reaching 2.6 ppbv, in agreement with the observations. For HCl and ClO, the improvement is most pronounced in the Southern Hemisphere at 40–50 km where WACCM-D predicts a decrease of HCl and increase of ClO by 1.6% and 10%, respectively, similar to MLS data. Compared to WACCM, WACCM-D produces 25–50% less OH and 30–130% more NO<sub>x</sub> at 70–85 km which leads to better agreement with the observations. Although not addressed here, longer-term NO<sub>x</sub> impact of ion chemistry could be important for polar stratospheric ozone and middle atmospheric dynamics.

## 1. Introduction

Energetic particle precipitation (EPP) affects the mesosphere and lower thermosphere (MLT) in the polar regions and significantly influences neutral composition and dynamics of the atmosphere [Rozanov *et al.*, 2005; Seppälä *et al.*, 2009; Funke *et al.*, 2011; Rozanov *et al.*, 2012]. For example, ionization caused by solar electrons and protons leads to the production of odd hydrogen (HO<sub>x</sub> = H + OH + HO<sub>2</sub>) and odd nitrogen (NO<sub>x</sub> = N + NO + NO<sub>2</sub>) species that have significant implications for the ozone (O<sub>3</sub>) chemistry [Jackman *et al.*, 2001; Verronen *et al.*, 2006; Jackman *et al.*, 2008]. By absorbing a great part of UV radiation, ozone plays an important role in the energy budget and dynamics of the middle atmosphere. It has been shown that the ozone changes in the stratosphere, in general, contribute to the ground-level climate variability, particularly at high latitudes [Gillett and Thompson, 2003]. Ozone variability caused by EPP in the upper stratosphere and mesosphere has been proposed to have a similar effect, although more research is needed to establish the coupling all the way to the surface [Seppälä *et al.*, 2009; Baumgaertner *et al.*, 2011; Andersson *et al.*, 2014].

Understanding all observed atmospheric effects of EPP requires a good representation of ion chemistry in models [Funke *et al.*, 2011]. Due to its complexity, the lower ionosphere (*D* region) ion chemistry is typically parameterized in global atmospheric models, and only production of HO<sub>x</sub> and NO<sub>x</sub> is considered. However, both satellite observations and ion chemistry analysis have shown that EPP and ion chemistry affect also other important species, such as nitric acid (HNO<sub>3</sub>), hydrogen chloride (HCl), and chlorine monoxide (ClO) [Winkler *et al.*, 2009; Verronen *et al.*, 2011; Damiani *et al.*, 2012; Verronen and Lehmann, 2013]. These effects should not be neglected because it has been proposed that they, e.g., ionic production of HNO<sub>3</sub>, can lead to modulation of middle atmospheric dynamics in the polar regions [Kvissel *et al.*, 2012]. Although detailed 1-D ion chemistry models exist, global models including vertical and horizontal transport can improve our understanding of

ion chemistry impacts because they allow for long-term (e.g., solar cycle) studies and their results are more comparable to satellite observations.

The solar proton event (SPE) of 16–21 January 2005 was characterized by two solar eruptions which perturbed the middle atmosphere on both short (days) and long (weeks) time scales [Damiani *et al.*, 2008; Jackman *et al.*, 2011]. Satellite observations, as well as model simulations, showed significant enhancements in HO<sub>x</sub> and NO<sub>x</sub> in the polar mesosphere and, consequently, substantial ozone destruction [Seppälä *et al.*, 2006; Verronen *et al.*, 2006; Damiani *et al.*, 2008; Seppälä *et al.*, 2008]. Moreover, precipitation of solar high-energy protons elevated the amount of HNO<sub>3</sub> in the stratosphere/lower mesosphere and caused changes in chlorine species [Verronen *et al.*, 2011; Damiani *et al.*, 2012].

In this paper, we utilize a variant of the Whole Atmosphere Community Climate Model (WACCM) which includes a selected set of lower ionospheric (*D* region, <90 km) ion chemistry (WACCM-D, see Verronen *et al.* [2016] for a description). We will demonstrate how the ion chemistry in WACCM-D improves the modeling of several important middle atmospheric neutral species during the January 2005 solar proton event. This is done by comparing WACCM-D results to satellite observations as well as to the results from the standard WACCM.

## 2. Modeling

WACCM is a chemistry-climate general circulation model with vertical domain extending from the surface to  $5.9 \times 10^{-6}$  hPa ( $\sim 140$  km geometric height). The standard horizontal resolution used is 1.9° latitude by 2.5° longitude. The representation of WACCM physics in the MLT and simulations of the atmospheric response to solar and geomagnetic forcing variations are described by Marsh *et al.* [2007]. Details of recent centennial scale coupled simulations using the current version of WACCM (version 4) and an overview of the model climate can be found in the study by Marsh *et al.* [2013]. The chemistry module in WACCM is interactive with the dynamics through transport, radiative transfer, and exothermic heating. Photochemistry associated with ion species (O<sup>+</sup>, NO<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>+</sup>, and N<sup>+</sup>) is part of the standard chemistry package. The standard model uses a lookup table parameterization for HO<sub>x</sub> production, based on the work of Solomon *et al.* [1981]. For NO<sub>x</sub>, it is assumed that 1.25 N atoms are produced per ion pair with branching ratios of 0.55/0.7 for N(<sup>4</sup>S)/N(<sup>2</sup>D), respectively [Jackman *et al.*, 2005; Porter *et al.*, 1976]. This parameterization is strictly valid only in the heterosphere, because its fundamental assumption is a fixed N<sub>2</sub>/O<sub>2</sub> ratio, and it has been shown to underestimate NO<sub>x</sub> production above about 65 km [Nieder *et al.*, 2014].

WACCM-D is a variant of WACCM in which the standard parameterization of HO<sub>x</sub> and NO<sub>x</sub> production is replaced by a set of *D* region ion chemistry reactions, with the aim to reproduce better the observed effects of EPP on the mesosphere and upper stratosphere neutral composition. The ion chemistry set was selected based on the current knowledge of ion chemical reactions and their effects on the neutral atmosphere [Verronen and Lehmann, 2013], and it includes 307 reactions of 20 positive ions and 21 negative ions. More details about WACCM-D as well as its lower ionospheric evaluation are presented in the companion paper by Verronen *et al.* [2016].

In this study, we have used WACCM version 4 simulations with the preconfigured specified dynamics scenario (SD-WACCM), which is forced with meteorological fields (temperature, horizontal winds, and surface pressure) from NASA GMAO (GEOS5.1) [Reinecker *et al.*, 2008] at every dynamics time step below about 50 km; above this, the model is fully interactive (88 levels in total). Note, however, that the model dynamics at all altitudes (also above 50 km) are very much driven by the winds and wave fluxes applied below 50 km, such that the internal variability of SD-WACCM is small. For example, the root-mean-square of temperature differences between the runs with and without *D* region chemistry indicates that there is an agreement within 3 K (i.e., 2%) in the polar regions at 60–80 km. The runs include forcing from auroral electrons and solar protons but do not include higher energy electrons (>10 keV) or galactic cosmic rays. Two model runs were made: (1) a reference run (SD-WACCM) and (2) a run with *D*-region ion chemistry (SD-WACCM-D). Both runs covered the period 1 January–28 February 2005. In the modeling, we use the SPE ionization rates based on GOES-11 observations and described in Jackman *et al.* [2011]. Note, however, that we excluded the highest energy protons (300–20,000 MeV) affecting altitudes below 10 hPa.

