

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

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Reply to Reviewer's comments on

Fluxes of Nitrates Between Snow Surfaces and the Atmosphere in the European High Arctic

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Referees: E. Wolff (W) and J. W. Bottenheim (B)

Both referees comment on the lack of actual NO_x measurements and suggest down-playing the conclusions.

In the specific sections (see below) changes were made; in the conclusions the relevant paragraph now reads: ŞAt Alert and Summit, the snow was acidic. NO₃⁻ was

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thus mainly associated with H^+ . It was probably located on the surface of snow crystals and was available for physical exchanges and for photochemical reactions, that led to HONO and NO_x emissions by the snowpack. At Ny-Ålesund, HONO emission was not observed from alkaline snow. Although fresh snow was often acidic, deposition of sea salt and crustal aerosols in this marine environment made the snow alkaline, and NO₃⁻ was then associated with heavier cations. Although it is not clear whether NO₃⁻ was actually incorporated in the snow crystals or remained within aerosol particles, we suggest that it was not readily available for physical exchange or photochemical reactions. If such reactions did take place, formation and/or release of products was hindered by cage effects or trapping in solids. To confirm whether alkaline snow does not reactivate nitrates or whether photolysis paths and/or products are different, measurements of NO_x fluxes are still necessary.†

Specific comments:

P76, I8: Clarify that negative fluxes are onto the snow (W). Abstract; I7,8; § showed a significant flux on to the snow surface; a mean deposition of $8.7 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$

P79: calculation of detection limits of filter packs (W). Two recent publications (and references therein) concerning denuder/filter measurements in the Arctic discuss the derivation of detection limits at all stages in detail. We have therefore chosen not to reiterate the calculations and details here again. The text now reads: § The L.O.D. for denuder and filter measurements of various particulate and gaseous species (Table 1) are evaluated on the basis of the L.O.D. of the analytical method and of the standard deviations of field blanks [see Beine et al., 2001b and Ianniello et al., 2002 for details].† A. Ianniello, H. J. Beine, R. Sparapani, F. Di Bari, I. Allegrini, J. Fuentes, Denuder measurements of gas and aerosol species above Arctic snow surfaces at Alert 2000. Atmos. Environ., 36(34), 5299–5309, 2002. H. J. Beine, I. Allegrini, R. Sparapani, A. Ianniello, F. Valentini, Three years of springtime trace gas and particle measurement at Ny-Ålesund, Svalbard. Atmos. Environ., 35(21), 3645–3658, 2001.

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P81, I1: discrepancy of delta HNO₃ between text and figure (W). Figure 2 was corrected.

P84, I3: Mention that higher temperatures will favor volatilization of HNO₃ from the snow (W).
§At Ny-Ålesund higher temperatures favor volatilization of HNO₃ from the aerosol and the snow; ¶

P85: Discussion on Snow variability is confusing; Most obvious and likely reason is simply mixing of different snows due to the windy conditions (B). While this would also be our preferred interpretation, we have insufficient evidence to rule out other possibilities, as outlined in the text. The wind hypothesis is very clearly mentioned in the text (p. 8, l. 27-28). The paragraph was reworded to make it more readable.

P85, I29: The increased concentration in the wind-packed sub-layer might be due to loss of water vapor. Or due to wind pumping of ions into the snow (W). Yes, either or both. Certainly air circulation induces sublimation. If NO₃⁻ is present as particles, they will be less affected (or not at all) and their concentration will increase. Alternatively, snow will filter out particles and trap NO₃⁻ containing coarse particles. We have added, ¶This can be explained by sublimation induced by air circulation. If NO₃⁻ is present in particulate form as particles, it will not be affected by sublimation and its concentration will increase. Alternatively, it can also be suggested that the snow filtered out NO₃⁻ containing particles.¶

P85, bottom; the May 4 wind packed sub layer showed increase in NO₃⁻ concentration; interesting observation that could warrant more discussion about how this came about. (B) As we say on p 87, l 23 ¶Therefore surface snow that has been exposed to sea salt is a good sink for HNO₃. Deeper snow layers may remain acidic and release HNO₃, which immediately gets trapped in the alkaline surface layer.¶ Also see response to W's comment above.

