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## Microorganisms in dry polar snow are involved in the exchanges of nitrogen oxides with the atmosphere

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### 15 **Abstract**

The snowpack is a complex photochemical reactor that emits a wide variety of reactive molecules to the atmosphere. In particular, the photolysis of nitrate ions, NO<sub>3</sub><sup>-</sup>, produces NO, NO<sub>2</sub> and HONO, which affects the atmospheric oxidative capacity. We report measurements in the European High Arctic which reveal that microbial activity in dry snow also results in the emission of these reactive nitrogen species. NO, NO<sub>2</sub> and HONO production can therefore take place in the absence of sunlight, so that snow chemistry can affect atmospheric composition year-round. Furthermore, isotopic measurements indicate that microbial activity affects the budgets of nitrate and nitrite in the snow, demonstrating that dry snow can play a major role in the biogeochemical cycling of reactive nitrogen.

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30 Snow on the ground is an essential component of the climate system. It has an obvious impact on the  
radiative balance of the Earth's surface, the hydrology of snow-covered catchments and the activity of  
cold regions ecosystems. Snow is known to be a very active photochemical reactor, to the point that it  
significantly affects the reactive chemistry of the overlying atmosphere in remote regions (1,2). In  
particular, reactive nitrogen in snow ( $N_{RS}=NO_3^- + NO_2^-$ ) undergoes major transformations in the snow,  
35 from its atmospheric deposition mostly in the form of nitrate ions to the emission of reactive molecules  
to the atmosphere ( $N_{RA}=NO + NO_2 + HONO$ ). Snow therefore contributes to the biogeochemical  
cycling of reactive nitrogen, which exerts a strong influence on the Earth's surface as a key nutrient for  
many remote ecosystems.

Despite numerous field campaigns and laboratory investigations (2), many aspects of the processes  
leading to snow emissions of  $NO_x (=NO + NO_2)$  and HONO remain unclear, largely because we do not  
40 understand the interactions between  $N_{RS}$  chemistry and other snow chemical variables such as  
alkalinity and its content in organic species (2,3). Biotic contributions to the cycling of  $N_{RS}$  have so far  
been simply ignored, because they were never unambiguously detected under cold polar conditions.

To shed some new light on snow  $N_{RS}$  reactivity, we carried out a field campaign at Ny-Ålesund,  
Svalbard (78°55 N, 11°55 E, sea-level) in the European Arctic, from February to April 2006. We  
45 measured the fluxes of NO,  $NO_2$ , HONO and  $HNO_3$  between the snow and the atmosphere, the  
chemical composition of the snow in mineral ions, and the isotopic composition of nitrate and nitrite in  
the atmosphere and in the snow, The conditions ranged from complete darkness in February to  
permanent sunlight in April. We observed  $NO_x$  and HONO emissions in the dark, implying that a non-  
photochemical source exists. The isotopic ratios of  $NO_3^-$  and  $NO_2^-$  in snow indicate that this source is  
50 microbial cycling of  $N_{RS}$  in the snow.

Measurements were carried out at the Ny-Ålesund International Arctic Research and Monitoring  
Facility, at about 400 m from the coast, between 19 February (DOY 50) and 21 April (DOY 111) 2006.  
Fluxes were derived from independent chemical measurements of HONO,  $HNO_3$ , NO and  $NO_2$  at two  
55 sampling heights above the snow surface (25 and 150 cm) and simultaneous measurements of  
atmospheric turbulence and temperature at the same locations (see Supplementary Online Material,  
SOM).

Triplicate samples of near-surface snow layers were obtained daily for on-site analysis of mineral ions  
using ion chromatography. The ionic balance was used to estimate the pH of the melted snow. Deeper  
layers were sampled less frequently. The  $^{15}N/^{14}N$ ,  $^{17}O/^{16}O$  and  $^{18}O/^{16}O$  isotopic ratios of nitrate and  
60 nitrite were measured in a fraction of the snow layers and in atmospheric samples (see SOM for  
details).

