Author's Response to Reviews of impact of chlorine ion chemistry on ozone loss in the middle atmosphere during very large solar proton events

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Answer to Referee 1

Dear referee,

Thank you for your thorough review of our work and the numerous comments. Here are our responses to your comments below.

5   – Major changes include: A comprehensive revision of the text concerning recent publications on ion-chemistry and chlorine species and revision of the abstract and summary. The figures are re-evaluated. Research implications and recommendations are also added in the conclusions.

    – The comments are numbered and in bold and each of them is followed by a response from the authors.

Yours sincerely and on behalf of all co-authors,

10   Monali Borthakur

1 Detailed Remarks:

1.1 L 91-92: "The chlorine negative ion is the most important ion of the lower D region during day and night time." I don't think this is true. In the winter polar region, large amounts of NO_x and lower level of dissociating solar radiation contribute to creation of NO_3^- and its clusters, for example. For daytime and at lower latitudes, 15   chlorine ions are abundant in the mesosphere but not dominant, I would say. The Authors could actually check this easily from their model results.

The composition and dominance of ions in different regions of the ionosphere vary depending on several factors, including altitude, latitude, time of day, and season. While chlorine ions can be present and play a role in the mesosphere, they are not typically considered the most important ions in the lower D region during both day and night. So, you are right and we

20 restructured the sentence to "The chlorine negative ion is an abundant ion of the lower D region during day and night time" in the revised manuscript.

1.2 L 170: "The ion-chemistry is based on the UBIC (University of Bremen ion-chemistry) model developed by Winkler et al. (2009) for the terrestrial middle atmosphere." The Authors could briefly describe the main development and changes between UBIC and Exotic, if any.

25 UBIC (University of Bremen Ion-Chemistry model) is a model developed by the University of Bremen to simulate ion-chemistry processes in Earth's atmosphere. The UBIC model as described by Winkler et al. (2009) simulates the time evolution of 137 species, 55 positive, 49 negative and 33 neutral species and computes more than 600 reactions. ExoTIC (Exoplanetary Terrestrial Ion-chemistry) builds upon the foundations of UBIC but is extended to study the ion-chemistry of exoplanetary atmospheres with a wide range of orbital parameters, stellar systems and base compositions as discussed by Herbst et al 2019.

30 In the ion-chemistry part of ExoTIC, we have added more neutral species compared to what was present in Winkler et al 2009. Some details have been added to the revised manuscript.

1.3 Section 3.1. There are indeed methods for estimation of the polar vortex edge vortex from the gradient of daily CO mixing ratio (e.g. Harvey et al. 2018, https://doi.org/10.1029/2018JD028815). Also, Funke (2005) and the gradient method is mentioned by the Authors, so why use a fixed CO mixing ratio? Also, CO is good for the

35 mesosphere but the Authors also show a lot of results from the stratosphere where the potential vorticity would be a better vortex measure, I assume. Please comment on this.

Funke et al. (2005) indeed use a vertically and temporally varying vortex boundary and this was determined from the CO latitudinal gradient. We think it was a mistake to use the Funke et al. (2005) paper as a reference for the method chosen here. Regarding the fixed CO threshold of 0.5 ppmv, a chemical vortex definition (via CO) is widely used in the mesosphere (70

40 km) as also studied by Harvey et al. (2015). And as you pointed out, below in the stratosphere the vortex is indeed commonly defined via the potential vorticity gradient from reanalysis data. Since we are determining the polar vortex in the MIPAS orbit, it is better to use MIPAS data as compared to reanalysis data. That is why we used MIPAS CO both in the stratosphere and the mesosphere and also due to the fact that MIPAS does not provide potential vorticity. We have included details and revised the manuscript accordingly.