In order to have the model results comparable to the satellite observations, WACCM profiles were output at Aura Microwave Limb Sounder (MLS) and SCISAT Atmospheric Chemistry Experiment-Fourier Transform

**Table 1.** MLS and ACE-FTS Data Characteristics

Data	Vertical Range (hPa/km)	Vertical resolution (km)	Precision	Accuracy (%)
MLS OH	1–0.003/49–84	2.5–5	$0.5–3.3 \times 10^6 \text{ cm}^{-3}$	10
MLS O <sub>3</sub>	1–0.02/49–76	3–5.5	0.2–1.4 ppmv	5–35
MLS HNO <sub>3</sub>	10–0.01/32–80	3–5	0.7–1.2 ppbv	10–50
MLS ClO	22–1/26–50	3–4.5	0.1–0.3 ppbv	5–20
MLS HCl	22–1/26–50	3–4	0.2–0.5 ppbv	10
ACE NO <sub>x</sub>	4–0.005/40–85	3–4	0.6–250 ppbv	10–35

Spectrometer (ACE–FTS) observation times and locations. From these, daily averages were calculated for polar latitudes. In the case of HNO<sub>3</sub>, the Aura/MLS averaging kernels have been applied to the model output, which decreases the HNO<sub>3</sub> mixing ratios at 65–75 km and increases them at 45–55 km (e.g., by a factor of 1.5–4 and 1.25–1.75, respectively, as shown by *Verronen et al.* [2011, Figure 2]). For the other species, the model results (daily averages) were simply interpolated to the same vertical grid with the observations before making a direct comparison or calculating differences between the model results and observations.

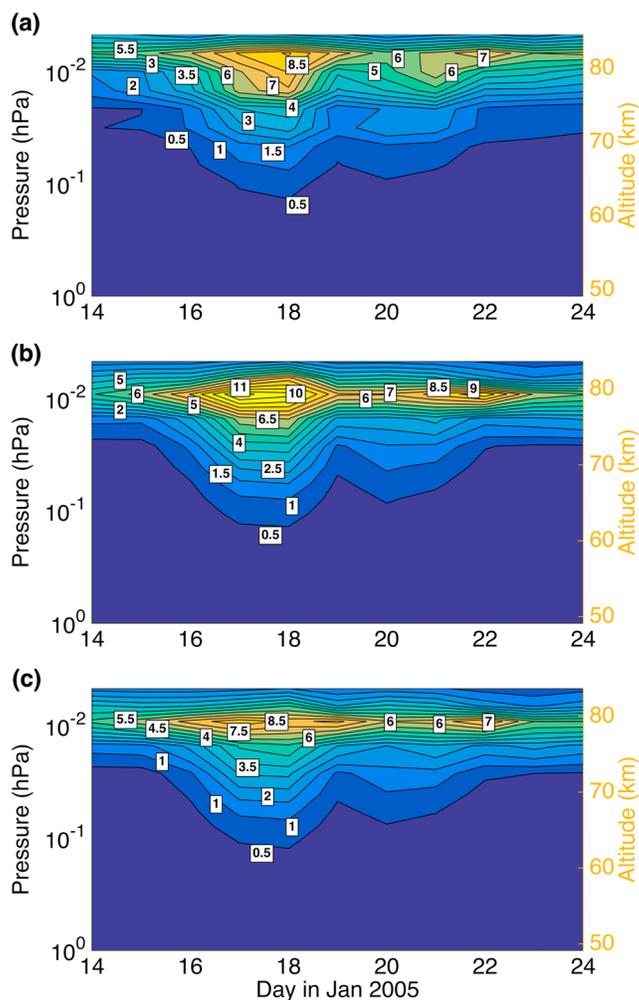
### 3. Satellite Observations

The Microwave Limb Sounder (MLS, <http://mls.jpl.nasa.gov>) is an instrument on board the Aura satellite [*Waters et al.*, 2006]. Aura is in a near-polar 705 km altitude orbit. As Earth rotates underneath it, the Aura orbit stays fixed relative to the Sun and gives daily global coverage with about 15 orbits per day. The local solar time is nearly the same for each orbit on a given day and at latitudes 60–90°N varies between about 1 A.M. and 1 P.M. The equatorial crossing time of the Aura satellite is about 1:30 in the afternoon. We use Version 3.3 Level 2 daily mean OH, O<sub>3</sub>, and HNO<sub>3</sub> data for the period 1–31 January 2005, concentrating on latitudes 60–82.5° in the Northern Hemisphere (NH). Additionally, we use HCl and ClO observations at latitudinal band 60–82.5° in the Northern Hemisphere (NH) and in the Southern Hemisphere (SH). Before the analysis, the data were screened according to the MLS data description and quality document [*Livesey et al.*, 2011]. More information on these MLS data products is given in Table 1 and in *Pickett et al.* [2008], *Jiang et al.* [2007], *Santee et al.* [2007, 2008], and *Froidevaux et al.* [2008]. Note that we use HNO<sub>3</sub> observations outside the recommended altitude range, i.e., between about 40 and 80 km (2.15–0.01 hPa) [*Santee et al.*, 2007; *Livesey et al.*, 2011]. At these altitudes, the signal-to-noise ratio of the measurements is typically low because the HNO<sub>3</sub> mixing ratios are low. However, the HNO<sub>3</sub> enhancement during the SPE improves the signal-to-noise ratio and allows us to study the changes in the upper stratosphere/lower mesosphere. The HNO<sub>3</sub> observations contain real atmospheric signal up to about 70 km (0.046 hPa), as discussed in *Verronen et al.* [2011].

The Atmospheric Chemistry Experiment-Fourier Transform Spectrometer (ACE-FTS, <https://database.scisat.ca/level2/>) is an instrument on board the SCISAT satellite [*Bernath et al.*, 2005]. The principle of ACE measurement is the solar occultation technique. A high inclination (74°), low Earth orbit (650 km) gives coverage of tropical, midlatitudes, and polar regions. The instrument observes the wavelengths between 2.2 and 13.3 μm during sunset and sunrise and measures vertical profiles (10–150 km) of temperature, pressure, density, and 18 atmospheric constituents, including NO and NO<sub>2</sub>. We use NO<sub>x</sub> observations (version 3) for the period 1 January–28 February 2005. The ACE observations were taken in the latitude range from about 57 to 66°N. More information on ACE-FTS NO<sub>x</sub> is given in Table 1 and in *Kerzenmacher et al.* [2008]. We use NO<sub>x</sub> observations (version 3) for the period 1 January–28 February 2005. Measurement errors for NO<sub>x</sub> vary with altitude and time. Between 25 and 45 km, the errors are quite small (less than 20%) but increase above 45 km (less than 35%).

