

# 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 2:

Dear referee,

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

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- 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 Major Comments

**1.1 Figures 5-8: The panels are far too small, the font is too small, the changing colour scale in each column makes comparisons extremely difficult, and the contour intervals are impossible to read in the figures (please add interval to caption). When using set contour intervals, I recommend also using set intervals in the colourbar.**

15 **Please don't change the colour scale between the vertical panels.**

We enlarged the figure panels and the fonts and also put the same colour scale for the vertical panels. We added the colour intervals to the caption. As part of our response to referee 1, we decided to remove the plots for full ion-chemistry for figures 5-8 since the ion-chemistry model with O(<sup>1</sup>D) in photo-chemical equilibrium works better with the MIPAS comparison. We

added more discussions on why model with O(<sup>1</sup>D) in photo-chemical equilibrium is better in the model description. However,  
20 we added the full ion-chemistry plots in a supplement to the revised manuscript but kept the discussion of results in the text.

**1.2 Figures 9-15: These figures are easier to read, but why are the full ion chemistry results not shown? Again there contour intervals are not clear here.**

We wanted to mainly show the comparison for the sensitivity studies that matched best with the MIPAS observations. But keep  
the discussion of the results from full ion-chemistry model without setting O(<sup>1</sup>D) to photo-chemical equilibrium. We have  
25 included the comparison of full ion-chemistry for the two events along with the other sensitivity studies in the supplement for  
your reference. And we have updated the figures in the revised manuscript.

**1.3 Figure 17 and 19: Why is an interpolated colour scale used here? However, the fontsize in the axis used in these figures is the best of all the many contour panel figures and I encourage you to implement this in the above mentioned figures.**

30 A discrete colour scale is used for these figures in the revised version.

**1.4 All figures from Figure 4 onwards: Please consider the use of “\_” in the figure titles, this does not help the reader.**

“\_” has been removed from all the figure titles in the revised manuscript.

**1.5 1D ion-chemistry modelling of the Halloween event has been done in the past, but these studies (e.g. Verronen, et al (2005), Diurnal variation of ozone depletion during the October – November 2003 solar proton events, J. Geophys. Res., 110, A09S32, doi:10.1029/2004JA010932) were not discussed. The previous studies focused on here were those involving 3D models, with limited or no ion-chemistry. Some discussion on ion-chemistry studies would be relevant to add.**

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The diurnal variation of HO<sub>x</sub>/NO<sub>x</sub> as well as ozone depletion increase during solar proton events have been reported in Verronen et al. (2005). We have included discussions from the same and also details about the differences of the magnitude of  
40 depletion with respect to the diurnal cycle and altitude in Sect. 4.3. Regarding ion-chemistry studies, discussions were added,  
for example, from Kalakoski et al. (2020), also as a part of our response to referee 1.

**1.6 Overall references should be added to where previous work is discussed. For example where in the text you discuss “Recent studies...” you need to actually include the references. One such example is the sentence on lines 39-40.**

45 We have added a couple of references overall throughout the different sections. In particular for this line 39-40, the reference Verronen et al. (2005) has been added.

## 2 Minor Comments/typos

### 2.1 Pay attention to use of “Figure” and “figure” throughout the text.

Only "figure" is used in the revised text except if it's at the beginning of a sentence.

- 50 **2.2 There are several mentions of “significant” as a measure in the text. What do you mean by significant, did you use some measure for this? For example in section 3.2 you talk about “significant low values”, you probably mean clearly low values etc.**

In section 3.2, using “significant low values” for HOCl daytime was meant as a measure against MIPAS observations, as in "significantly low values compared to what MIPAS observed". However, we replaced it with "much lower values were  
55 observed...compared to MIPAS observations" here. And removed the word "significant" in some other places, for example, line 320, caption in figure 5 and line 438. However, for example, in line 502, it means noteworthy ozone depletion even though the event stops. So we didn't remove it there and some other places concerning ozone depletion.

### 2.3 “Earth” (the planet) always starts with a capital letter.

In the new version, we have used "Earth" everywhere in the text.

- 60 **2.4 67.5°N. There should not be a space after the number and before the degree sign, or between the degree sign and N/S.**

The space after the number and before the degree sign has been removed in 67.5°N.