P86, bottom: it seems unwarranted in light of the discussion p85, l8/9 that surface snow had the same NO₃⁻ content than falling snow. Since there are no measurements

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of falling snow this should be mentioned (B). On 29 april, it snowed the whole day. At 13:00, FD sampled surface snow, while snow was falling. So this is as close as we got to sampling falling snow. We reckon that the sampled snow had been on the ground for less than 1 hour. The nitrate content was 140 ± 9 ppb. This is hereafter called the 'middle layer', and, from Fig 5b, its nitrate content did not show any significant variation after that, so that we can essentially say that the nitrate content of the 29 april layer was determined by the initial content of the snow, + what was wet-scavenged during precipitation. Dry deposition after that did not result in a significant increase in snow nitrate, as evidenced by Fig 5b. But again, we do have noisy data. Regarding dry dep, it is obvious that the physical process did take place but affected other species, such as sea salt. This 29 april snow was initially very poor in sea salt: 17 ± 10 ppbw of Cl^- for the middle layer, sampled fresh at 13:00, and 68 ± 11 ppbw of Cl^- for the top layer, sampled fresh at 18:30. After that, the NaCl content of the snow increased very fast for the top layer, exposed to the atmosphere: 905 ± 112 on 30 april, 10:30, and 1302 ± 153 ppbw Cl^- on 30 april, at 14h. The increase for the unexposed middle layer was on the contrary, insignificant. We changed the text slightly: 'The nitrate content in the falling snow corresponds to the surface snow layers later sampled; We sampled on April 29 surface snow while snow was still falling, and hence saw a good approximation of falling snow. The NO_3^- content of this surface snow did not change afterwards.'

P87, l28 on: imply that the same 5 cm of snow are at the surface throughout winter. More direct way: $8.7 \text{ nmol hr}^{-1} \text{ m}^{-2} = 1.2 \text{ ng cm}^{-2} \text{ day}^{-1}$. 5 cm of snow at density 0.2 is $1 \text{ cm}^3 \text{ cm}^{-2}$. The loss in a 5 cm layer is thus 1.2 ppb/day for the observed days (W). The paragraph was changed: 'Under the crude assumption that our observed mean HNO_3 fluxes hold true for an entire winter season (September to May) we can assess the influence of this atmospheric deposition to the snow surface. The accumulation of snow NO_3^- from atmospheric HNO_3 was on the order of $8.7 \text{ nmol hr}^{-1} \text{ m}^{-2}$, or $1.2 \text{ ng cm}^{-2} \text{ day}^{-1}$. If this affected the surface layer (top 5 cm) of the snow, of mean density of 0.2 g cm^{-3} , the increase was $1.2 \text{ ppbw (ng/g) day}^{-1}$. This change is virtually impossible to detect in the snow.'

