Atmospheric
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Discussions

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Interactive comment on "HO$_2$NO$_2$ and HNO$_3$ in the coastal Antarctic winter night: a "lab-in-the-field" experiment" by A. E. Jones et al.

Anonymous Referee #1

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The paper by Jones et al describes field measurements of HNO$_3$ and HO$_2$NO$_2$ at the Antarctic coast. The unique aspect of this study is the presentation of winter data and the identification of physical exchange processes in the field environment. This is an innovative approach as earlier field studies span summer month, where photochemistry dominates fluxes of nitrogen oxides. This data set and the discussion of the results in this study are a highly valuable contribution to the scientific community and allow learning about physical exchange processes for the first time in complex and undisturbed field settings. So far, physical exchange processes have mainly been quantified in laboratory studies.

The paper is clearly structured; conclusions seem sound and well justified. I fully support publication in ACP after considering some minor aspects:

- My current understanding is that HO$_2$NO$_2$ is formed in-situ in the gas-phase and this is the first time I hear that emissions from snow are discussed as source. This is inline with your introduction. I wonder about the ultimate origin of this HO$_2$NO$_2$, that would presumable be adsorbed HO$_2$NO$_2$? This must have been formed during summer: I wonder if it is stable enough to last all winter, taken that HO$_2$NO$_2$'s thermal lifetime in the gas-phase is limited? Even more, the reservoir of HO$_2$NO$_2$ seems to be very stable from June throughout July - as Figure 5 indicates very similar gas-phase concentrations indicating similar fluxes from the snow indicating stable snow concentrations during those 6 weeks.

  Could you comment on this, and may I suggest elaborating on HO$_2$NO$_2$ and HNO$_3$'s origin in winter snow in the introduction?

- This work states that fluxes form the snow fuel the observed HO$_2$NO$_2$ and HNO$_3$ mixing ratio during winter.

  Would one then not need to know the boundary layer height to be able to compare the strength of this exchange during different days of your study and in particular when comparing with findings of other studies (page 12774 for example)?

- This work focuses on adsorption of HNO$_3$ and HO$_2$NO$_2$ to snow, in fact this is the only exchange process that is discussed. Agreement of the heat of adsorption derived in this study to earlier laboratory based finding support this hypothesis

  - Could you discuss why uptake to liquid NaCl aerosols that might be present down to temperatures of - 40°C or to the solid ice forming a solid solution are not equally well able to explain the data?

– What is the error range of the laboratory based heat of adsorption measurements taking into account other studies, and are those really well enough known to clearly favour adsorption vs. solid solution (DH of -68 kJ/mol; Thibert & Domine 1998) vs. solution in liquid aerosol droplets.

Smaller things:

Page 12774 "The details of this uptake will differ somewhat between the two molecules, as the enthalpy of adsorption for HO_2NO_2 is greater than for HNO_3 (Ulrich et al., 2012), and both adsorption processes are temperature-dependent (Crowley et al., 2010; Ulrich et al., 2012)." This sounds a little confusing to me: I miss a statement that the main difference is that the partitioning coefficient of $HNO_3 > HO_2NO_2$. Thus HNO_3 is much more sticky than HO_2NO_2 and one can expect a higher fraction of HNO_3 on the ice surface compared to HO_2NO_2.

P 12776: How did you quantify HNO_3 and HO_2NO_2 using the CIMS? How was calibration done? What is the reaction time in the CIMS, i.e. are you as sensitive to humidity and to form $H2O$ clusters as Slusher 2001 was?

12779 „Given our understanding of the interaction between acidic gases and ice gained through laboratory studies (e.g. Huthwelker et al., 2006), the most likely mechanism is temperature-dependent adsorption/desorption at the snow surface." Why not diffusion and solid solution or uptake to liquid aerosol particles

17782 "The average Hads for HNO_3 is 42±7 kJ mol1 which can be compared with the laboratory-derived value (Bartels-Rausch et al., 2002) of 44kJmol1;" What is the error bar on the laboratory derived values taking all studies into account?

Figure 1: Maybe add wind speed to this graph.

Figure 6: The folding depth for data in B) was higher than for A) and C). Does this mean that the BL was lower and that fluxes were actually higher to reach the same

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mixing ratio?

Hope you find this comments helpful

Thank you very much for this stimulating manuscript.