### 4. Results and Discussion

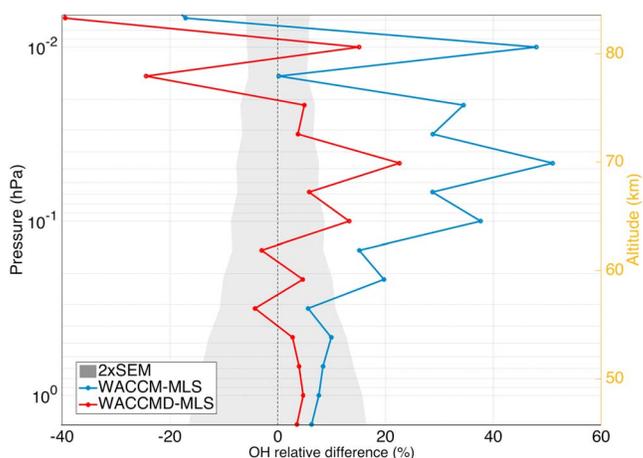
Significant perturbations were observed in short-lived species, such as OH and ozone, as a consequence of the January 2005 SPE. Figure 1 shows the MLS OH measurements (Figure 1a) together with WACCM (Figure 1b) and WACCM-D (Figure 1c) model predictions for 14–24 January 2005 in the latitude band 60–82.5°N. Both MLS and the models show large OH enhancement during the SPE. The observed and modeled increase of OH occurred on 17–18 January at altitudes between 60 and 82 km. In general, WACCM and WACCM-D agree well with observations. However, it is clear from Figure 1 that WACCM predictions overestimate OH values by about



**Figure 1.** Daily averaged OH mixing ratio (ppbv) from (a) Aura MLS measurements and model predictions from (b) WACCM and (c) WACCM-D for the 60–82.5°N band for the period 14–24 January 2005. The contour intervals are: 0.25, 0.5, 0.75, 1, 2, 4, 6, 8, 9, 10, and 11 ppbv. MLS data uncertainty ( $2 \times \text{SEM}$ ) varies between 0.05 and 0.25 ppbv (2–8%).

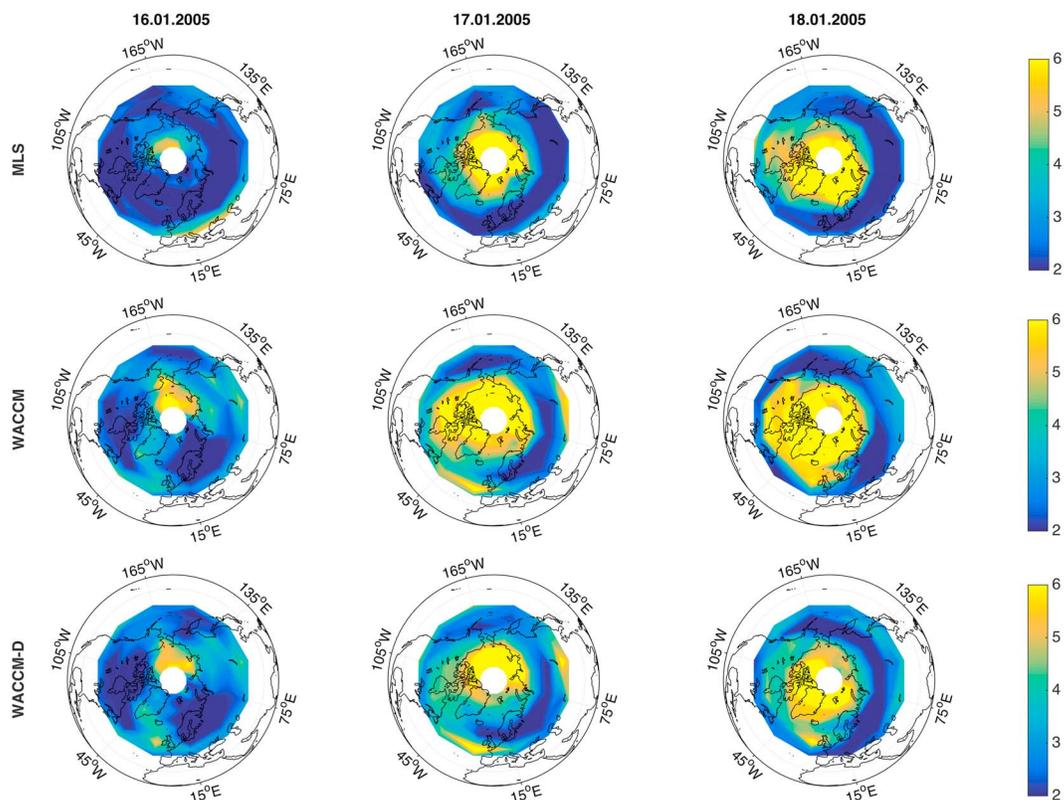
1–2.5 ppbv (20–50%) at altitudes between 60 and 80 km. The relative differences between the simulated and observed OH presented in Figure 2 indicate that during the main peak of the SPE (17 January), WACCM overestimates the OH enhancement by up to about 55% at altitudes between 60 and 80 km. The agreement between WACCM-D and observations is much better with a maximum 22% OH overestimate for the same altitudinal range. Between 60 and 80 km, WACCM-D fits better inside the MLS standard error of the mean (SEM) than WACCM which is outside SEM for almost all altitudes. Due to the short lifetime of OH [Pickett *et al.*, 2006], the changes caused by the SPE lasted only for couple of days. After 21 January, the OH observed/predicted enhanced values returned to the levels before the event.

Similar behavior in OH can be seen in Figure 3, where we compare the MLS polar maps of OH at 70–80 km with the model predictions. For clarity, measurements and predictions are shown in the latitude range 40–82.5°N, gridded into 5° latitude  $\times$  30° longitude bins. Before the SPE on 16 January, the observed and predicted OH values are low, however, both model versions seem to overestimate the OH values. On 17 January (peak of SPE), a substantial increase of OH inside the polar cap area (poleward 60°) is observed by MLS and predicted by WACCM and WACCM-D. However, WACCM-D is in better agreement with the observations compared to WACCM, which overestimates the OH amounts over the entire polar cap, in average by about 15–35%. As discussed by Verronen and Lehmann [2013], the standard parameterization of HO<sub>x</sub> production used in WACCM (and many other models) is dependent upon altitude and ionization rate only and neglects the effects of negative ion chemistry (e.g., HNO<sub>3</sub> production) and seasonal variation caused by different atmospheric conditions. At the altitudes shown in Figure 3, there is less direct HO<sub>x</sub> production in WACCM-D, mostly because the ion

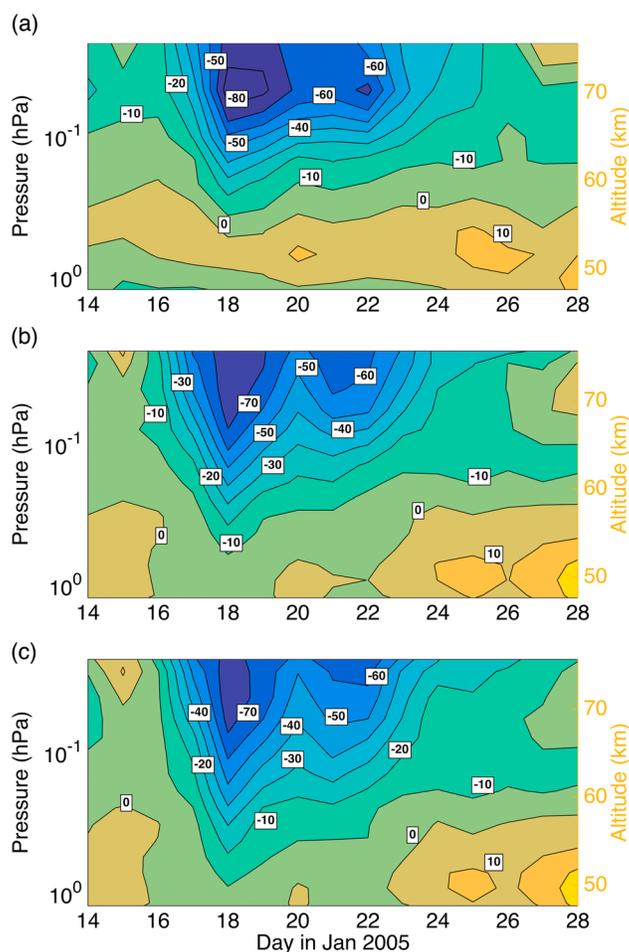


**Figure 2.** OH relative differences (%) between WACCM and MLS (blue line) and WACCM-D and MLS (red line) in the NH polar region on 17 January 2005. Grey area indicates MLS data uncertainty ( $2 \times \text{SEM}$ ).

chemistry is affected by the modeled wintertime amount of water vapor, while the standard parameterization assumes a fixed summertime amount (the latter being higher). The ionic  $\text{HO}_x$  production is especially sensitive to water vapor at 70–80 km because  $\text{H}_2\text{O}$ , decreasing with increasing altitude, gradually becomes the limiting factor for water cluster ion formation. A much smaller proportion of the OH difference comes from OH/H partitioning which in WACCM parameterization is 50/50 but depends somewhat on ionization rate and altitude in WACCM-D.



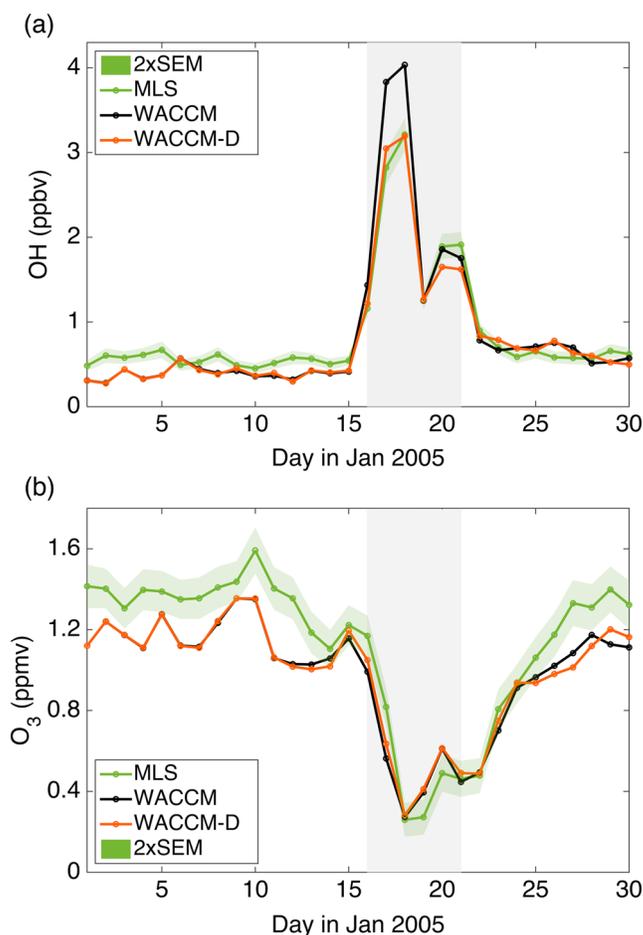
**Figure 3.** Polar maps of daily averaged OH mixing ratio (ppbv) from (top row) Aura MLS measurements and model predictions from (middle row) WACCM and (bottom row) WACCM-D averaged between 70 and 78 km altitude for three selected days: 16–18 of January 2005. For clarity, measurements are shown in the latitude range 40–82.5°N. MLS data uncertainty ( $2 \times \text{SEM}$ ) varies between 0.5 and 1.5 ppbv.



**Figure 4.** Daily averaged  $O_3$  changes (%) from (a) Aura MLS measurements and model predictions from (b) WACCM and (c) WACCM-D for the 60–82.5°N band. An observed/predicted  $O_3$  profile for the period 1–14 January 2005 was subtracted from the observed/predicted  $O_3$  values for the plotted days (14–28 January 2005). The contour intervals for the ozone changes are –80, –60, –50, –40, –30, –20, –10, 0, 10, and 20%. MLS data uncertainty ( $2\times$ SEM) varies between 0.02 and 0.06 ppmv (5–20%).

An important consequence of the SPE-induced short-term OH enhancement is ozone loss in the upper stratosphere and mesosphere, as shown in Figure 4. The observed and modeled  $O_3$  anomalies (%) are calculated on a daily time scale with respect to the 1–14 January average (a quiet, non-SPE period). During the SPE, ozone decreases of up to about 80% are observed by MLS and up to about 70% predicted by both WACCM and WACCM-D. Both models are in reasonably good agreement with the observations considering the magnitude of the ozone changes. At altitudes between 70 and 75 km, the observed relative ozone changes are slightly larger than predicted by WACCM and WACCM-D; however, the differences are within data uncertainty which is about 10–20%. The predicted ozone loss extends deeper than in the observations, down to about 50–55 km, as already noted earlier by *Jackman et al.* [2011, Figure 7]. The ozone depletion lasts for about 6 days (16–21 January), after which there is a gradual recovery to the levels seen before the event. The timing of ozone loss and recovery is well captured by both models. It has been shown before that the short-term mesospheric ozone depletion during SPEs can be reasonably well modeled using a simple parameterization of  $HO_x$  production [e.g., *Funke et al.*, 2011]. Our results, i.e., the relatively small differences between the WACCM and WACCM-D ozone responses, confirm this and also indicate that the water cluster ion chemistry in WACCM-D is working as expected and causing an effect which is in agreement with observations.

