

Interactive comment on “Diurnal variations of reactive chlorine and nitrogen oxides observed by MIPAS-B inside the January 2010 Arctic vortex” by G. Wetzel et al.

Anonymous Referee #2

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General comments

The paper discusses measurements of chlorine and nitrogen species during a balloon flight in activated air in the Arctic vortex in January 2010. This is a very interesting situation regarding polar ozone loss and the measurements are of high quality. The paper presents a unique case study of the temporal development of the species N_2O_5 and Cl_2O_2 from night time equilibrium into daylight. A comparison of model results and observations is presented. There are discrepancies observed between model results and observations, which are interesting rather than disturbing (in my opinion) as they might help us to learn more about the atmosphere. But I suggest a more detailed

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discussion of the discrepancies. I have the following major points:

1. Regarding the photolysis cross sections for Cl_2O_2 it would be good to do a sensitivity run with the model using e.g., the Papanastasiou et al. (2009) cross sections (see also the most recent WMO report). This would allow questions to be addressed regarding the onset and the rapidity of ClO rise after (or even before in the model) sunrise. This would be important to clarify the discrepancies regarding conclusions on this issue between the present paper and Sumińska-Ebersoldt et al. (2012).
2. Related to point 1), I suggest that more discussion is presented in the paper regarding the relative importance of the direct and diffusive radiative flux. Do we really (even in cloud free air) expect the photolysis of the ClO dimer to start at the sunrise terminator? Isn't the UV in the direct beam mostly absorbed in the long atmospheric path at large zenith angles? In Fig. 5, it seems that the rise of ClO starts even before sunrise.
3. The paper reports a huge discrepancy between measured and observed N_2O_5 . If this observation is correct, the EMAC model (and very likely most other stratospheric chemical models) strongly overestimates the heterogeneous reaction of N_2O_5 with water vapour. If this is a result of the paper, a stronger statement should be made. On the other hand, it would be very helpful corroborate the MIPAS observation with independent measurements.
4. The model is able to reproduce the observed chlorine activation correctly and to reproduce the observed ClO values. This is an important point. Therefore, I suggest more discussion on this issue in the paper. This would mean focussing in a section on the temporal development of active chlorine and chlorine reservoir species over the winter until January, rather than focussing only on the day of the balloon measurement. But I think this would be worthwhile.

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5. I also suggest somewhat more discussion on PSC characteristics in the paper. Are the observed PSC characteristics consistent with other observations (Pitts et al., 2011; Khosrawi et al., 2011)? Further, regarding the heterogeneous scheme: which assumptions are made for NAT formation and surface area? Which parameterisation is used for the heterogeneous reactivity of liquid aerosol (STS) and NAT particles? Is the heterogeneous reactivity in the model dominated by NAT or liquid particles? Are reactions on ice surfaces included in the model and are they important for the simulated chlorine activation?

The paper is well written and structured overall. The observations and the model simulations are of high quality. I suggest that a revised version of the paper should be accepted for publication in ACP after revision along the lines suggested here.

Comments in detail

p. 4868 l. 4: the reservoir gases are activated, not ClO_x

- l. 11: quickly → rapidly
- l. 16: its → the chlorine
- l. 19: can you quantify 'fairly well'?
- l. 22: 'less quickly' – explain why this could be the case, what in the conclusion from this finding?

p. 4869 l. 2 drop 'to produce'

- l. 3: add 'to be produced' after Cl₂
- l.5 drop 'being'; 'subsequently'

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- l.24 perhaps also discuss in-situ observations of ClO during daytime under activated conditions?
- l. 26: change to 'polar winter'

p. 4870 l. 5: change to 'Arctic winter'

- l. 10: N₂O₅ is converted to HNO₃ also in warm winters
- l. 12: the 'sequestration' also (and more importantly) happens through *condensation* of HNO₃
- l. 18: 'ozone budget' unclear whether polar or global ozone is meant here.

p. 4872 l. 27: change to 'place already'

p. 4873 l. 16: The discussion about PSCs is very brief. It would be good to extend the discussion. For example to give an indication how reliable the attribution of the particle type is. Also it would be interesting to state in how far the presence of PSC will influence the quality of the MIPAS retrieval. Are the PSC observations (and possibly conclusions on denitrification) consistent with earlier studies on the Arctic winter 2009/10 (Pitts et al., 2011; Khosrawi et al., 2011)?

p. 4875 l. 7: suggest considering also a citation to ECHAM as well (as the basis of EMAC)

- l. 23: 'condensation' → 'existence'
- l. 24: Further details about the heterogeneous chemistry schemes should be given here. What is the assumed NAT number density (this is important for the resulting surface area)? Which particles are assumed in the scheme to form first (STS I assume)? Which particles are most relevant for heterogeneous chlorine activation?

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- p. 4876 l. 10: The release of ClO from Cl₂O₂ is an important issue for the paper. Therefore, it would be very important to test the impact of using recently measured cross sections for Cl₂O₂. For example, using the cross sections reported by Papanastasiou et al. (2009), should result in a more rapid increase in ClO after sunrise in the model improving the agreement with the observations. It should not be too difficult to perform such a test in EMAC (only a one day run is required). It would be interesting to see in how far the conclusions from such a run agree with those by Sumińska-Ebersoldt et al. (2012), who investigated the problem for the same winter based on in situ ClO measurements. Finally, the recommendation in Sander et al. (2006) is unchanged since JPL02-25, so there is no need to list the 2006 report separately.
- l. 26: How complete is the activation? I suggest showing also EMAC results for HCl. What fraction of the available chlorine (Cl_y) is in the form of ClO_x. Could MLS measurements be considered to check the model results?
- p. 4877 l. 5: it would be important to know the MIPAS-B ClO values at 20 km for better comparison with the Geophysica measurements (Sumińska-Ebersoldt et al., 2012). Are the measurements consistent?
- l. 13: Which radiative transfer model was used for these calculations?
 - 23: 'slower velocity' – why? Could this deficiency be due to underestimating the cross sections for Cl₂O₂?
- p. 4878 l. 4: '... starts at sunrise'. This finding is in contrast to the results reported by Sumińska-Ebersoldt et al. (2012), who find a delay between sunrise and the rise of ClO and no strong impact of shadowing by clouds in their simulations. The reason for this apparent discrepancy should be discussed.
- l. 15: drop 'typically'

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- l. 21: state how close to zero
 - l. 27: Could tracer measurements be used to check if the modelled Cl_y is correct?
- p. 4879 l. 11: This is true, but even if there were significant NO₂ production it would not show up in the presence of high ClO values because of the rapid formation of ClONO₂ under such conditions.
- l. 18: weaker 'than'
 - l. 22: comparison between observations and model results are not good at 26–26 km.
- p. 4880 l. 10, 11: There is a huge discrepancy here between measured and observed N₂O₅. If these observations are correct, it means that the EMAC model (and very likely most other stratospheric chemical models) strongly overestimate the heterogeneous reaction of N₂O₅ with water vapour. If this is a result of the paper, a stronger statement should be made. On the other hand, it would be very helpful to have support from independent measurements for the MIPAS observation.
- p. 4881 Is it really that important to get the PSCs right in a model to obtain a good representation of chlorine activation? How well do the observed and simulated PSC characteristics agree in this case study?
- Fig. 5: It looks to me that the build-up of ClO starts *before* sunrise in the model. Is there an explanation? Further, it looks like the model underestimates ClO at 32–34 km.

References

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