1.4 **Figure 5 (and similar figures of MIPAS comparisons). For clarity, I would suggest to remove the model data without-averaging-kernels-applied and harmonize the color scales. Firstly, the x axis is almost unreadable. Secondly, if averaging kernel impact needs to be shown then one good example should do it. Thirdly, changing the color scales makes the plot confusing (at least to me). Finally, it's not necessary to plot the same MIPAS data four times. Maybe it would make sense to plot the difference between the model runs and MIPAS?**

We decided to keep the model calculations without without-averaging-kernels-applied for the following reason: what MIPAS sees, is a distorted picture of the "truth". We apply the same distortion when applying the averaging kernels. If AK-convolved model results and MIPAS observations fit, then the original model results represent the "truth" (at least one of the possible ones). Therefore, not the MIPAS results represent the true distribution of trace gases in the atmosphere, but the original model result. The data plotted here are the differences w.r.t. 26th October 2003, a day before the event. However, we also added the absolute differences between model and MIPAS data in the supplement. In the revised manuscript, the figures are enlarged and we decided to keep the format with MIPAS data along each row because we thought it's better for the comparison of the different sensitivity runs. The color scales are harmonized in the revised version and the x-axis ticks are also enlarged.

1.5 **Figure 5 (and similar figures). It seems to me that plotting the results from the "full ion chemistry" simulation makes no sense because that model setup cannot handle O(1D) properly. The Authors basically admit this and it's something that was already noted by Winkler (2009, and the follow-up correction paper). Therefore, I would suggest to remove all data from the "full ion chemistry" simulation and clarify in the model description why "O(1D) in photo-chemical equilibrium" is necessary and sound approach.**

We removed the full ion-chemistry plots from the main text and put them in a supplement but kept the discussion of the results from full ion-chemistry in the main text. We made some changes in the model description discussing more on "O(1D) in photo-chemical equilibrium" as a necessary and sound approach in Sect. 2.2.1.

1.6 **Figure 5. Why is there a strong peak in HOCL increase at about 35 km in the daytime simulation panels?**

The enhanced HOCl production is due to the increased availability of chlorine atoms due to the catalytic ozone destruction cycle. The strong peak in HOCl increase at about 35 km during daytime is because this altitude represents the optimal conditions for the ClO_x cycle to occur. More details are included in the revised manuscript in Sect 1.3 and Sect 3.2.

1.7 **Figure 6. The data above 50 km could be excluded from the figures because nothing is going on.**

The new figures upto 50 km are included in the revised manuscript.

1.8 Figure 8. Is the modeled ozone data sampled at MIPAS measurement local times? There could be variability with local time in the mesosphere.

We did not sample the modelled ozone data at the MIPAS measurement local times. It is a 1D model and doing that probably makes better sense for a 3D model. Instead we sampled in the solar zenith angle range of MIPAS. To sample the model data at the MIPAS measurement local time, a 3D model is needed. We are in the process of implementing the ion-chemistry into a global 3D chemistry climate model EMAC (ECHAM/MESSy) to test that.

1.9 Figure 9. I don't understand why the parameterised NOx production makes more NOy than the ion chemistry. The parameterization uses a fixed value of 1.25 NOx molecules/ion pair while it was shown by e.g. Nieder et al. (J. Geophys. Res. Space Physics, 119, 2137-2148, doi:10.1002/2013JA019044, 2014) that this number is an underestimation in the upper mesosphere and lower thermosphere. Also, Andersson et al. (J. Geophys. Res. Atmos., 121, 10328–10341, https://doi.org/10.1002/2015JD024173, 2016) and Kalakoski et al. (Atmos. Chem. Phys., 20, 8923-8938, https://doi.org/10.5194/acp-20-8923-2020, 2020) have shown that in the mesosphere, the ion chemistry produces more NOx than the fixed parameterization during SPEs. Please discuss and clarify this issue.

The rate of formation of NO_x=N+NO is higher in the mesosphere if ion-chemistry is used but the ratio between N and NO to the initial formation is more to N and that means that the rate of loss is also faster and one ends up with less NO. It is the absolute numbers of NO that determines if the rate of loss or the rate of formation is larger. Nieder et al. (J. Geophys. Res. Space Physics, 119, 2137-2148, doi:10.1002/2013JA019044, 2014) indeed showed that in terms of mixing ratio that is less. More discussions are added in the revised manuscript and also discussion of results from Andersson et al. (J. Geophys. Res. Atmos., 121, 10328–10341, https://doi.org/10.1002/2015JD024173, 2016) and Kalakoski et al. (Atmos. Chem. Phys., 20, 8923-8938, https://doi.org/10.5194/acp-20-8923-2020, 2020) are included in Section 4.1.