Winter and spring 2006 at Ny-Ålesund were exceptionally warm. The monthly mean temperatures  
from January to May were 10.7, 3.8, 1.4, 10.3, and 4.2°C above means since 1969 (4). Relevant  
consequences include: (1) the icepack did not form near Ny-Ålesund; (2) heavy rains in January led to  
65 the formation of an ice layer up to 20 cm thick at the base of the snowpack all over our study area,  
totally isolating the ground from the atmosphere. Many melt-freeze structures were also present in the

snowpack, mostly near the base. During the campaign, snow temperature never reached 0°C, as detailed in the SOM.

70 Median values of HONO, HNO<sub>3</sub>, NO and NO<sub>2</sub> atmospheric mixing ratios during the campaign were 4.2, 1.8, 1.8 and 20.2 pmol/mol (pptv). These values are within the ranges found for these species in the coastal Arctic boundary layer at this time of year, in the absence of ozone depletion events (5). Fluxes of these gases are shown in Figure 1. NO<sub>2</sub> and NO fluxes are almost always positive, and the only episode with significantly negative fluxes (DOY 103) is discussed subsequently. HONO fluxes are mostly positive, while HNO<sub>3</sub> fluxes are mostly negative as observed at other polar sites.

75 Surprisingly, fluxes of NO, NO<sub>2</sub> and HONO coming out of the snow are observed in the absence or near absence of sunlight (Figure 1), and the magnitude of fluxes in February, with zero sunlight, and early March (DOY 50 to 75) was similar to that in early April (DOY>90), with 24 hours sunlight. Our data therefore demonstrate the existence of a non-photochemical source of NO<sub>x</sub> and HONO from the snow to the atmosphere.

80 At this coastal site, the snow had a marked marine signature and Na<sup>+</sup> and Cl<sup>-</sup> dominated snow ionic composition, with Na<sup>+</sup> concentrations up to 2.7 mM. The Na<sup>+</sup>/Cl<sup>-</sup> ratio was within 5% of the sea salt ratio of 1.165 for >95% of the samples. Terrigenous dust also impacted snow composition, as expected from the ubiquitous outcrops of sedimentary rocks all over Spitsbergen. Plots of Ca<sup>2+</sup> vs. Na<sup>+</sup>, and a comparison with sea salt ratios indicate that dust contributed up to 50 % of the snow Ca<sup>2+</sup>.  
85 As a result of those inputs of sea salt and dust, the ionic balance of snow revealed a marked alkaline character for almost all snow samples.

NO<sub>3</sub><sup>-</sup> concentrations ranged from 0.5 to 4 μM, except a few samples reaching 14 μM. A noteworthy observations is the unusually high NO<sub>2</sub><sup>-</sup> concentrations. Although about half of all values were below 1 μM, many values were between 1 and 5 μM, with some values reaching 10 μM. NO<sub>2</sub><sup>-</sup> was correlated to Na<sup>+</sup> and Ca<sup>2+</sup>, but not to non-sea-salt Ca<sup>2+</sup>, suggesting that NO<sub>2</sub><sup>-</sup> was associated with sea salt particles in the snow. Over half of the NH<sub>4</sub><sup>+</sup> snow concentrations were below detection limit (0.1 μM). Most other values were between 0.1 and 3.1 μM, and the highest value was 11 μM. NH<sub>4</sub><sup>+</sup> concentrations showed no significant correlation with any other ion.

95 The oxygen and nitrogen isotopic composition of N<sub>RS</sub> (nitrate and nitrite in the snow) provide diagnostic information on its source (6, 7). The oxygen isotopic composition of N<sub>RS</sub> is reduced here to the oxygen anomaly Δ<sup>17</sup>O (or <sup>17</sup>O excess), defined as the deviation from the terrestrial fractionation line (Δ<sup>17</sup>O = δ<sup>17</sup>O - 0.52 δ<sup>18</sup>O). Briefly, only deposition of atmospheric nitrate to the snow can induce a positive Δ<sup>17</sup>O in N<sub>RS</sub>, because atmospheric nitrate stems from interactions between ozone (possessing a high Δ<sup>17</sup>O) and NO<sub>x</sub> (6, 7). The deposition of atmospheric nitrite contributes negligibly to the budget of N<sub>RS</sub>. Δ<sup>17</sup>O values for tropospheric nitrate range from 20 to 40 ‰ (7, 8). If nitrate or nitrite are produced under non-atmospheric conditions, their O atoms originate from H<sub>2</sub>O and/or O<sub>2</sub>, and therefore the Δ<sup>17</sup>O signature is between 0 and -0.3 ‰. In contrast to δ<sup>17</sup>O and δ<sup>18</sup>O, Δ<sup>17</sup>O is not modified by mass-dependent fractionation, which makes it a powerful tracer of atmospheric nitrate  
100

