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Evidence for a snowpack biological source of NO_x and HONO to the Arctic boundary layer in Svalbard

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Nitrogen oxides (NO + NO_2) and HONO are among the most reactive species in the polar boundary layer. About a decade ago, the discovery of photochemical production of NO_x and HONO in the polar snowpack forced us to consider the role of snowpack emissions to understand the composition of the polar boundary layer. Here we present evidence that NO_x and HONO can be emitted by the snowpack to the polar boundary layer in the absence of sunlight. NO_x and HONO fluxes were measured at Ny Alesund, Svalbard (79°N) from mid February (no sunlight) to late April (24 h sunlight). Values were mostly positive (i.e. species transferred from snow to atmosphere) and up to 800 and 120 nmol m^{-2} h^{-1}, respectively, with the highest values observed in the near absence of sunlight. Mineral ions in surface snow were also analyzed continuously, and snow chemistry data led us to suspect that bacteria were involved in those emissions. The measurements of nitrate isotopic data ($\delta^{15}N$ and $\Delta^{17}O$) confirmed that a large fraction of nitrate in most snow layers was not of atmospheric origin, and our interpretation is that is was produced from ammonium by nitrifying bacteria. NO_2^- is an intermediate in nitrification, and can lead to NO emission by bacteria. NO can be rapidly oxidized to NO_2 by ozone in the snowpack. Physical release of HONO from NO_2^- by the snow also takes place. We therefore suggest that microbial activity in cold snowpacks can lead to the release of significant amounts of reactive species, and deserves consideration in the understanding of polar boundary chemistry and of polar snow chemistry.