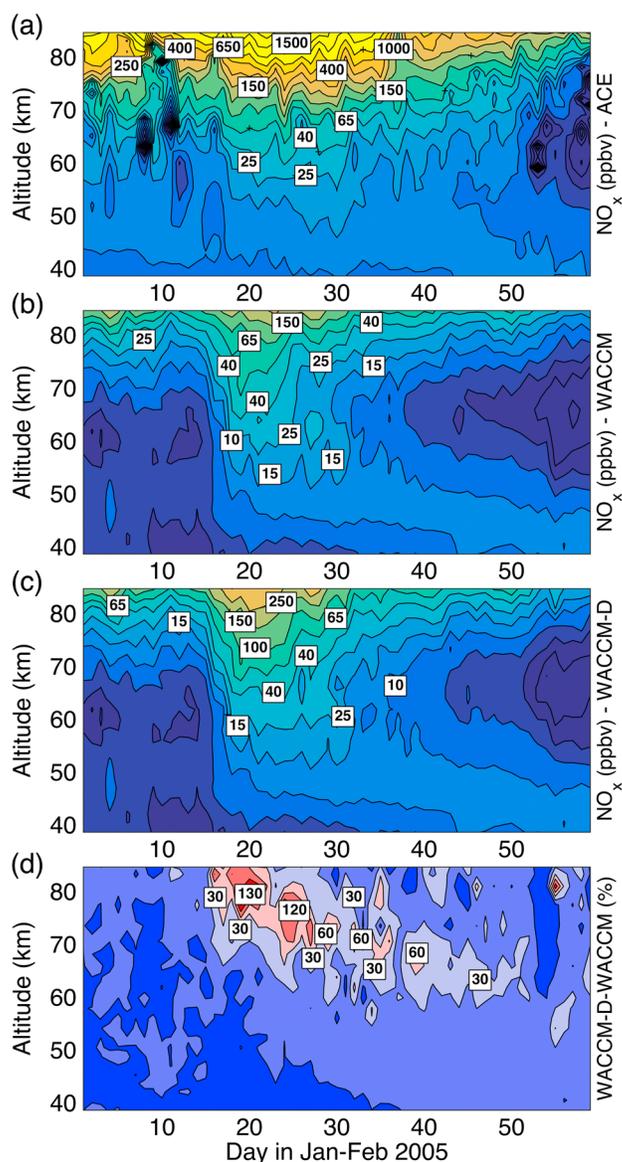
To summarize the short-term SPE effects, Figure 5 shows the observed and predicted OH (Figure 5a) and  $O_3$  (Figure 5b) mixing ratios averaged between 70 and 76 km altitude and latitudes between 60 and 82.5°N. The increased OH values between 16 and 21 January coincide closely with decreased  $O_3$  as seen from satellite



**Figure 5.** Daily averaged (a) OH mixing ratio (ppbv) and (b) O<sub>3</sub> mixing ratio (ppmv) from Aura MLS measurements together with model predictions from WACCM and WACCM-D for the 60–82.5°N band and altitudes between 70 and 76 km. SPE days are marked as a grey area. Green area indicates MLS data uncertainty ( $2 \times \text{SEM}$ ).

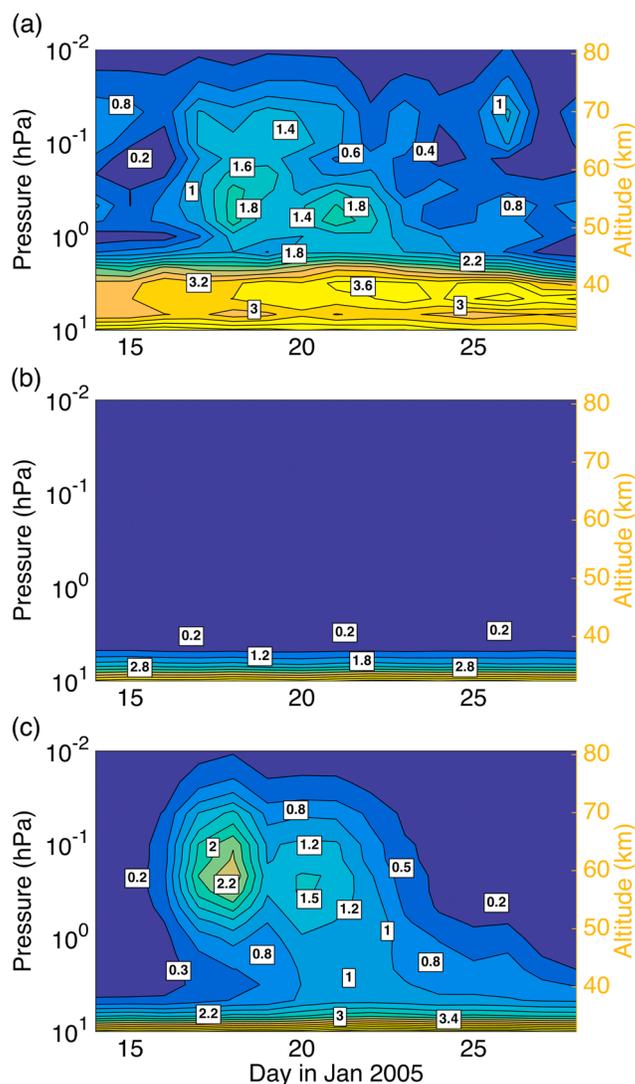
measurement and model predictions. The predicted OH enhancement by WACCM is about 35% higher than OH predicted by WACCM-D and measured by MLS. As already mentioned, the OH differences between the models are related to differences in direct HO<sub>x</sub> production and HO<sub>x</sub> partitioning. In the case of ozone, both WACCM and WACCM-D agree very well with observations (within data uncertainty) during and a few days after the SPE, while at other times the models predict smaller amounts of ozone.

In addition to the short-term effects, the SPE has an impact on constituents that have longer lifetimes (such as NO<sub>x</sub>, HNO<sub>3</sub>) and can significantly affect the atmosphere for several weeks following the event. In the absence of solar radiation, e.g., during polar winters, NO<sub>x</sub> is chemically long-lived throughout the middle atmosphere and can be transported down from the mesosphere-lower thermosphere to the stratosphere. Once in the stratosphere, it is always long-lived and can cause catalytic ozone loss in solar illuminated conditions. During the whole of January, large amounts of NO<sub>x</sub> were observed (Figure 6a) with a rather moderate response during and after the SPE between 16 and 31 January. In comparison, the simulated NO<sub>x</sub> (Figures 6b and 6c) exhibits a distinctive peak corresponding to the SPE event. Moreover, during the whole period under consideration (1 January–28 February 2005), the NO<sub>x</sub> values predicted by WACCM (Figure 8b) and WACCM-D (Figure 8c) are considerably smaller than the ACE-FTS measurements. These results confirm previous studies by *Jackman et al.* [2011] where ACE-FTS data and WACCM version 3 were used. One possible reason for model underestimation is the omission of medium energy electrons, because energetic electron precipitation (EEP) could produce a considerable amount of NO<sub>x</sub> in situ in the mesosphere [e.g., *Newnham et al.*, 2011]. In the present case, the beginning of the year was characterized by strong geomagnetic activity and EEP events that occurred during 2–7 January. Work is ongoing to include this source of EEP and it will be the topic of a future study.



**Figure 6.** Daily averaged  $\text{NO}_x$  mixing ratio ( $\log_{10}(\text{ppbv})$ ) from (a) ACE measurements and model predictions from (b) WACCM and (c) WACCM-D in the NH polar region for the first 60 days in 2005. The contour intervals are: 0.8, 1.2, 1.6, 2, 2.4, 2.8, and  $3.2 \log_{10}(\text{ppbv})$ . Daily averaged  $\text{NO}_x$  relative differences (%) between (d) WACCM-D and WACCM in the NH polar region for the first 60 days in 2005. The contour intervals are: 0, 30, 60, 90, and 120%.