input to marine and terrestrial ecosystems (6). The nitrogen isotopic ratio ( $\delta^{15}\text{N}$ ) traces the origin of N  
105 (6, 8).

$\Delta^{17}\text{O}$  of atmospheric nitrate at Ny-Ålesund during February to April 2006 ranged between 31 and 37‰  
(8 and Fig. 2).  $\Delta^{17}\text{O}$  ( $N_{\text{RS}}$ ) spanned a much wider range: 3 to 37 ‰. The monthly averages of  
 $\delta^{15}\text{N}(N_{\text{RS}})$  were -17, -12 and -14‰ in February, March and April, respectively (8). Measurements in the  
110 snow ranged between -14 and 3‰, in agreement with previous studies (9-11). Plotting snow  $\Delta^{17}\text{O}$  vs.  
 $\delta^{15}\text{N}$  (Fig. 2) reveals that the isotopic composition of  $N_{\text{RS}}$  is well described by the mixing of two widely  
different reservoirs, possessing end-members compositions that are about (-13 ‰; 36 ‰) and (5 ‰; 0  
‰) in the  $\delta^{15}\text{N} \times \Delta^{17}\text{O}$  space. While the first end-member obviously corresponds to the deposition of  
atmospheric nitrate, the isotopic data clearly confirms the existence of another source of  $N_{\text{RS}}$  within the  
115 snowpack, possessing a zero  $\Delta^{17}\text{O}$  and a positive  $\delta^{15}\text{N}$  ( $\approx 5\text{‰}$ ), which represents almost 100% of the  
burden of some snow layers. This observation contrasts with measurements from polar ice-caps,  
where the isotopic data could be explained with just an atmospheric nitrate source (12).

Explaining our observations requires a mechanism that produces nitrate and/or nitrite within the  
snowpack. Nitrification, i.e. the oxidation of ammonium to nitrite and then nitrate by micro-organisms  
acting in cascade (13), has been recognized as the most probable non-atmospheric source of  $N_{\text{RS}}$  in  
120 the Arctic subglacial environment (11) or in the snow (14). Ammonium can originate from various  
reservoirs with different  $\delta^{15}\text{N}$ : ammonification of organic nitrogen (-4.8 to -3.3 ‰), clay particles (-1.6 to  
7.7 ‰), atmospheric deposition ( $\delta^{15}\text{N}$  of ammonium in the snow is -5.8 and -1.7 ‰) (11). Assuming  
that isotopic fractionation during nitrification has a negligible impact given the low availability of  
ammonium (6, 11), the only source of ammonium consistent with the observations is the clay particles  
125 that originate from outcrops in the vicinity of the sampling site through atmospheric deposition onto  
snow surfaces. We therefore propose that the oxidation of clay-bound ammonium occurs at a  
significant rate in this Arctic snowpack. We now need to discuss the likelihood of a microbial  
metabolism leading to nitrite and nitrate production in the snow, and how it can explain the gas fluxes  
of Fig. 1.

130 Bacteria involved in the transformation of  $N_{\text{RS}}$  are common in aquatic and terrestrial environments of  
cold to tropical regions (15). An array of autotrophic, ammonium oxidizing bacteria (AOB), and  
archaea (AOA), have the ability to oxidize  $\text{NH}_4^+$  into  $\text{NO}_2^-$  (13). During this first step of nitrification, NO  
can be either released as such (16), and thus account for the observed NO fluxes (Fig. 3), or further  
reduced into  $\text{N}_2\text{O}$ , depending on  $\text{O}_2$  availability (17). Nitrite can further be oxidized to nitrate by nitrite  
135 oxidizing bacteria (NOB) that likely live in close symbiosis with AOB or AOA during nitrification (18).  
AOB, AOA and NOB metabolism can thus explain the presence of  $N_{\text{RS}}$  with a non-atmospheric  
isotopic signature.