### 2.5 Check where you need to use comma before the word “which”.

We checked that and revised accordingly.

- 65 **2.6 Abstract: Last sentence: This currently reads as there was only 10/20% ozone loss and it was all due to chlorine chemistry. I know you mean that you specifically found that the inclusion of chlorine ion chemistry ADDED 10/20% to the ozone loss, so this sentence should be revised.**

That is true. In figure 19, for the Halloween SPE and the extreme event, we calculated the additional ozone loss that was due to the already present chlorine ion-chemistry in the ion-chemistry model. We basically switched it off to assess that. The sentence  
70 has been restructured in the abstract accordingly.

### 2.7 Line 33: “..and HEAVIER nuclei”

We included the word "HEAVIER" in this sentence.

**2.8 Introduction: SPEs are currently defined to mean Solar Particle Event and well as Solar Proton Event. In your case you I think you only mean the latter.**

75 In this case, we are mainly considering solar proton events. So yes, SPEs stand for that.

**2.9 Can you comment on observed amounts of chlorine ions in the mesosphere? For example, how do we know that Cl<sup>-</sup> and Cl-(H<sub>2</sub>O) are the most abundant?**

Few older studies of chlorine ion-chemistry of the D-region like Turco (1977), Chakrabarty and Ganguly (1989) and Kopp and Fritzenwallner (1997) indicate that Cl<sup>-</sup> and Cl-(H<sub>2</sub>O) are the most abundant chlorine anions in the mesosphere for both  
80 night-time and daytime conditions. Some further explanations are also provided by Holger Winkler, Justus Notholt (2013). We included more details and revised the introduction.

**2.10 Line 106: Shanklin (1985), remove the full stop after Shanklin and before bracket.**

The full stop after Shanklin and before bracket was removed.

**2.11 Lines 125-126: This sentence needs to be rearranged to that the three statements are in correct order: circumpolar cyclone, formed due to solar insolation, dominates circulation (rather than circulation, use dynamics).**

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We have re-arranged the sentence in the revised manuscript accordingly.

**2.12 Line 185: Space before the reference.**

We have added that.

**2.13 Section 2.2.2 and conclusions: So why is the rate of O(1D) too large and how would you assure this was not an issue if the ion chemistry was applied to a climate model? That is, can you offer a working solution from the results of this paper which you could state in the conclusions?**

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In the ExoTIC model, the ions are brought into photo-chemical equilibrium. And for the neutrals, the rate of formation is then calculated from the ion-chemistry. The neutrals in the ion-chemistry are long lived with the exception of N(<sup>2</sup>D) and O(<sup>1</sup>D).  
95 N(<sup>2</sup>D) is treated like one of the ions, so it is not transferred to the neutral chemistry but is brought into equilibrium. O(<sup>1</sup>D) however is not brought into equilibrium and hence the rate of formation is large. So if O(<sup>1</sup>D) is put into equilibrium, it is definitely formed in the ion-chemistry and then the rate of formation is zero. For a climate model, at least in the chemistry climate model EMAC, the ion-chemistry is part of the normal chemistry solver and in that case, the O(<sup>1</sup>D) formation rate should be not too large. So the ion-chemistry implementation should work without doing anything to O(<sup>1</sup>D). We have revised  
100 the "conclusions" section and discussed some implications and future work.

**2.14 Averaging kernels: The text uses both A and AK, figures use AK. Please change these so that the use is consistent.**

We have changed it to A everywhere in the text and figures.

105 **2.15 Section 3: Using the averaging kernels: Do you mean that the model is first sampled only at MIPAS altitude grid locations, then averaging kernels are applied. This just need a clarification in the text where currently it's a bit mixed up. Same section, you need a reference here for the MIPAS tracer aspects.**

Yes, the model is first sampled only at the MIPAS altitude grid locations and then averaging kernels are applied. We have clarified that in the text. The references for the MIPAS tracer aspects are present in Sect. 2.3. But we have also added them in Sect. 3.