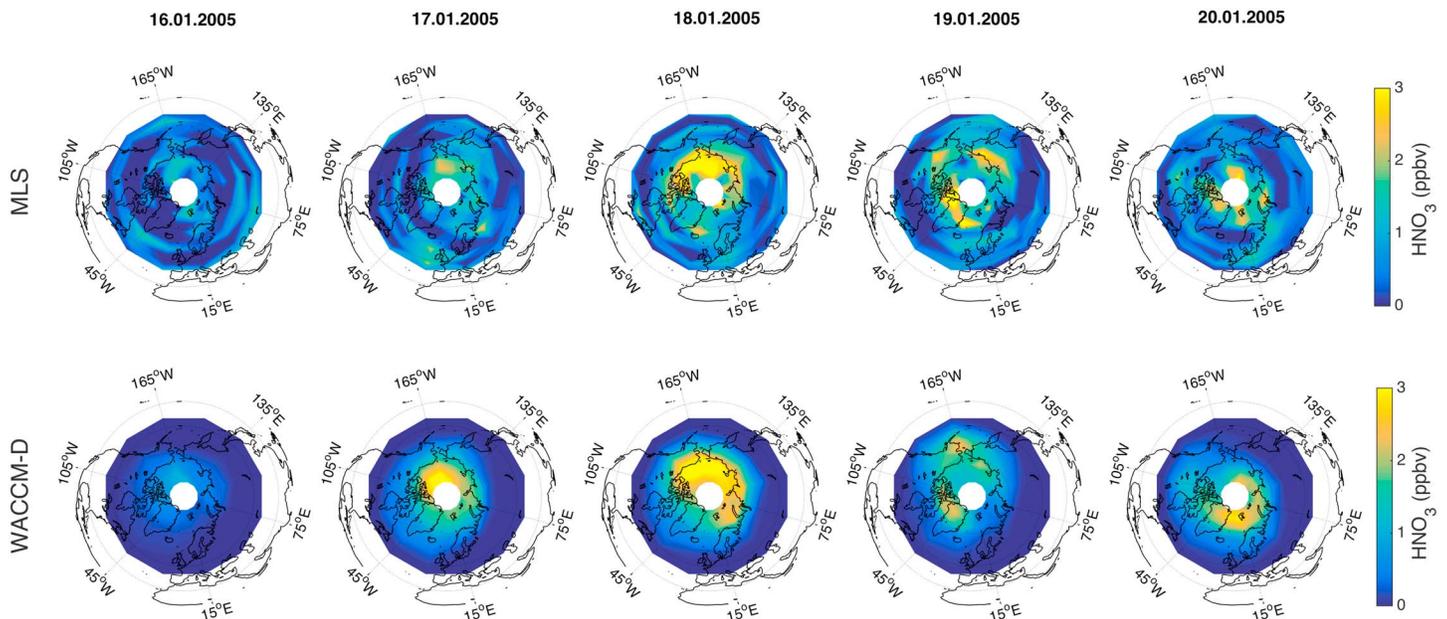
Compared to WACCM, at 60–85 km WACCM-D predicts more  $\text{NO}_x$  between days 16 and 50 (Figure 6d), caused by larger  $\text{NO}_x$  production during the SPE. As shown by *Nieder et al.* [2014], the standard parameterization used in WACCM (and many other models) underestimates  $\text{NO}_x$  production at altitudes above 65 km. This is confirmed by the differences in  $\text{NO}_x$  production between WACCM and WACCM-D: compared to the altitude-independent production of 1.25 N atoms per ion pair in WACCM, in WACCM-D the production increase with altitude reaching 2 and 2.5 N atoms per ion pair at 80 km and 100 km, respectively (not shown). These numbers are also about 50% higher than those presented by *Nieder et al.* [2014], mostly due to enhanced production from  $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$  which subsequently leads to more production from  $\text{NO}^+ + \text{e}^- \rightarrow 0.2\text{N}(^4\text{S}) + 0.8\text{N}(^2\text{D}) + \text{O}$  as well. Note that the former reaction produces NO directly, instead of N, and was not considered in their model by *Nieder et al.* [2014]. The difference in  $\text{NO}_x$  production is not caused by the temperature difference (which is small, only about 3 K or 2% between the models, not shown), and not



**Figure 7.** Daily averaged  $\text{HNO}_3$  mixing ratio (ppbv) from (a) Aura MLS measurements and model predictions from (b) WACCM and (c) WACCM-D for the  $60\text{--}82.5^\circ\text{N}$  band and for the period 14–28 January 2005. The contour intervals are: 0.2, 0.4, 0.6, 1, 1.4, 1.8, 2.6, and 3.6 ppbv. MLS data uncertainty ( $2 \times \text{SEM}$ ) varies between 0.01 and 0.15 ppbv (10–20%).

likely by the difference in atomic oxygen (up to 35% difference, not shown) because the  $\text{NO}_x$  production is not sensitive to O below about 85 km [Nieder *et al.*, 2014]. The large differences below 70 km, after the SPE, are caused by  $\text{NO}_x$  descent from above.

Atmospheric models using an EPP lookup table parametrization, such as WACCM, significantly underestimate  $\text{HNO}_3$  values during SPEs when compared to observations [Jackman *et al.*, 2008; Funke *et al.*, 2011]. In WACCM-D,  $\text{HNO}_3$  is directly produced by ion-ion recombination reactions (as described in Verronen and Lehmann [2013]). As an example of the WACCM-D evaluation, Figure 7 shows daily averaged MLS  $\text{HNO}_3$  (Figure 7a) together with the WACCM and WACCM-D predictions (Figures 7b and 7c, respectively) for the latitudes  $60\text{--}82.5^\circ\text{N}$ . During the SPE, significant enhancement of MLS  $\text{HNO}_3$  was observed at altitudes between about 40 and 75 km. Elevated  $\text{HNO}_3$  values (0.6–1.8 ppbv) lasted for about 10 days (16–24 of January) with the maximum increases on 17 and 21 January, when the proton fluxes were high. For comparison, the  $\text{HNO}_3$  values predicted by WACCM are almost 100 times lower (0.03–0.04 ppbv) than those seen from satellite observations. In contrary, WACCM-D and its ion chemistry are able to reproduce the observed changes in  $\text{HNO}_3$ . The SPE effects predicted by WACCM-D, i.e., the magnitude of the observed  $\text{HNO}_3$  changes (0.6–2.5 ppbv), duration of the enhancement ( $\sim 10$  days) as well as affected altitudes (40–75 km), are all in good agreement with observations (within data uncertainty). Note that because the mesospheric production of  $\text{HNO}_3$  is