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P88, last; p89, first lines: Big assumption that NO_x and HONO fluxes are equal. Mechanism for NO_x is understood, but not for HONO; and there is no particular reason that these two should be emitted 1:1. The discussion is revised for this; the initial statement now reads: HONO emissions were observed at both Alert and Summit [Zhou et al., 2001; Honrath et al., 2002] and were attributed to the photolysis of the nitrate ion contained in snow, and subsequent reaction of the primary photolysis products with water in the acidic snow environment. NO_x at Alert was also produced by nitrate photolysis in the snow in a ratio NO_x : HONO of 1:1 [Beine et al., 2002a], however, it is conceivable that in the alkaline snow environment of Ny-Ålesund HONO formation from primary photolysis products was not occurring. No measurements of NO_x were made during the spring of 2001 at Ny-Ålesund. If, however, the release mechanisms and ratios are similar at Ny-Ålesund to those at Alert, we may speculate that NO_x was not emitted from the snowpack at Ny-Ålesund. Further; comment that surface snow content of nitrate did not decrease is irrelevant, since loss elsewhere is certainly due to emissions of HNO₃, not due to photolysis. We have shown that at Alert up to 45% of HNO₃ is released by photolysis, and not directly as HNO₃ [H. J. Beine, R. E. Honrath, F. Dominé, W. R. Simpson, J. D. Fuentes, NO_x During Background and Ozone Depletion Periods at Alert: Fluxes Above the Snow Surface. J. Geophys. Res., 107(D21), 4584, doi:10.1029/2002JD002082, 12 Nov. 2002.]. The discussion on page 89 does not relate only to the loss of HNO₃ through photolysis, but to any loss of HNO₃ (or the lack thereof). Soften conclusions; in particular that nitrate at Ny-Ålesund must be bound in a way that the products of photochemistry cannot escape. (may be correct, but don't yet have evidence to support it) (W). This particular result is not derived from the assumption that NO_x emissions are zero or that HNO₃ is lost through photolysis, but through the discussion of the observed fact that surface NO₃- concentration do not change with time, even though the specific surface area of the snow does. Hence we feel that the suggestion of a Scage effect is valid, and may be discussed with our data. We have, however, softened the language of the discussion. P90; if the snow on 4/29 was initially acidic would we not have expected to see a flux of NO_y out from the

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snow, at least for a day or so after the fall? (B) Indeed, this is an interesting suggestion. It turns out that by DOY 120.6 the surface snow was alkaline; the snow fell on April 28 and 29 (DOY 118, 119), and during times of snow precipitation the denuders do not always work reliably (snow gets sucked in the denuders). We have thus one single set of denuder measurements for DHONO for the time in question. This was a 24h sample, centered around DOY 119.9, and DHONO was 0 pmol/mol. Since it includes the transition of the surface snow from acidic to alkaline we would regard this sample as inconclusive with respect to the question.

P92, l15-20: Additional reason to understand these issues because it affects how we see nitrate in ice cores from the much dustier last glacial period (Rothlisberger et al., JGR 105, 20,565, 2000; Ann.Glaciol., 35, in press) (W). A sentence & references were added.

P92, l24. fact that pH appears to influence NO_y emissions does not confirm, but at most supports suggestions by Dominé & Shepson (B). Wording was changed.

Edits

Add a table w/ units & conversion factors to ease reading (B)

Atmospheric values and fluxes are expressed in mixing ratios and mol/h m⁻²; while snow values are expressed in ng/g. To compare them to each other, atmospheric mixing ratios were converted to concentrations. Since this requires the knowledge of p and T for each datapoint, there is no easy conversion factor. The conversion equations can further be found in any introductory text for Atmospheric Chemistry.

Replace Šwet depositionŤ with Šprecipitation scavengingŤ (B) A sentence was added: Š(in this work the term Šwet depositionŠ includes all precipitation scavenging).Ť

Title: Cap. Arctic (W). I agree; it was capitalized in the original manuscript that we submitted

P76, l6/7: add commas after ŠfjordŠ, ŠspeciesŠ (W) Commas added

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P78, l5: 20 m ŠĚca. 20 m distance from the fjordĚĚ

P78, l6: cap. Arctic (W) ĚAs in the title

P79, l8: ŠNylasorbĚ (W) changed

P81, l18: ŠduringŠ, not until (W) ŠĚ increased only slightly until the beginning of the light intensive,ĚĚ

P83, l22: remove comma between pmol & mol (W) removed

P84, l17: lower case ŠsouthŠ (W) changed

P90, l20: ŠloseŠ (W) changed

REF: Jones et al in list, but not text. corrected

Table 1: first 2 columns; alignment? (W) The table was corrected

Fig. 2: explain box-and-whisker plot symbols (W) The box-and-whisker plot is explained in caption to Fig. 1

Fig. 3, caption, correct to um symbol (W) mm

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

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