110 **2.16 Page 13: numbered point 1. What do you mean by this? numbered point 2. degrees North. numbered point 3. What do you mean by the model temperature profile being fixed? Fixed the whole time?**

Numbered point 1: It means we selected the model profiles from the entire time series, one at a time. Numbered point 2: Yes that is correct. 57.5 to 77.5 degrees North. Numbered point 3: The model temperature profile is fixed for the entire time series. It doesn't change with time. In the revised version, we did some rewording.

115 **2.17 Section 3.1. Lines 294-295: This needs rearranging or clarifying.**

We restructured the sentence and also added more details on why CO was used as a tracer of vortex air.

**2.18 Section 3.1. Later you talk about latitude bands relating to vortex edge and deep in the vortex, but you never actually define these regions. Please add the relevant information and how these were determined here.**

120 We defined the regions "edge of the vortex" as 57-77N and "deep in the vortex" as 70-90N. The boundary of the "edge of the vortex" was determined using a fixed threshold of CO that was 0.5 ppm. More discussion is added in the revised manuscript in Sect. 3.1 explaining how we determined the vortex boundary where we also defined these regions.

**2.19 Section 3.2. Line 310: Initially, MIPAS looks to be much higher. However, this is a good example where the current figure is difficult to read with the changing colour scale and multiple panels. After careful examination the statement in the text is probably correct, but you need to clarify the figures.**

125 Line 310: With full ion-chemistry, the original model results are much higher compared to MIPAS for both day and night. But for the other three sensitivity runs, for daytime, MIPAS is higher and for night-time, model shows higher values. We have updated the figures keeping the same color scale for the vertical panels and also added the colorbar intervals in the figure captions.

**2.20 Section 3.2. Line 315-316: I don't see this removal of a peak in the figure.**

130 The word 'peak' is probably not right to use here. What we meant was that there was excess HOCl observed in the mesosphere around 60 km for the night-time plots with ion-chemistry considering O(<sup>1</sup>D) in photo-chemical equilibrium. This excess value just disappears when the chlorine ion-chemistry is switched off. We have removed the word 'peak' and restructured the sentence.

**2.21 Section 3.3: I do not understand where the 57N-77N = "vortex edge" and 70N-90N = "deep in the vortex" comes from. This is something you need to clarify in the earlier section according to my previous comment. The overlapping latitudes are particularly strange here.**

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As you pointed out before, we have clarified this in the revised version in Sect. 3.3. The latitude bands do overlap but we defined the regions "vortex edge" and "deep in the vortex" based on the experiments conducted with different samplings of the latitude bands for the zonal averages. This was done as an attempt to check which sampling works better for the different chemical species. For HOCl and ClONO<sub>2</sub>, using a sampling of 57-77N showed better agreements with the model results with averaging kernels applied, whereas for ozone 70-90N worked better.

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**2.22 Lines 387-388: Where does this arise from? Adding a reference could be sufficient.**

We added some references for this in the revised version, for example, Funke et al. 2011, <https://doi.org/10.5194/acp-11-9089-2011>.

**2.23 Lines 395-396: You need to include references here.**

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We have added a citation Meraner et al. 2018, <https://doi.org/10.5194/acp-18-1079-2018> in this sentence.

**2.24 Lines 401-402: Does this information come from examination of the reaction rates, or from a reference (not included)?**

The loss in the mesosphere being related to HOx catalytic cycle is taken from references, Funke et al. (2011) and Bates and Nicolet et al. (1950).

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**2.25 Lines 410-412: Why do you expect the AISstorm ionisation rates being different to real ones for the event? Particularly the precipitating proton fluxes are were well known for the Halloween event.**

The proton fluxes for the Halloween event are known from different satellites indeed, for example, GOES 10 and GOES 11. However, AISstorm here uses GOES 10 and the ionisation rates should be a lower estimate. The SPE ionization is already happening in the denser atmosphere, therefore the conversion from particle fluxes into ionization should be more or less precise in terms of total ionization and altitude. The main uncertainty of SPE ionization in AISstorm is the size of the area that is affected by high energetic particle precipitation. This cannot be derived from these channels but is taken from a lower energy

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channel on another satellite and thus it might be an underestimate of the polar cap size. However if that would be important for the spatial average 70-90N, we should see an underestimation of the ionization (and NO<sub>y</sub>) as well, which doesn't seem to be the case (and which is unlikely anyway as the equatorward boundary should be at about 60N).

**2.26 Section 4. What latitude is modelled here?**

It is the same latitude of 67.5N as in the previous section.

**2.27 Why are both NO<sub>y</sub> and HO<sub>x</sub> defined different to previous sections of the paper for this comparison? Why not use the same definition (the initial ones) throughout? Seems like the macron was added to NO<sub>y</sub> to distinguish it from the previous definition, but the same was not done for HO<sub>x</sub>?**

NO<sub>y</sub> was indeed defined using a macron in this section as  $\tilde{\text{NO}}_y$  because we wanted to add N and NO<sub>3</sub> to  $\tilde{\text{NO}}_y$  for the Halloween SPE and extreme event comparison. Since MIPAS doesn't measure these species of N and NO<sub>3</sub>, we used a different definition of NO<sub>y</sub> in the previous section. HO<sub>x</sub> studies are mainly shown in section 4 and wasn't calculated for section 3 due to the same reason as H and OH not being provided by MIPAS.

**2.28 Lines 445-446: The results for the full ion-chemistry model results are not shown so we can't see where this comparison result comes from.**

We didn't include the full ion-chemistry results because we wanted to mainly show the sensitivity studies that compared best to the MIPAS observations. But discussions of the full ion-chemistry results are included in the text. We added the full ion-chemistry results along with the other sensitivity runs as a comparison in the supplement to the revised manuscript.

**2.29 Lines 463-464: This is repetition of previous sentences, remove.**

This sentence has been removed.

**2.30 Figure 14: Looking at this figure, it would seem that the chlorine ion chemistry is not important for ClONO<sub>2</sub>? Perhaps you can comment in the text?**

The chlorine ion-chemistry plays a small role for ClONO<sub>2</sub> around 45-50 km during the event as seen from this figure. However the impact is indeed very small. We have clarified this in the text.

**2.31 Figure 15-16: It's impossible to see any detail in these figures. I think you should be able to easily clarify these by making lines thicker and adjusting the y-scale. The labelling font is far too small.**

The figures are updated with thicker lines and larger labelling font. The y-scale in figure 15 is the same for the top and the bottom row for each column (species). The axes font are also enlarged.

185 **2.32 Lines 488-489: Not clear. Perhaps: “Because there are not enough chlorine atoms during nighttime...”?**

Yes, because there are not enough chlorine atoms during night-time.

190 **2.33 Section 4.3: The discussion of ozone loss in the mesosphere and stratosphere is a bit mixed. Perhaps you can clearly distinguish between the HOx and NOx driven losses to clarify this section. In this section it would also be useful to contrast the Halloween ozone loss to previously published model results (e.g. Verronen et al. I mentioned earlier) as well as observations since this is a very well studied event.**

We have included 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. The HOx and NOx driven losses in the mesosphere and stratosphere are also clarified and revised. Details about the differences of the magnitude of ozone depletion with respect to the NOx and HOx related loss and altitude have been included as well.

195 **2.34 Section 5: Lines: 516-517: Why is this expected?**

We believe that this is related to the diurnal cycle of ClO which is different for daytime and night-time. During the event, ClO formation is seen for night-time at 50-70 km whereas it is not present during day-time. Explanations regarding this are added in the revised manuscript in section 5 and a figure for the same in the supplement (Figure 15).

200 **2.35 End of Conclusions: Based on your work, can you discuss lessons learned that should be considered for inclusions of D-region ion chemistry in EMAC.**

205 We have revised section 6 discussing the implications and recommendations of the work. In a nutshell, the validated D-region ion-chemistry in ExoTIC consists of important chemical reactions involving water, chlorine and NO<sup>+</sup> cluster ions. We are implementing these reactions from ExoTIC into EMAC and also using the same ion pair production rates that are based on Porter, J. N. (1976). One lesson that we learned from our ion-chemistry model is to consider O(<sup>1</sup>D) in photo-chemical equilibrium. But for the global chemistry climate model EMAC, this shouldn't make much of a difference as also discussed in the previous comment "section 2.2.2 and conclusions". The next step would be to evaluate the performance of the ion-chemistry comparing it with MIPAS observations and considering that for experiments involving atmospheric dynamics.