1.10 Figure 10. The ionic HOx production depends on the level of H2O at least in the upper mesosphere, but the parameterised HOx production is calculated with a fixed H2O profile (Andersson et al., J. Geophys. Res. Atmos., 121, 10328–10341, https://doi.org/10.1002/2015JD024173, 2016). Could H2O explain some of the differences between the parameterized-HOx and the other runs?

The way we include the parameterisation is not using that of Andersson et al., J. Geophys. Res. Atmos., 121, 10328–10341, https://doi.org/10.1002/2015JD024173, 2016, but as 2 HO_x, one H and one OH per ion pair. In the upper mesosphere, above 80 km, water vapour is low. So if the ionisation rate is not present, the HO_x will go into pre-event very quickly. The high value of HO_x are only maintained by the continuing destruction of water vapour. So if the water vapour is completely destroyed, then there will be no more HO_x formation and it will break down. This means H_2O does explain some of the differences. Details about the HO_x parameterisation and some explanation have been added to the description of the model in Sect. 2.2.4 and in Sect. 4.1.

1.11 Figure 10. The Authors discuss HOx recovery but I think it's worth to note that the SPE ionization stays at an elevated level for the duration of the simulation, i.e. also after the peak on day 302, as shown in Figure 1. Therefore, the recovery is only partial as EPP-HOx production continues albeit with a lower rate.

For figure 10, we have applied the mean ionisation rate of October 28/29 for day 301 (just one profile), i.e. those shown in Figure 1 (right). Nevertheless, even after the ionisation/event stops, the recovery of HOx is indeed partial.

1.12 L 458: "due to the same" => due to the chlorine ion chemistry

We replaced "due to the same" to "due to the chlorine ion chemistry" in the revised manuscript.

1.13 Figure 11. Also Andersson et al. (J. Geophys. Res. Atmos., 121, 10328–10341, https://doi.org/10.1002/2015JD024173, 2016) have previously reported a HCl decrease from ion chemistry between 40 and 50 km in during an SPE. However, the Authors show here that a quite similar decrease is seen below 50 km even without ion chemistry. Also, the decrease at 40-50 km seems to be much larger than what was reported by Andersson et al. Perhaps the Authors can briefly discuss this matter.

In Figure 11, the ion-chemistry shows an HCl decrease of around 10-15 % at 40-50 km for the Halloween SPE of 2003 which is indeed larger compared to what is reported by Andersson et al. (2016). Below 50 km, a 5-10 % decrease is observed even without ion-chemistry. A figure for the relative changes of HCl for the different sensitivity runs w.r.t. the reference run is included in the supplement (figure 16) to the revised manuscript. Further discussions are added in Sect. 4.2.

1.14 Figures 12,13,14. It seems to me that the extended ClO decrease below 50 km seen in the EXT run is balanced by increase and buildup of ClONO2, not HOCl. Could it be that NOx plays a more important role at these altitudes than HOx?

You are right. NOx does play a more important role than HOx below 50 km. We have revised and corrected the explanations.

1.15 Figure 17. "NO is quite long lived down at 40 km altitude and below so the ozone loss due to the NO catalytic cycle seems to be persistent." Based on the figure, it looks more like "at 60 km and below".

We changed from "40 km altitude and below" to "60 km altitude and below" in the sentence which seems to be the case.

1.16 Figure 17. It could be useful the extend the altitude range upwards to fully see the ozone depletion region.

The figures are updated with extended altitude region in the revised manuscript.

1.17   Line 503: "ozone depletion which stays on and produces a diurnal cycle as seen from the Figure 17." The diurnal variability of ozone depletion has previously been discussed by, e.g., Verronen et al. (J. Geophys. Res., 110, A09S32, https://doi.org/10.1029/2004JA010932, 2005).