An alternative biological pathway for NO production is denitrification under oxygen-limited conditions,  
i.e. the respiratory reduction of  $\text{NO}_3^-$  into  $\text{NO}_2^-$ , and then into NO,  $\text{N}_2\text{O}$  and finally  $\text{N}_2$  (12 and Fig.3).  
140 Since the snowpack volume is ventilated, and because snow crystals were at the most 1 mm in size,  
this may seem unlikely. However, it is known that in natural biofilms or soils, oxic and anoxic

microenvironments co-exist within submillimetric distances (20). Such short distance redox variations can be imagined in snow, with bacteria surrounded by organic particles or trapped within ice crystals, with sufficiently low  $O_2$  partial pressure to allow anoxic oxidation pathways. In any case, the presence  
145 of denitrifying bacteria or fungi is not mandatory to explain our observations of NO fluxes in the dark, as AOA or AOB activity suffices (21).

NO may be oxydized in snowpack interstitial air by  $O_3$  in a few minutes to explain  $NO_2$  fluxes (Fig.1 & 3). In acidic media,  $NO_2^-$  can be released to the atmosphere as HONO. Because of the ubiquity of sea salt and of mineral dust, our bulk snow samples were alkaline, but we hypothesize that in the vicinity  
150 of bacteria, acidic microenvironments exist because ammonium oxidation produces  $H^+$ . A fraction of the HONO produced can be captured by sea salt particles trapped in the snow, which explains the large  $NO_2^-$  concentrations and the correlation to sea salt.

Bacteria can therefore explain emissions of NO,  $NO_2$  and HONO in the dark.  $NO_3^-$ , produced by nitrifying bacteria can be released to the atmosphere as  $HNO_3$  in acidic media, thus explaining  
155 snowpack  $HNO_3$  emissions in the dark.

As enzymes require the presence of liquid water for catalysis, it could be argued that no bacterial activity could have taken place, since snow temperatures remained negative. However, biomass increase and tannin catabolism in alpine soils at  $-6^\circ C$  have been reported (22). Furthermore, Price and Sowers (23) compiled evidences for metabolically active bacteria and fungi at temperatures down to -  
160  $40^\circ C$ . The study of  $N_2O$  in Antarctic ice cores has led to the discovery of artifacts (24) correlated with high concentrations of dust and high bacterial counts. It was therefore suggested that metabolically active bacteria, presumably brought to the ice caps with the dust, had produced sufficient  $N_2O$  over the years to alter the composition of the archived air.

Uptake of atmospheric HONO and  $HNO_3$  were occasionally observed (Fig.1), which cannot be  
165 accounted for by biological processes. In Italy, large uptakes of atmospheric HONO have been reported in snow that was rendered alkaline by the deposition of Saharan dust (25). A similar uptake may be invoked for our alkaline snowpack. Photochemical  $N_{RA}$  production is not expected to be important in alkaline snow (26, 27).

Regarding the uptake of  $NO_2$  uptake by snow on DOY 103, we propose that this was caused by the  
170 reaction of  $NO_2$  with organic particles (28) deposited to the snow. On DOY 103, an unusually high concentration of organic aerosols was observed at Ny-Ålesund, caused by a biomass burning plume from central Europe. That negative  $NO_2$  flux indeed coincides with a positive flux of HONO, the expected product of such reactions.

A quantitative test of the role of microbes in the observed fluxes would require the identification and  
175 quantification of bacteria in the snow samples studied. The involvement of microorganisms was totally unexpected and such studies will require further campaigns. However, bacteria have been found in summer snow near Ny-Ålesund (29). Wynn et al. (11) described nitrifying bacteria in the subglacial hydrosphere near Ny-Ålesund, and it is easy to suggest that such bacteria can be transported to wind-exposed soils by proglacial streams and from there onto the snow by wind.

