Response to Reviewer 1

We thank Reviewer 1 for his/her comments on our paper, which we address in the following.

- My current understanding is that HO_2NO_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 in line with your introduction. I wonder about the ultimate origin of this HO_2NO_2, that would presumable be adsorbed HO_2NO_2? This must have been formed during summer: I wonder if it is stable enough to last all winter, taken that HO_2NO_2's thermal lifetime in the gas-phase is limited? Even more, the reservoir of HO_2NO_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_2NO_2 and HNO_3's origin in winter snow in the introduction?

- Our work suggests that HO2NO2 in the atmosphere is in equilibrium, both with gas phase atmospheric HO2 and NO2, but also with HO2NO2 adsorbed to the snowpack. As the year moves from the warmer summer months, towards the colder temperatures of autumn and winter, the lifetime of gas-phase HO2NO2 with respect to thermal decomposition, will increase. Similarly, with the lower temperatures, the air/snow HO2NO2 equilibrium will shift towards snowpack-adsorbed HO2NO2. The ultimate origin of the snowpack-adsorbed HO2NO2 could thus be gas-phase production in the atmosphere.

The stability of the reservoir through June/July can thus be considered in terms of equilibrium. During the cold dark winter months, the lifetime of HNO3 and HNO4 is relatively long. Without a photochemical sink, and with an equilibrium between air and snowpack, the reservoir can be maintained. It is also possible that transport from inland Antarctica (where higher mixing ratios of gas-phase HNO3 and HNO4 are measured) of snow rich in HNO3 and HNO4 could contribute to the snowpack reservoir. The scale of the snowpack reservoir is demonstrated by the calculations by Bartels-Rausch (shown in Fig 1 of his Short Comment to our paper) which show that the vast majority of both HNO3 and HO2NO2 (>99% of all molecules) is associated with the snow at temperatures below 250K. A change in atmospheric mixing ratios would thus not greatly affect the snowpack reservoir under these conditions.

We have included discussion on this topic into the Conclusions section of our revised manuscript.

- This work states that fluxes from the snow fuel the observed HO_2NO_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)?

- The Reviewer is of course correct, that in order to compare strength of exchange on different days, and with other studies, then the boundary layer height would need to be known. In paragraph 3, page 12774, the discussion is intended to describe the situation in general, and the different mixing ratios that have been observed in different years. It is not designed to address the reasons for/mechanisms behind these differences. To, convey this, we have altered our

manuscript to read: "While the specific mixing ratios will be strongly influenced by boundary layer height, overall, these high mixing ratios are fuelled by in situ production from elevated levels of NOx and HOx..."

- This work focuses on adsorption of HNO_3 and HO_2NO_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?

In our paper we considered only exchange driven by adsorption/desorption. In his Short Comment to our paper, T. Bartels-Rausch (http://www.atmos-chem-phys-discuss.net/14/12771/2014/acpd-14-12771-2014-discussion.html) considered also uptake to solid ice. He found that reversible solid-solution/air partitioning was not able to predict the measured gas phase mixing ratios of HNO_3 as well as Langmuir adsorption. Further, the reservoir of HNO3 stored as solid solution in the outer part of the snow crystals was too small to explain the observed increase in mixing ratio. He thus concluded that uptake to a solid solution was not able to explain our data. This is now discussed in the Conclusions section of our revised manuscript.

– 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.

Ullerstam et al. (2005) report heat of adsorption of HNO3 of -30.3 +/- 6.0 $kJmol^{-1}$, i.e. somewhat lower than the Bartels-Rausch et al (2002) values that we refer to in our manuscript. We now refer also to the Ullerstam et al results in our manuscript. Again, the Short Comment by Bartels-Rausch demonstrates that the solid solution mechanism is not able to explain our field data, as we mention in our revised manuscript.

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.
Text amended to read: The details of this uptake will differ somewhat between the two molecules because the partitioning coefficient of HNO_3 is greater than that for HO_2NO_2. HNO_3 is thus more sticky than HO_2NO_2, and a higher fraction of HNO_3 can be expected on the ice surface compared with 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?

As the method to quantify HNO3 and HO2NO2 is fully described elsewhere, we chose not to repeat what is already published. However, as this section was not clear to the Reviewer, we now include additional references to clarify this. The section now reads:

“The instrument employed the SF_6^- method to detect both HNO_3 and HO_2NO_2, using the NO_4^-(HF) cluster at m/z 98 to detect HO_2NO_2, and NO_3^-(HF) at m/z 82 to detect HNO_3 (as per Slusher et al., 2001, 2002). ***Calibration was achieved using the SO_2 method as described by Slusher et al. (2001) and Kim et al. (2007).*** Background measurements, or zeros, were obtained every 10 minutes. These were achieved by passing sampled air for 3 minutes through a customized filter filled with activated coarse charcoal and nylon glass wool coated in $NaHCO_3$. This scrubbing method has previously been shown to be efficient at removing both HO_2NO_2 and HNO_3 from sampled air (Slusher et al., 2001). The instrument detection limit derived from background data averaged over 10-minutes was 0.7 pptv for HNO_3 and 0.4 pptv for HO_2NO_2. ***Total estimated uncertainty in the CIMS observations is ±40%.***

While the SF_6^- method has been used successfully in previous field campaigns (e.g. Slusher et al., 2002; Slusher et al., 2010), it has been demonstrated in laboratory studies (Slusher et al., 2001) that SF_6^- reacts with H_2O in the sample air flow. This introduces an interferent into the technique, the non-linearity of which is evident in the unfiltered data (not shown). ***However, with their instrument reaction time of ~25 ms, Slusher et al. (2001) also concluded that this interferent was significant only at dewpoints greater than -25^{o}C, and that at lower dewpoints, the interferent was negligible. During the period of measurements at Halley, the CIMS instrument also operated with a reaction time of ~25 ms, such that the interferent would be equivalent to that of Slusher et al. (2001).*** At Halley, dewpoint temperatures varied from -12^{o}C to -52^{o}C (mean -31^{o}C), but were below -25^{o}C for 81% of the time. To remove the potential for H_2O interference in our data, all measurements made at dewpoints above -25^{o}C are filtered out from the dataset.”

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

The sentence has now been changed to: “Given our understanding of the interaction between acidic gases and ice gained through laboratory studies (e.g. Huthwelker et al., 2006), one possible mechanism is temperature-dependent adsorption/desorption at the snow surface.”

12782 “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?

We have now included information on error assessment in our text: “The values of ΔH_{ads} derived from these fits are given in Table 2. The average ΔH_{ads} for HNO_3 is -42±2 kJ.mol^{-1} which can be compared with laboratory-derived values of Bartels-Rausch et al. (2002) and Ullerstam et al. (2005). Bartels-Rausch et al. (2002) derived ΔH_{ads} of -44 kJ.mol^{-1} (based on 4 measurements, with random error 2.3 kJ.mol^{-1}, systematic error 13 kJ.mol^{-1}); Ullerstam et al. (2005), working at lower concentrations of HNO_3, relevant to the natural atmosphere, derived ΔH_{ads} of -30.6 ± 6.0 kJ.mol^{-1} (based on measurements at 3 temperatures). For HO_2NO_2, the average ΔH_{ads} derived from our field data is -56±1 kJ.mol^{-1} which can be compared with the laboratory-derived value (Ulrich et al., 2012) of -59 kJ.mol^{-1}.”

Figure 1: Maybe add wind speed to this graph.

The reviewer suggested that we could maybe add wind speed to this graph. We prefer not to do so, as we feel this would merely clutter what is already a rather full graph, thereby reducing the clarity of the information. Certainly in Antarctica the arrival of storm systems raise ambient temperatures, but there is of course not a 1-to-1 correlation between temperature and wind speed. Our Fig 6 and Fig 7 focus on periods with low and invariant wind speeds and changes in mixing ratios are strongly associated with changes in temperature. We therefore prefer to focus on temperature, and not include wind speed in Fig 1.

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 mixing ratio?

We assume that the reviewer is asking here about the slopes on the plots, and suggesting that B has a greater slope than either A or C. If we re-scale the figures, so that they all extend for the same time duration, the slopes of B and C in mixing ratio are very similar, as they are in temperature. Figure 6A is different for both parameters. To address the reviewer's question in more detail would be interesting, but for this we would need more data on either surface u* or a profile of the mixing efficiency through the boundary layer, and these are not available.

Response to Reviewer 2

We thank Reviewer 2 for his/her review. We respond to issues/questions here:

1) Atmospheric measurements indicate rather unchanged HNO4 mixing ratios over all the winter (see Figure 1). Since no atmospheric HNO4 sources are likely at that season a overall positive net flux out of the snow would be needed to maintain the atmospheric HNO4 mixing ratios unchanged over this long period in view of the limited lifetime due to thermal decomposition of this species (to my knowledge around 10 to 20 hours at -30_C). If true, the question would arise how this HNO4 winter reservoir in the snow has been built up ? Is it possible that this is created during summer, in spite of an even shorter lifetime in summer than in winter and a rather restricted available amount of NO2 to proceed with the NO2 plus HO2 production reaction (a few pptv of NO2 at noon at Halley in summer, Bauguitte et al. 2012)? Could drifted snow from inner Antarctic sites (more rich in HNO4) can contribute to the HNO4 snow reservoir at the coast ?

This is an interesting question, and indeed one raised also by Reviewer 1. Our work suggests that HO2NO2 in the atmosphere is in equilibrium, both with gas phase atmospheric HO2 and NO2 (R1 in our manuscript), but also with HO2NO2 adsorbed to the snowpack. As the year moves from the warmer summer months, towards the colder temperatures of autumn and winter, the lifetime of gas-phase HO2NO2 in the atmosphere with respect to thermal decomposition, will increase. Similarly, with the lower temperatures, the air/snow HO2NO2 equilibrium will shift towards snowpack-adsorbed HO2NO2. One can therefore imagine a general conduit, whereby HO2 and NO2 in the atmosphere become snowpack-adsorbed HO2NO2. The suggestion of the reviewer, that snow drifting from inner Antarctica could carry HNO4 towards the coast, is also likely, and indeed this mechanism is discussed in our manuscript (P12783, 21-25). The scale of the snowpack reservoir is demonstrated by the calculations by Bartels-Rausch (shown in Fig 1 of his Short Comment to our paper) which show that the vast majority of both HNO3 and HO2NO2 (>99% of all molecules) is associated with the snow at temperatures below 250K. A change in atmospheric

mixing ratios would thus not greatly affect the snowpack reservoir under these conditions. In order to respond to the reviewer's comment, we have expanded our discussion in the Conclusions section.

Is it possible that the snow reservoir is refilled (also in winter) due to precipitation events which wash out the atmospheric HNO4 ?

As per our response to the question above, it seems quite likely that the snow reservoir of HNO4 is added to during the winter by precipitation events and transport of snow from further inland.

Did you detect a change of HNO4 (and HNO3) mixing ratios after a precipitation event?

Meteorological observations are made at Halley every 6 hours. We have looked at the data to see if there is a change in HNO4 and HNO3 after a precipitation event, as suggested by Reviewer 2. It's very hard to make a clear statement whether there is or not – the mixing ratios are so tightly constrained by temperature, this appears to control the mixing ratios over and above any other environmental factor.

2) You assume that measurements made at 5 m height are representative to interstitial concentrations. What makes you sure of that? Was it possible to do any measurements on site in the snow interstitial air ? Couldn't it be possible that at least for HNO4 interstitial concentrations are systematically enhanced in view of the expected overall net flux out of the snow (see comment above)? Is it possible to estimate the gradient (and with that the net flux) between atmosphere and the interstitial air via the atmospheric lifetime of HNO4 and the diffusive coefficients in atmosphere and the interstitial air?

It was not possible to make measurements of interstitial air. However, it's important to be clear: we assume that measurements made at 5 m height are effectively proxies of interstitial concentrations specifically under conditions of low and constant wind speeds. We are then interested in how these concentrations would vary as a function of changing temperature. While temperature changes at depth within the snowpack will be damped compared with those at 5m, the magnitude of temperature changes in the top layers of snowpack are likely to be similar. We explain this (P12782, line 10) by writing that "over several hours, and under low and constant wind conditions, the concentration at our inlet tracks the concentration in the firn..." i.e. we believe that delta concentration at 5m can be a proxy for delta concentration within the firn under conditions of low and invariant wind speed. Further discussion/justification of this approach is given in the manuscript in section 3.3.

3) Could you report an error estimation for the enthalpy calculations?

We thank the Reviewer for his/her question, which made us realise there was a small error in our previous calculation (now corrected). The uncertainty on the enthalpy for each derivation (as per Fig 7) is simply the uncertainty on the slope which is given in the paper (Table 2). As we consider 3 cases for deriving averaged enthalpy of adsorption, both for HNO3 and HO_2NO_2, we use the uncertainty on the line for each case to propagate through to the overall uncertainty,

$$\mathit{overall\,uncertainty} = \frac{\sqrt{(\sigma 1^{2}+\sigma 2^{2}+\sigma 3^{2}}}{N}$$

Where: σ is the error on the line for each line fit; N is the number of lines considered (i.e. 3)

4) Is it straight forward to compare the ratio of HNO3 and HNO4 obtained at Halley with the one obtained at the South Pole since species do not have the same lifetime?

The aim of the comparison was only intended to demonstrate the differences between the two systems. If we were to present ratios in our paper, it would be strange not to in some way refer/compare them to the South Pole results. In response to the reviewer's question, we have amended our manuscript to read: "Differences between South Pole summer and Halley winter are also evident in the ratio of HNO_3:HO_2NO_2, arising through differences in the species' lifetime."

Response to Reviewer 3

We thank Reviewer 3 for his/her comments on our paper, which we address in the following.

1. Introduction: Please provide specific information about typical lifetime of HO2NO2 and HNO3 from specific reaction channels (R2a to R5). Some of those listed reactions may or may be not important in the tropospheric conditions especially conditions like Antarctica. Please discuss further about the implications of each reaction channel specifically in the lower troposphere!

The reviewer suggests providing information about typical lifetimes of HO2NO2 and HNO3 from the reaction channels (R2a to R5) described in our manuscript. As our paper deals with Antarctic winter, none of these reaction channels are likely to be operative and influencing our data. The information is included only to introduce HO2NO2 and HNO3 chemistry in general terms. Indeed, we state, at the end of P12774, that under the conditions of our observations (24 hour per day darkness), atmospheric chemistry stalls. However, to clarify earlier in the manuscript that this is the case, we have included the following above where the reactions are introduced:

"There are a number of photodissociation pathways which drive HO2NO2 and HNO3 chemistry under sunlit conditions. The most important are thought to be:"

2. Page 12775 Line 15: This section is describing CIMS instrumentation so the title would be better for going by either "CIMS instrumentation" or "CIMS".

We have made the change suggested by the Reviewer

3. Page 12783 Line 15-20: Once HNO3 and HO2NO2 molecules are adsorbed in the ice surface, how long would it be stayed as it is? I would think that it will be dissolved into the ion phase then nitrate and nitrite in ice would be regenerated into the gas phase species as described in Domine and Shepson (2002 Science 297 pp 1506). Please add a detailed discussion on the specific relevant heterogeneous mechanisms.

We have added considerable discussion about exchange mechanisms in the Conclusions section of our revised manuscript.

Response to Short Comment by Thorsten Bartels-Rausch

We are extremely grateful to Thorsten Bartels-Rausch for his detailed Short Comment, which presents calculations using our field data that both support our paper and provide an extension to it.

While it is not appropriate to include completely new issues in our revised manuscript, we now refer to this Short Comment in our revised manuscript as well as in response to reviewers.