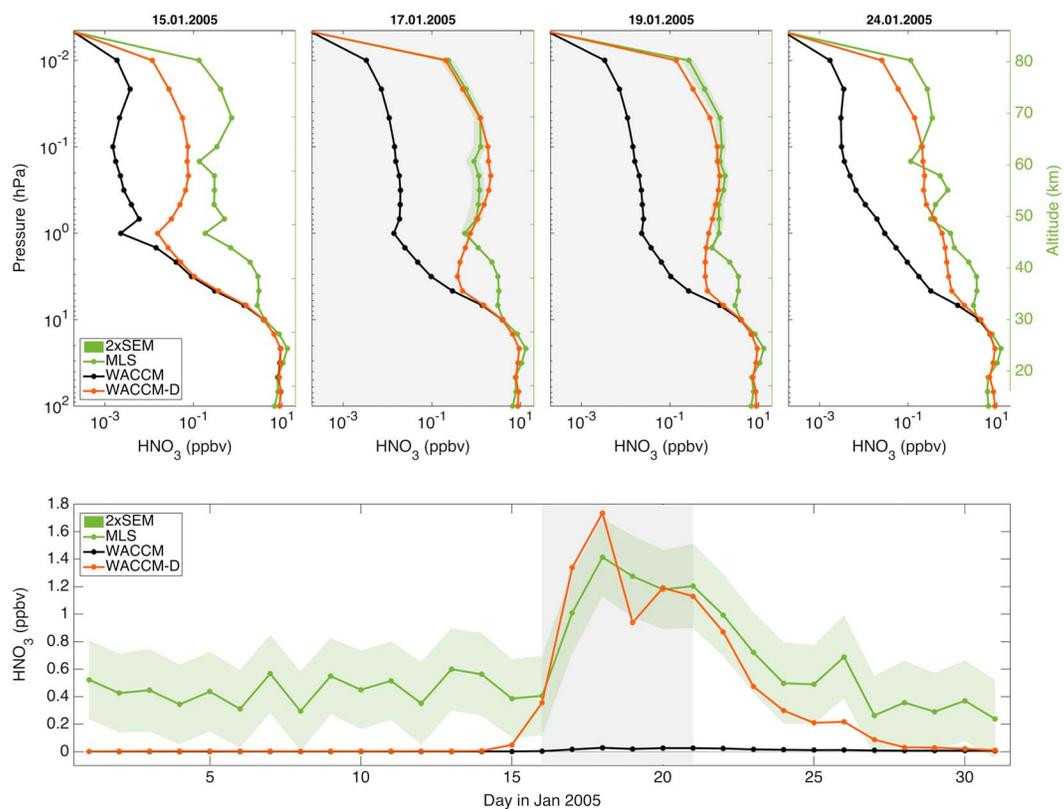


**Figure 8.** Polar maps of daily averaged  $\text{HNO}_3$  mixing ratio (ppbv) from (top row) Aura MLS measurements and model predictions from (bottom row) WACCM-D averaged between 45 and 80 km altitude during the SPE between 16 and 20 January 2005. For clarity, measurements are shown in the latitude range 40–82.5°N. MLS data uncertainty ( $2 \times \text{SEM}$ ) varies between 0.5 and 1 ppbv.

dominated by ion chemistry during large EPP events, measurements of  $\text{HNO}_3$  changes are also a direct indicator of the EPP ion pair production rates such that they can be used as a proxy for the EPP fluxes. In the present case, the reasonably good agreement between WACCM-D and MLS gives confidence in the SPE fluxes used in the model.

This agreement between WACCM-D and the satellite observations of  $\text{HNO}_3$  can be seen throughout the whole SPE in Figure 8. It illustrates a comparison between the observed and predicted polar maps of mixing ratios averaged between 45 and 80 km for the period 16–20 January. Around the SPE peak (17–18 of January), WACCM-D  $\text{HNO}_3$  values are overestimated, but the differences with MLS are small. Overall, the  $\text{HNO}_3$  distribution over the polar cap and the magnitude of the  $\text{HNO}_3$  changes during the SPE are similar in the WACCM-D results and the observations. As already noted by *Verronen et al.* [2011], the observed  $\text{HNO}_3$  enhancements show inhomogeneous longitudinal distribution, with a clear day-to-day variation due to atmospheric dynamics. Figure 8 shows that WACCM-D is reproducing this longitudinal variability reasonably well. Note that for reasons of clarity, the WACCM results are not shown in the figure, as the  $\text{HNO}_3$  changes are negligible.

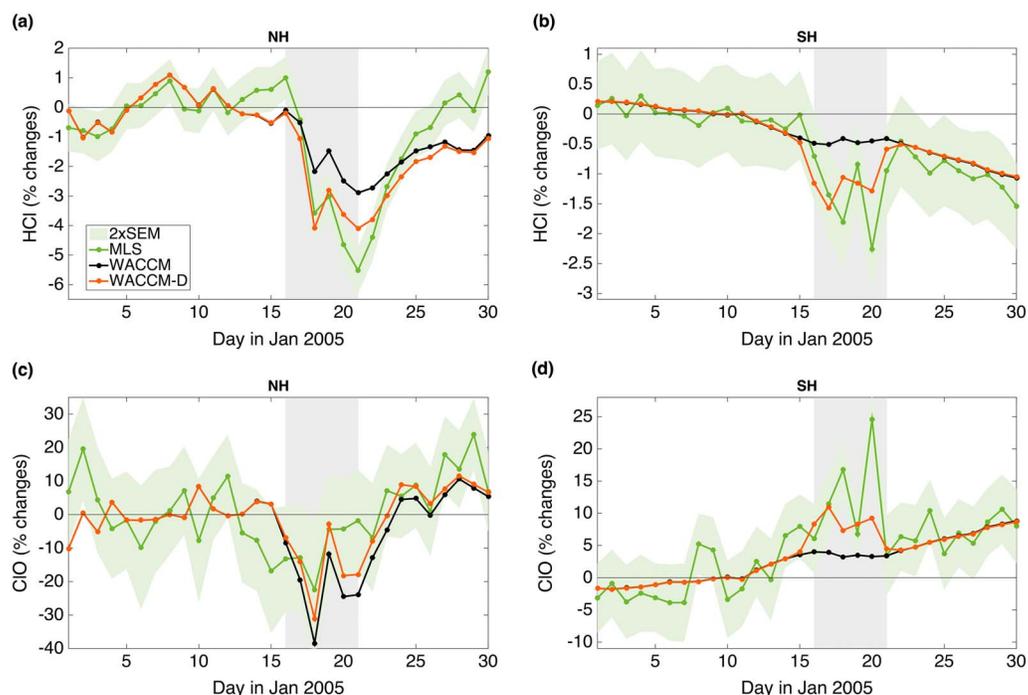
In general, the differences between observed and predicted  $\text{HNO}_3$  vary with altitude and ionization levels. To demonstrate this dependency, daily averaged  $\text{HNO}_3$  profiles from MLS measurements and model predictions from WACCM and WACCM-D for the 60–82.5°N are shown in Figure 9 (top row). It is clear that the best agreement between WACCM-D and the MLS measurements coincides with the highest ionization levels (around 17–19 January) and two altitude ranges: 45–85 and 15–35 km. In the absence of strong proton ionization, the differences are larger (e.g., on 15 and 24 January). This can also be seen in Figure 9 (bottom row), which shows the daily mean  $\text{HNO}_3$  averaged between 45 and 80 km in January 2005. WACCM-D reproduces the enhancement in  $\text{HNO}_3$  around the SPE period quite well (15–27 January), and the differences are within the standard error of the mean. During the quiet time conditions (no SPE ionization), the  $\text{HNO}_3$  levels are too low compared to the MLS observations. Again, this is likely due to the omission of medium energy electron ionization in the WACCM-D model. Part of the observed  $\text{HNO}_3$  variation at the beginning of January could be connected to the EEP event that occurred between 2 and 7 January. In comparison to WACCM-D, WACCM is unable to reproduce any changes seen in  $\text{HNO}_3$  and the values are substantially underestimated during the whole period under consideration. Note that at around 35–45 km both models underestimate the



**Figure 9.** (top row) Daily averaged  $\text{HNO}_3$  profiles (ppbv) from Aura MLS measurements and model predictions from WACCM and WACCM-D for the 60–82.5°N band for four selected days: 15 of January (before SPE event), 17 and 19 of January (during SPE event), and 24 of January (after SPE event). (bottom row) Daily averaged  $\text{HNO}_3$  mixing ratio (ppbv) from Aura MLS measurements together with model predictions from WACCM and WACCM-D for the 60–82.5°N band and altitudes between 45 and 80 km. SPE days are marked as a grey area. Green area indicates MLS data uncertainty ( $2 \times \text{SEM}$ ).

measured  $\text{HNO}_3$ . This is explained by previous studies, which have shown that WACCM fails to reproduce the polar  $\text{HNO}_3$  enhancements reaching the stratopause due to a low bias in the climatological distribution of  $\text{N}_2\text{O}_5$  in the upper stratosphere [Kvissel *et al.*, 2012].

Finally, we test the capabilities of WACCM-D to reproduce the changes in chlorine species, particularly hydrogen chloride (HCl) and chlorine monoxide (ClO) which play an important role in the  $\text{Cl}_y$  family. HCl is an important reservoir of active chlorine and has been shown to respond to SPEs, partly because chlorine ion chemistry converts it to Cl, ClO, and HClO [Winkler *et al.*, 2009]. Previously, the impact of the January 2005 SPE on the chlorine family has been studied in detail by Damiani *et al.* [2012] using satellite measurements and model simulations. They found that mixing ratios of both HCl and ClO decreased in the NH during the event. Comparing WACCM-D with WACCM and the MLS observations, Figure 10 shows daily averaged anomalies of HCl and ClO for the latitudinal band 60–82.5° in the NH and SH, at altitudes between 40 and 52 km. During the SPE, satellite observations and model results show a rapid HCl decrease of about 2–6% in both hemispheres due to uptake into negative ions ( $\text{Cl}^-$ ,  $\text{Cl}^-(\text{H}_2\text{O})$ ,  $\text{ClO}^-$ , and  $\text{NO}_3^-(\text{HCl})$ ), starting from 16 of January. WACCM-D agrees better with the MLS HCl measurements and is able to reproduce the loss of about 4% and 1.6% in the NH and SH, respectively, during the SPE. WACCM underestimates the HCl decrease compared to MLS, especially in the SH where no response to the SPE is seen. The improvement from WACCM to WACCM-D is due to the ion chemistry converting HCl to other chlorine species. This is seen also in ClO, with WACCM-D producing a clear increase of about 10% in the SH and less decrease in the NH compared to WACCM, which leads to better agreement with the MLS observations. In the NH, the decrease of HCl and increase of ClO due to ion chemistry are only part of the change in these species (the part indicated by the difference between WACCM-D and WACCM), with a decrease of ClO beginning already a few days before the SPE in the MLS observations.



**Figure 10.** Daily averaged (a, b) HCl and (c, d) ClO anomalies (%) from Aura MLS measurements and model predictions from WACCM and WACCM-D for the 60–82.5°N (Figures 10a and 10c) and 60–82.5°S (Figures 10b and 10d) band and altitudes between about 40 and 50 km. An observed/predicted HCl/ClO profile for the period 1–14 January 2005 was subtracted from the observed/predicted HCl/ClO values for the plotted days (1–30 January 2005). SPE days are marked as a grey area. Green area indicates standard error of the mean (SEM). Green area indicates MLS data uncertainty ( $2 \times$  SEM).

## 5. Summary

WACCM-D is a variant of the Whole Atmosphere Community Climate Model, including a selected set of  $D$  region ion chemistry. Here we have evaluated WACCM-D capabilities by examining its ability to reproduce the atmospheric effects of the January 2005 solar proton event. We have validated the WACCM-D results against Aura/MLS and SCISAT/ACE-FTS satellite observations and compared the WACCM-D results to those from standard WACCM (including no  $D$  region ion chemistry). The results indicate that including an ion chemistry scheme in the atmospheric models can improve the EPP response of important neutral species.

The most pronounced improvement is in the modeling of  $\text{HNO}_3$ , which is produced during SPEs mostly by ion-ion recombination reactions. Northern Hemispheric  $\text{HNO}_3$  values above 45 km from WACCM-D are almost 100 times higher (0.6–2.6 ppmv) than those from WACCM (0.03–0.04 ppbv). Compared to MLS observations, WACCM-D was able to reproduce not only the magnitude of the observed  $\text{HNO}_3$  changes but also the altitude distribution of the SPE-driven enhancement. The generally good agreement between WACCM-D and satellite observations (within MLS data uncertainty at most altitudes between 45 and 80 km) can be seen throughout the SPE period. Outside the SPE period and below 45 km, there is still an underestimation of  $\text{HNO}_3$  in WACCM-D.

Ion chemistry affects also the chlorine species. Compared to MLS observations, WACCM-D ion chemistry improves the modeling of HCl and ClO. The improvement is most pronounced in the SH at 40–50 km where WACCM-D predicts a decrease of HCl and an increase of ClO by 1.6% and 10%, respectively, in general agreement with MLS observations. WACCM, without  $D$  region ion chemistry, does not predict any SPE-related changes in the SH.

WACCM-D simulated OH enhancement was compared to the MLS OH observations and found to be in better agreement than predictions from WACCM. During the SPE, mean OH values at altitudes 70–76 km are within the data uncertainty. Both WACCM and WACCM-D predictions show quantitatively similar  $\text{O}_3$  depletion, which agree well with the observed MLS  $\text{O}_3$ .

In the case of  $\text{NO}_x$ , the WACCM and WACCM-D simulations generally reproduce well the production below 70 km during the SPE. At 70–85 km, WACCM-D produces up to 130% more compared to WACCM which leads to better agreement with ACE-FTS observations. However, at these altitudes the  $\text{NO}_x$  values from both WACCM and WACCM-D are substantially smaller than ACE measurements. Underestimation of  $\text{NO}_x$  in WACCM and WACCM-D can be partially connected to the fact that the electron precipitation event in early January is not considered in the model experiments.

Although the short-term ozone response does not change much, we must emphasize that there is evidence of longer-term impact of ion chemistry on  $\text{NO}_x$  and ozone [Kvissel *et al.*, 2012] which cannot be modeled with the ion chemistry parametrization used in WACCM. During polar winter,  $\text{NO}_x$  produced by EPP in the MLT region descends to lower altitudes [e.g., Seppälä *et al.*, 2007; Randall *et al.*, 2009; Salmi *et al.*, 2011; Funke *et al.*, 2014]. Observations have shown that, gradually over the winter, the descending  $\text{NO}_x$  can be converted first to  $\text{N}_2\text{O}_5$  and then to  $\text{HNO}_3$  by cluster ion reactions, which can lead to modulation of stratospheric ozone and polar vortex dynamics in model simulations [Kvissel *et al.*, 2012, and references therein]. Since ozone is the most likely connector between EPP, atmospheric dynamics, and climate variability, it is thus important to describe ion chemistry adequately in models. Although in this paper we only consider the short-term effects of EPP, to validate the WACCM-D ion chemistry, the longer-term impacts of ion chemistry will be the topic of a future study.

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