

Interactive comment on “Coupling of HO_x, NO_x and halogen chemistry in the Antarctic boundary layer” by W. J. Bloss et al.

Anonymous Referee #1

Received and published: 27 August 2010

I think this is a very interesting photochemical modeling study performed in a unique environment. I think the paper has a variety of strong points.

1) The ability of the model to explain NO_x levels in the presence of halogens is a nice achievement and demonstrates the importance of halogen nitrate formation in this environment. This work indicates that these processes are pretty well understood. Along these lines I am interested to know which process dominates IONO₂? BrONO₂? etc
2) The importance of iodine and its role in the HO_x cycle – especially as impacting the HO_x partitioning is well described. A lot of the uncertainties in the iodine mechanism are mentioned and this provides a nice overview for the reader. 3) An excellent review of polar HO_x measurements is provided and I feel the work is well motivated. 4) I also think it is very interesting that the assumption of a constant iodine source seems to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Interactive
Comment

deliver IO well – The BrO assumption seems to be less good but is still reasonable. Although it clearly doesn't work at all on one day. The amount of BrO and IO data is not that much so this assumption may not be validate over a wider range of data. I don't understand the data coverage of BrO and IO. If both are measured by DOAS why do you have data for one on one day and not the other?

I think the paper has a few areas that could be improved. 1) Chlorine may also be present in this environment – it could have a role especially in cross radical reactions, etc. BrCl may be important – I doubt if it would change HOx partitioning that much and would only seem to increase the concentration of radicals. However, I think its potential role should be mentioned or perhaps there are some constraints on the levels 2) The HOx measurements are troubling. At some level the HOx levels are going to be very hard to budge in any kind of model treatment as they will be buffered. The loss will depend on the square of radical concentrations (i.e. HO₂+HO₂, etc) and there is nothing that any model is going to do that will decrease HO₂ to the observed levels during the early period given the known radical sources. The authors do need to address the possibility of a flaw in the HOx data that may be alleviated with time (i.e. the measurement improves over the course of the campaign). Model case A where the full mechanism is used and the NOx is constrained seems to be the most appropriate. This Case really doesn't agree with the observations and I must admit that I find the other cases to be much less compelling. I think this is a very high quality measurement group and this is a delicate point but I don't think uncertainties in the boundary layer and the iodine measurement will ever reconcile the first part of the measurement period. 3) If the authors feel the HOx data is correct they should discuss the possibility that IO does not increase OH levels via enhanced partitioning from HO₂. This goes against the model predictions and the general impression in the community. At some level this seems to be the key issue of the paper – how does iodine chemistry impact HOx as bromine chemistry is going to have less of an impact at the levels observed. 4) I would like to see a table that compares mean noontime HOx levels along with the predictions of the model test cases. I think it would also be good to show the comparison results

C6890

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

when IO measurements are present i.e. you are constrained to NO_x and IO – these seem to be the key species in my mind. 5) Since RO₂ radicals are not measured is there any possibility the HO₂ is ending up there?

In summary, this manuscript describes an impressive body of both experimental and theoretical work. I highly recommend publishing but would like to see a more critical discussion of the HO_x measurements and the role of iodine.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 15109, 2010.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper