

## ***Interactive comment on “” by***

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Received and published: 5 August 2011

We thank Reviewer 2 for his/her comments. As suggested we have waited until the primary papers have been published, and have now included into this manuscript details of alkyl nitrate flask sampling conducted as part of the budget, but not previously published elsewhere. We agree that this is an improvement in approach. The PAN results are now published in a peer-reviewed publication and is closely referred to in this manuscript. The HONO data have been called into question sufficiently for us to discard them for the budget analysis. The reasons are fully explained/discussed in the revised manuscript.

Possible sources of organic nitrates are discussed in the PAN paper (and referred to in the text here), but additional discussion regarding sources of alkyl nitrates is now also given within in the new section 3.1 about the alkyl nitrate flask samples.

Measurements of  $\text{HNO}_4$  have subsequently been made at Halley, and we refer to these, as yet unpublished, data in the “Discussion and Conclusions” section. We refer also to the observations made at South Pole by Slusher et al.

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The reviewer questions why there is not a tighter correlation between surface snow nitrate and boundary layer atmospheric particulate nitrate, given that we have evidence that suggests a peak in surface snow nitrate was driven by aerosol scavenging by snowfall. Previous work has shown that, on a day-to-day basis, a tight correlation between aerosol and surface snow composition is not found (e.g. Wolff et al., 1998). A study by Rankin and Wolff (2002) has shown that aerosol loading can display large variability with height, sometimes with higher concentrations at the ground than aloft, and sometimes with lower concentrations. For this reason, ground based-measurements of aerosol are not always a great surrogate for atmospheric loading, and the amount of aerosol available for scavenging (and thence deposition) by snowfall. To go some way to address this concern in the paper, we have adjusted the text to read as follows: “Previous analyses of surface snow chemistry and ground level aerosol, sampled at daily resolution, did not find the two to be consistently highly correlated (Wolff et al., 1998). This suggests that impurities in surface snow can be determined by factors other than the ground level aerosol composition (as discussed above). Indeed, a limited number of profiling measurements subsequently showed that aerosol concentration varied quite markedly with height, and that air masses aloft ( 200 m above the ground) could have an aerosol loading quite different to that measured on the ground (Rankin and Wolff, 2002). Variability in the aerosol profile may go some way to explain why, for this event, it appears that the source of surface snow nitrate was wet deposition and scrubbing of boundary layer  $p\text{-NO}_3^-$ , while on a seasonal basis, there is no obvious link between the two. We note, however, that Wolff et al. (2008) further explored the role of snowfall in depositing aerosol nitrate during the CHABLIS campaign and found that spikes in the surface snow nitrate data were regularly accompanied by fresh snowfall.”

The reviewer suggests that the  $p\text{-NO}_3^-$  seasonal cycle is odd in comparison with other coastal Antarctic records. The stations referred to by the reviewer have published records from high-volume aerosol samplers, which are considered to capture both particulate and gaseous nitrate (one directly and the other by exchange reactions). So, a comparison of Halley lo-vol data (which is unlikely to have captured gaseous nitrate)

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with high-vol data even from Halley, of course will give a different seasonality. However, a composite of the monthly-averaged  $p\text{-NO}_3^-$  and the gaseous  $\text{HNO}_3$  measured at Halley during CHABLIS is provided in the Overview paper (now published in ACP, and referenced in this revised manuscript) which is therefore more comparable with the datasets referred to by the reviewer. While there is a summer peak in the CHABLIS data, there is also a shoulder suggesting a possible secondary peak in August. Of note also is that the hi-vol records discussed by the reviewer display considerable variability between stations and between years. Take for example the Savoie et al. 1993 paper that compares N-species in aerosol at Mawson and Palmer station. Figure 3 shows nitrate measured at Mawson over 5 years – the details of the seasonality is not consistent year-on-year. Similarly, Figure 5 compares the cycles at Mawson and Palmer – the timing of peaks are quite different between the records. Rankin and Wolff present cascade impactor data and the distribution of  $p\text{-NO}_3^-$  across different particle ranges. Yes they show a December peak within a particular size range, but if this were averaged across all size ranges this peak would not be so conspicuous. They did not do this averaging, so it's not possible to make a real comparison between the CHABLIS data and theirs. With regards halogens, yes, they were operative in the springtime, as is discussed by Bauguitte et al., (2009).

Although Grenfell (1991) is now dated, the main uncertainty in the actinic flux with depth is actually embodied in the e-fold depth. The depth that was output by Grenfell's model matched that group's earlier data. It is undoubtedly the case that higher e-fold depths have been found at central Antarctic sites since then implying greater actinic fluxes. We have therefore reacted to this change in knowledge (that has occurred also since this paper was first submitted) by scaling the output in line with the e-fold depth (which is a reasonable assumption given the other uncertainties). We have used a value that, with our quoted uncertainty, encompasses the range of likely values. This does imply a large range of possible emissions, but without narrowing down the e-fold depth or using direct measurements, this range is a realistic estimate of our uncertainty.

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Page 4131 line 3 – this text has been adjusted

Page 4131 line 8: The aim is to assess whether a particular month is significantly different from another. This is done using the standard error of the mean. The standard deviation of the mean would address the distribution of values within a month. The standard error is the right uncertainty to report when the aim is to assess whether one monthly mean is significantly different from another monthly mean.

Page 4131 line 22 – the reference has been changed to Weller et al., 2002.

Page 4133 line 4 – Savarino et al reference now updated

Page 4133 line 8 – Bauguitte pers. comm.. is removed

Page 4135 line 13: The equivalent to Table 2 has subsequently been published in Grannas et al (2007), so Table 2 has been removed from this manuscript, referring instead to the Grannas et al version.

Page 4136 line 2: this section has been removed.

Page 4138 ppbv corrected to pptv

Page 4140 line 8: the additional references are now included.

Page 4141 line 15 reference corrected to Weller et al., 1999, and added to reference list

Section 4.3: Snow at Halley is acidic so will not be subject to mineral effects to the same extent as was observed at Browning Pass. We have now included text to explain this in the paper. Further, the reason that the model was used in the way it was is because it was compared with measured fluxes made at Neumayer station, and good agreement was found. As Neumayer and Halley are very similar in location and snow structure, it was assumed that this model, set up in the same way, would also be appropriate for Halley. However, the real point here is to compare sources of NO<sub>x</sub> to the boundary layer. Given that the boundary layer at Halley, although highly variable

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from day to day lies somewhere between 10 and a few hundred meters, the uncertainty on calculated snowpack emissions does not alter the conclusion that the snowpack source dominates over the gas-phase sources, and indeed to a considerable extent. We have further emphasised this point in the text.

Page 4146 line 11: My reading of this goes as follows: Savarino et al report measurements made using a high volume aerosol sampler. At a coastal site, given the loading of sea salt in the atmosphere, hi-vols are generally considered to capture both particulate and gaseous nitrate (see e.g. Wagenbach et al, 1998, Savoie et al., 1989). However, as Savarino et al do indeed present their arguments in terms of  $p\text{-NO}_3^-$ , we have adjusted our manuscript as suggested – thanks for pointing this out.

Page 4146 line 26: the data presented here could be used for a variety of model studies and indeed ought to be at some point. A study of BL chemistry driven by air/snow exchange would indeed benefit from a box model. We present an initial approach to such an assessment with the calculations of  $\text{NO}_x$  production. The suggestion of a 3D study was to probe the larger-scale issues concerning source/sinks and the role of transport. This however, and unfortunately, does go beyond the scope of the present paper.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4127, 2007.

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