180 Further work is needed to assess the geographical extent of bacterial involvement in  $N_{RS}$  cycling in dry  
snow. Available data on  $N_{RA}$  fluxes to the atmosphere suggest that it does not take place in much  
colder places such as Alert (Canadian High Arctic, 82°N, 26) and in places much poorer in nutrients  
such as Summit (Greenland, 72°N, 3250 m a.s.l., 12). However, the processes detected here could be  
widespread in moderately cold seasonal snowpacks, both in Arctic and Alpine settings. In non-alkaline  
185 snow however, such bacterial activity may not lead to increases in  $NO_2^-$  concentrations in snow,  
because it may be immediately released to the atmosphere as HONO. Bacterial activity in snow could  
also lead to  $N_2O$  emissions that are expected along the same metabolic pathways. Biologically-  
mediated  $N_2O$  emissions from the Earth's surface could therefore occur year round in cold and remote  
environments, helping close the currently unbalanced  $N_2O$  budget (30).

190 **References**

1. F. Dominé, P.B. Shepson, *Science* **297**, 1506 (2002).
2. A.M. Grannas *et al.*, *Atmos. Chem. Phys.* **7**, 4329, (2007).
3. F. Domine *et al.*, *Atmos. Chem. Phys.* **8**, 171 (2008).
4. A. Stohl *et al.*, *Atmos. Chem. Phys.* **7**, 511 (2008).
- 195 5. H.J. Beine, D. A. Jaffe, J. A. Herring, J. A. Kelley, T. Krognes, F. Stordal, *J. Atmos. Chem.* **27**, 127 (1997).
7. S. Morin *et al.*, *Science* **322**, 730, (2008); 10.1126/science. 1161910.
8. S. Morin *et al.*, *Geophys. Res.* **114**, D05303 (2009); 10.1029/2008JD010696.
9. T. H. E. Heaton, P. Wynn, A. Tye, *Atmos. Environ.* **38**, 5611 (2004);  
200 10.1016/j.atmosenv.2004.06.028.
10. P. M. Wynn, A. Hodson, T.H.E Heaton, *Biogeochemistry* **78**, 173 (2006); doi:10.1007/s10533-005-3832-0.
11. P. M. Wynn, A. Hodson, T.H.E Heaton, S.R. Chenery, *Chem. Geol.* **244**, 88 (2007).
12. S. A. Kunasek *et al.*, *J. Geophys. Res.* **113**, D24302 (2008); 10.1029/2008JD010103.
- 205 13. M. G. Klotz, L.Y. Stein, *FEMS Microbiol. Lett.* **278**, 146 (2008).
14. J. L. Wadham, K. R. Hallam, J. Hawkins, A.O'Connor, *Tellus* **598**, 229 (2006); 10.1111/j.1600-0889.2006.00180.x.
15. B. B. Ward, *Internat. J. Earth Space* **3**, 25 (1996).
16. D. Zart, I. Schmidt, E. Bock, *Antonie van Leeuwenhoek* **77**, 49 (2000).
- 210 17. A. Bollmann, R. Conrad, *Global Change Biology* **4**, 387 (1998).
18. D. J. Arp, P. J. Bottomley, *Microbe* **1**, 229 (2006).
19. W. G. Zumft, *Microb. Mol. Biol. Rev.* **61**, 533 (1997).
20. L. J. Monrozier L. *et al.*, *Sci. Total Environ.* **136**, 121 (1993).
21. R. Conrad, *Microbiol. Reviews* **60**, 609, (1996).
- 215 22. F. Baptist *et al.*, *Environ. Microbiol.* **10**, 799 (2008).
23. P.B. Price, T. Sowers, *Proc. Natl. Acad. Sci. USA* **101**, 4631 (2004).
24. T. Sowers, *J. Geophys. Res.* **106**, 31903 (2001).
25. H. J. Beine *et al.*, *Geophys. Res. Lett.* **32**, L10808 (2005); 10.1029/2005GL022589.
26. H. J. Beine, R. E. Honrath, F. Dominé, W. R. Simpson, J. D. Fuentes, *J. Geophys. Res.* **107**, 4584,  
220 (2002); 10.1029/2002JD002082.