The diurnal variation of HO_x/NO_x related ozone depletion during solar proton events have been reported by Aikin and Smith (1999) as well as in Verronen et al. (2005). Discussion from Verronen et al. (2005) who studied the diurnal cycle of ozone loss during the Halloween SPE using the Sodankylä Ion Chemistry Model (SIC) and Rohen et al. (2005) who studied it using SCHIAMACHY observations have been included. We have also included details about the differences of the magnitude of depletion with respect to the diurnal cycle and altitude in Sect. 4.3.

1.18   Line 504: "continuing ozone loss in the middle and upper stratosphere, after the event stops, is found to be still 80-100% for the extreme scenario". Based on the figure, I would say it's 60-80%. I think a brief discussion on this would be needed because ozone changes quite a lot compared the the impact calculated, e.g., for the Carrington event. See, e.g., Calisto et al. (Environ. Res. Lett. 8 (2013) https://doi.org/10.1088/1748-9326/8/4/045010), Rodger et al. (J. Geophys. Res., 113, D23302, https://doi.org/10.1029/2008JD010702, 2008).

The ozone loss during the event is 80-100% whereas the continuing ozone loss is indeed around 60-80%. Significant ozone variations that can occur during extreme space weather events are discussed by Calisto et al. (2013) and Rodger et al (2008). They investigated the Carrington event of August/September 1859 using SOCOL 3D model and SIC model respectively. They found that SPEs can cause localized ozone depletion in the polar regions, primarily through the production of NOx and HOx. Discussions related to these studies have been added in Sect. 4.3.

1.19   Figure 18: I don't quite see any use for this figure. There is no comparison to observations, so what advantage is gained from averaging the model data for day-time and night-time? I would suggest to remove Figure 18.

Figure 18 is one of the main result to assess the impact of chlorine ions on ozone loss calculated from the model after its validation. Since we applied temporal ionisation rates for the MIPAS comparison using the Halloween SPE, we wanted to check the contribution of the included chlorine ion-chemistry for the sensitivity run that compared best with MIPAS observations. That would be the run "ion-chemistry with $O(^1D)$ in photo-chemical equilibrium". It is not possible to calculate that from the observations. We decided to keep figure 18.

1.20 **Figure 19: "A very small impact of the chlorine ions around 10-20 % is observed on the event day." I would not call a 10-20% impact small. Also there should be an explanation why the EXT run shows no impact from chlorine ion chemistry at 70-75 km while the other run does. I suspect it would better to use the same control run as the reference for all runs when calculating ozone depletion percentages, and then compare those numbers. Otherwise some of the differences shown could be simply from using different references.**

We restructured the sentence and removed the words "very small". Regarding why the extreme run shows no impact from chlorine ion chemistry at 70-75 km while the other run does, we think it is mainly to do with the ClO response to the SPEs. Comparing the ClO for both the events, more discussion on this has been added to Sect. 5. Regarding the usage of the same control run as the reference for all runs when calculating ozone depletion percentages, that is something we did for Figure 17. Figure 19 was however to assess the impact of the included chlorine ions in the ion-chemistry model on the ozone loss for the two events. Due to this reason, we calculated the percentage difference of the model run, ion-chemistry with $O(^1D)$ in photo-chemical equilibrium (with chlorine ion-chemistry included) w.r.t. the same model run when chlorine ion-chemistry is switched off.

1.21 **Figure 19. Kalakoski et al. (Atmos. Chem. Phys., 20, 8923-8938, https://doi.org/10.5194/acp-20-8923-2020, 2020) have reported stronger ozone depletion around 60 km when D-region ion chemistry is included. The results presented here seem to agree qualitatively, particularly in the EXT case. Perhaps a brief comment on this can be added.**

Kalakoski et al. (2020) studied ozone depletion during SPEs in both the hemispheres with WACCM-D. They found the ozone depletion to be larger for about 5 days after the onset of the SPE at around 0.5-1 hPa. Both the duration and altitude range of this extra ozone loss correspond to enhanced Cl_x. Some details on this are added to Sect. 5.