Atmos. Chem. Phys. Discuss., 3, S4–S7, 2003
www.atmos-chem-phys.org/acpd/3/S4/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Fluxes of nitrates between snow surfaces and the atmosphere in the European high arctic" *by* H. J. Beine et al.

E. Wolff (Referee)

e.wolff@bas.ac.uk

Received and published: 16 January 2003

This paper summarise some work on nitrogen compounds (nitrate, nitrite and corresponding acids) in the atmosphere above snow at Ny Alesund. Although the measurements are rather limited in scope (no NOx measurements for example), they provide a nice complement to previous studies at Alert and on the Greenland and Antarctic ice sheets, adding to our knowledge of the complex range of behaviours that these compounds can exhibit over snow. The paper addresses an important topic since snow emissions can have a big effect on the boundary layer over snow, and it is important to determine whether the same effects are seen over snow in all regions. The data can be quite complex to interpret but the authors have done quite a good job of picking out some of the essential measurements so that a coherent picture starts to emerge.

The authors conclude that the form of nitrate in Ny Alesund snow makes it less available for further transformation or emission (compared to other sites). This is an interesting conclusion, but not really well-supported (again in part because of the lack of NOx data, so that assumptions have to be made). The authors may need to downplay their conclusion a little (my comment re page 88/89 refers). I am also a little concerned that the authors make the analysis itself sound routine - I think there are many concerns over how easy it is to measure these compounds, and especially the partitioning between them, with a filter/denuder technique. Perhaps the authors could comment on this (they acknowledge M. Legrand, and he would certainly be able to add comments on this issue). However, otherwise the data make a useful addition to the literature, and apart from a few minor comments and technical issues the paper should be published.

Detailed comments

Page 76, line 8: please clarify early on that negative fluxes are into the snow (the way you have worded this, I would normally have assumed that if a deposition was negative it was an emission)

Page 79: In calculating detection limits, how do you handle the filter packs? You get a number from the Teflon filter, but then presumably there is also a number for each of the backup filters. I don't see how you get an overall detection limit out very easily.

Page 81, line 1. The value you give here (-5.5) cannot be right. On Figure 2, the median looks like about -3. Please check and correct either the text or the figure.

Page 84, line 3: I know you will argue that volatilisation from the snow is not so important, but it's worth mentioning that higher temperatures may also favour volatilisation of HNO3 from the snow.

Page 85 line 29: One possibility is that the increased concentration in the windpacked sub-layer might be due to loss of water vapour (concentrating the remaining ions). Or due to windpumping of ions into the snow.

ACPD

3, S4–S7, 2003

Page 87, line 28 onwards. By doing the calculation this way, you implicitly imply that the same 5 cm of snow is at the surface throughout the winter. You can easily avoid this by going more directly: 8.7 nmol hrˆ-1 mˆ-2 is 1.2 ng cmˆ-2 dayˆ-1. 5 cm of snow at density 0.2 is 1 cmˆ3 cmˆ-2, so the loss in a 5 cm layer is 1.2 ppb/day for the days you observed.

Page 88, last lines/page 89 first lines: Here you assume that because you measured no HONO emissions there are no NOx emissions. This is a very big assumption. There is no particular reason to expect the ratio of the two to be 1:1, since we don?t really have a good mechanism for the HONO, whereas we do for the NOx (so we have no basis to assume the same ratio at Ny Alesund as at Alert). Furthermore your comment that the surface snow content of nitrate did not decrease is irrelevant since the loss elsewhere is almost certainly due to emissions of HNO3 not due to photolysis (photochemical calculations show that the expected loss of nitrate through photolysis is negligible in the snow even though it has a big effect on the boundary layer ? as you comment later). I therefore think you must soft-pedal on all the conclusions that come from this. In particular, you conclude that nitrate in Ny Alesund snow must be bound in a way that the products of photochemistry cannot escape ? this may be correct but I don?t think you have evidence to support it yet.

Page 92, lines 15-20. An additional reason to understand these issues is because it affects how we see nitrate in ice cores from the much dustier last glacial period (see Rothlisberger, R., Hutterli, M.A., Sommer, S., Wolff, E.W. and Mulvaney, R. (2000) Factors controlling nitrate in ice cores: evidence from the Dome C deep ice core. J. Geophys. Res., 105:20565-20572; Rothlisberger, R., Hutterli, M.A., Wolff, E.W., Mulvaney, R., Fischer, H., Bigler, M., Goto-Azuma, K., Hansson, M.E., Ruth, U., Siggaard-Andersen, M.-L. and Steffensen, J.P. (In Press) Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes. Ann. Glaciol., 35,).

I have not checked the Appendix, but hope someone more attuned to this theory has done.

ACPD

3, S4–S7, 2003

Typos and technical comments

Title: Arctic should be capitalised

Page 76, line 6/7: add commas after "fjord" and "species" to make this sentence more easily readable.

Page 78, line 5: "ca. 20 m" - do you mean 20 m altitude, or 20 m from the fjord? Please clarify.

Page 78, line 6: Arctic capitalised.

Page 79, line 8: I think spelling is "Nylasorb"

Page 81, line 18: "during" not "until".

Page 83, line 22: remove comma between pmol and mol.

Page 84, line 17: "south" lower case.

Page 90, line 20: "lose" not "loose".

Reference to Jones et al is in list but not in text.

Table 1: the numbers in the left columns are not aligned to any row ? where do they belong? In the earlier version there were more numbers in these columns, have they been lost?

Fig. 2 and others - I assume the stars and circles are outliers. Please explain this in the caption.

Fig. 3 caption, "<2.5 mum" needs correcting to micrometer symbol.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 75, 2003.