27. H. J. Beine *et al.*, *Atmos. Chem. Phys.* **6**, 2569-2580, (2006); 1680-7324/acp/2006-6-2569.

28. K. Stemmler *et al.*, *Atmos. Chem. Phys.* **7**, 4237 (2007).

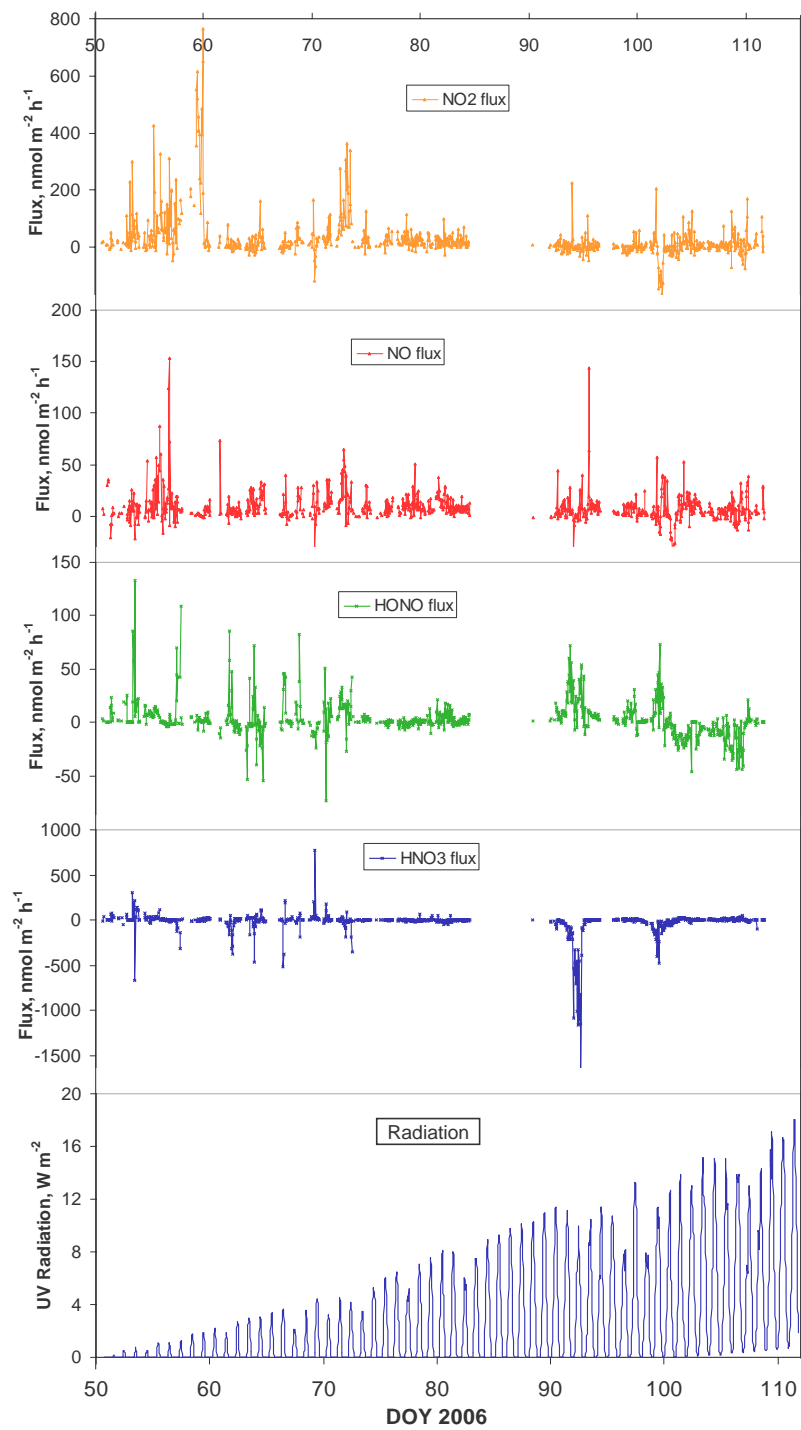
29. P. Amato *et al.*, *FEMS Microbiol. Ecol.* **59**, 255 (2007); 10.1111/j.1574-6941.2006.00198.x.

30. IPCC, *Climate Change 2007: Synthesis report*, (Cambridge Univ. Press, 2007).

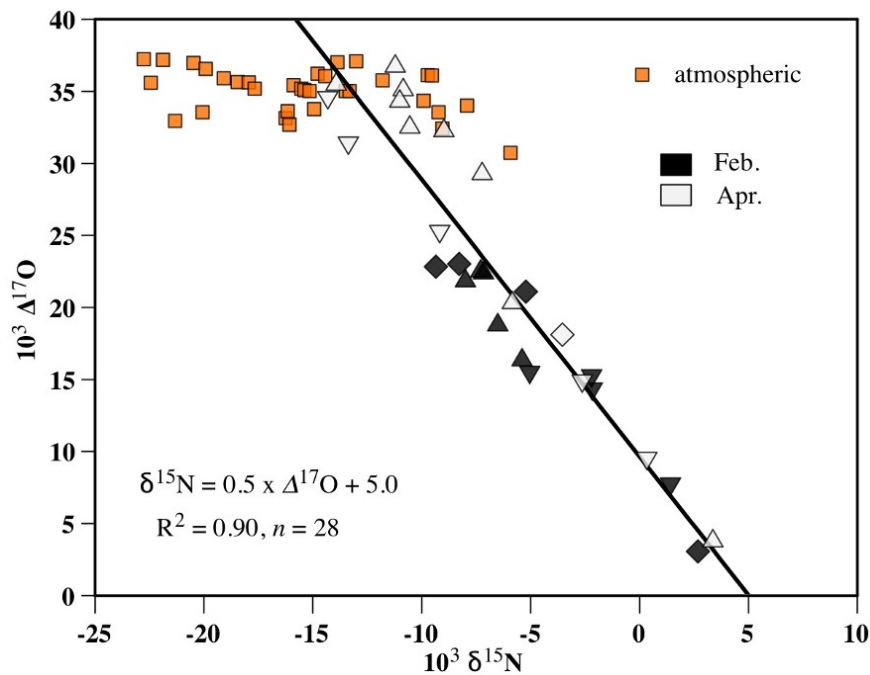
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## Figures

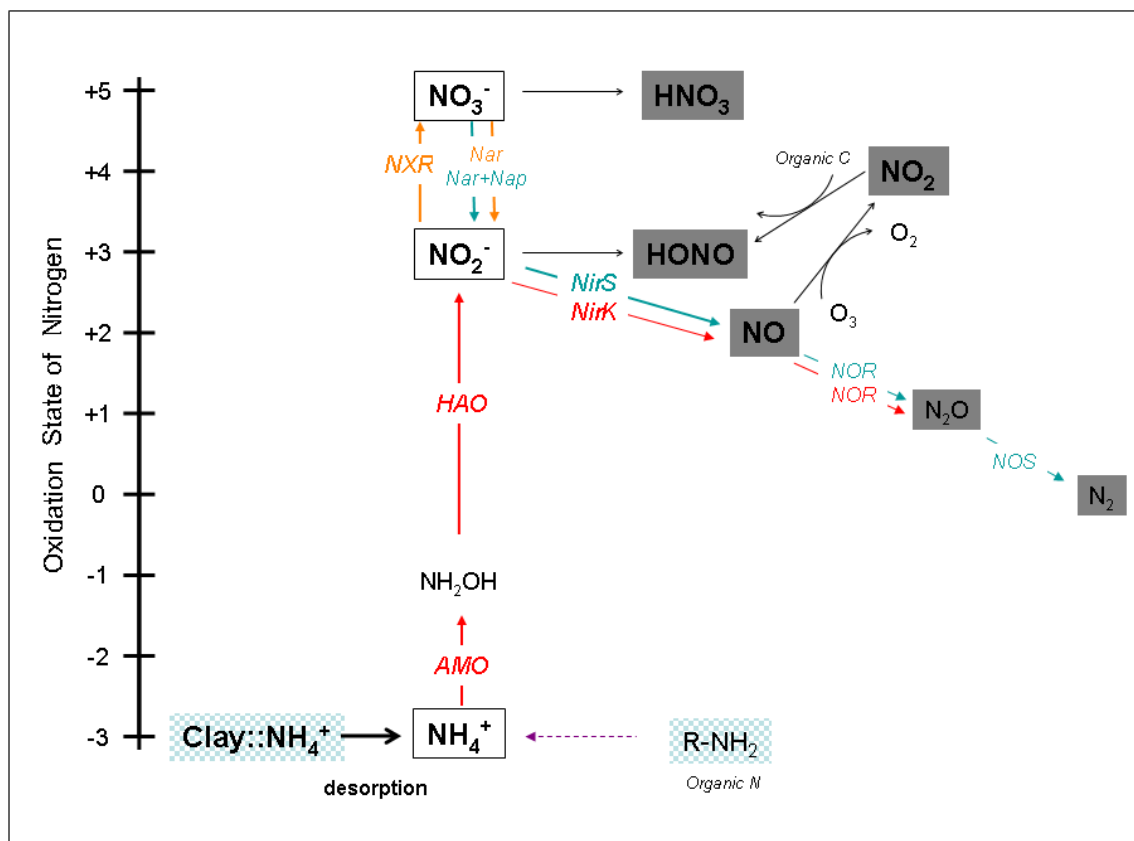


240 Figure 1. Time series of the fluxes of NO<sub>2</sub>, NO, HONO and HNO<sub>3</sub>, and of UV radiation. Positive fluxes are emissions by the snow, negative fluxes uptake by the snow.



245 Figure 2.  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  of  $\text{N}_{\text{RS}}$  (nitrate and nitrite) in the snow and of particulate nitrate in the atmosphere at Ny-Ålesund. Atmospheric data are represented as orange squares.  $\text{N}_{\text{RS}}$  is segregated as a function of depth in the snowpack (upward facing triangle: surface; diamonds: subsurface; downward facing triangles: bottom. Black (white) symbols represent samples collected in February (April). The variations in  $\text{N}_{\text{RS}}$  isotopic composition is interpreted as caused by the mixing between a reservoir of atmospheric origin and another reservoir produced by the biologically-mediated oxidation of ammonium to nitrite and nitrate in the snow.

250



255 Figure 3. Non-photochemical processes proposed to take place within the snowpack and leading to  
 the release of  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{HONO}$  and  $\text{HNO}_3$  to the atmosphere. Grey boxes: gaseous N forms; white  
 260 boxes: N ionic forms metabolized by microorganisms; checkerboard boxes: N forms contained in  
 particles trapped in the snow. Colored arrows denote biochemical reactions catalysed by three soil  
 bacteria whose genomes have been sequenced: red (*Nitrosomonas europaea*, an AOB), orange  
 (*Nitrobacter winogradskyi*, a NOB), and blue (*Pseudomonas stutzeri*, a denitrifier). The corresponding  
 enzyme names are in italics: *AMO*, ammonium monooxygenase; *HAO*, hydroxylamine  
 265 oxidoreductase; *NXR*, nitrite oxidoreductase. The blue arrows constitute the denitrification pathway  
 (*Nap*, *Nar*: periplasmic- and respiratory nitrate reductases, respectively; *NirK*, *NirS*:  $\text{Cu}^{2+}$ - and  
 cytochrome cd1 nitrite reductases; *NOR*: nitrous oxide reductase; *NOS*: nitrous oxide reductase).  $\text{NO}$   
 and  $\text{N}_2\text{O}$  can be produced by either denitrifying or nitrifying organisms. **Black** arrows denote abiotic  
 reactions: given adequate pH,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  can be released as  $\text{HONO}$  and  $\text{HNO}_3$ .  $\text{NO}$  can be  
 oxidized within minutes to  $\text{NO}_2$  by  $\text{O}_3$  in snowpack interstitial air.  $\text{HONO}$  can also be produced from  
 $\text{NO}_2$  and organic matter (see text).  $\text{HONO}$ ,  $\text{NO}$  and  $\text{NO}_2$  can therefore be emitted by the snow without  
 photochemistry.