

Snow atmospheric fluxes of reactive nitrogen species in the European high Arctic

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Introduction

Atmospheric nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), emitted from fossil fuel combustion, biomass burning, soil microbial activity, and lightning with a small contribution from downward transport from the stratosphere and high-flying aircraft, have adverse respiratory effects, contribute to the formation of atmospheric acidity, and play a pivotal role in regulating the oxidative capacity through their connections to ozone (O_3) and hydroxyl radical (OH).

Previous studies in the Arctic, Antarctic, and at mid-latitudes have demonstrated that the sunlit polar snowpack is an active reactor, where previously deposited chemical species can undergo photochemical processes that subsequently result in an efflux of trace gases to the overlying atmosphere, altering its composition and oxidative capacity with important implications for climate processes, including atmospheric oxidation and aerosol formation. In particular, the photochemical production of nitrogen oxides (NO_x) and nitrous acid (HONO) by nitrate (NO_3^-) photolysis within or at the surface of snowpack can significantly impact the NO_x , radical species (OH_x), and ozone (O_3) budgets in the overlying atmosphere and alter the preservation and concentration of trace species such as hydrogen peroxide (H_2O_2) and NO_3^- in ice cores (Beine et al. 2006; Björkman et al. 2014; Ianniello et al. 2016; Spataro et al. 2016). Factors known to affect the release of chemicals include the physical properties of snow, such as temperature, pH, ionic strength and specific surface area (SSA). However, the quantitative understandings of NO_x emissions from snow is still incomplete, but it is a research priority to be able to parameterize global chemistry climate models to assess for example global impacts of chemical air–snow exchange on tropospheric O_3 . In addition, knowledge of the natural background concentration and main sources of reactive nitrogen species ($\text{NO}_y = \text{NO}_x + \text{HNO}_3 + \text{HONO} + \text{particulate } \text{NO}_3^- + \text{PAN} + \text{etc.}$) is pivotal in determining their influence and the impact of human activity on the atmospheric photochemistry and on ecosystems in polar environments. Observations on atmospheric chemistry of NO_y in the global atmosphere are limited, in particular, in the polar regions due to limited sensibility of sampling techniques, and to a general lack of comparable measurements of NO_x emissions from surface snow across a wide range of environmental conditions. Hence, a better understanding of these processes controlling the fate of NO_y in the polar regions is needed.

As part of the PRIN2007 (“Dirigibile Italia”), PRIN2009 (“Arctica”) and ARCA projects, measurements of atmospheric concentrations and fluxes of reactive nitrogen species (NO , NO_2 , NO_x , HONO , HNO_3 and particulate NO_3^-), and chemical and physical properties of snow were carried out during spring time 2010 and 2011 at Ny-Ålesund (Svalbard Islands). Furthermore, automatic and continuous measurements of nitrogen oxides were performed throughout the year 2015.

The goals of this work were to determine the atmospheric concentrations, the partitioning and the budget of NO_y ; to quantify the direction and magnitude of NO_y fluxes at the snow-atmosphere interface; to identify chemical processes that control the NO_y redistribution and recycling in the snow; and, then, to investigate about the atmospheric sources of snow NO_3^- and the links with climate changes.

Experimental

All measurements were carried out from 29 March to 30 April 2010 and from 1 to April 2011 in a flat and undisturbed snow area near the Gruvebadet station, located at about 1 km south from the Ny-Ålesund International Arctic Research and Monitoring Facility, Svalbard (78°55'N, 11°54'E, 40 m msl). All the instruments had been located in a laboratory hut. This measuring site was chosen to minimize the influence of local pollution from the research community. The snowpack flux experiments were derived from independent chemical measurements of reactive nitrogen species at two sampling heights above the snow (0.3 and 1.5 m) using a multi-level gradient grid (scaffolding) tower at height of 10 m above the snow surface. This grid tower was installed at the site before the onset of the snow accumulation season and allowed to be covered by the precipitating snow without any disturbance throughout the snow-covered time period.

Simultaneous atmospheric turbulence measurements were made using a 3-dimensional sonic anemometer in order to determine the friction velocity (u^*) and eddy diffusivity between the reactive nitrogen measurement heights above the snow surface. The derivation of atmospheric reactive nitrogen fluxes from this mixed eddy covariance and gradient technique is fully described previously (Beine et al. 2003, Ianniello et al. 2016).

NO_x were detected every 6 min using a modified commercial two-channel high-sensitivity chemiluminescence detector (Sonoma Technologies, USA). Channel 1 sampled air at 0.3 m and channel 2 at 1.5 m above the snow in order to determine the concentration gradients of the nitrogen species. The 3σ detection limit for NO was 4.4 and 3.3 ppt for Channel 1 and 2, respectively, while the 3σ detection limit for NO_2 was 9 and 7 ppt for Channel 1 and 2, respectively, in a 1 min average.

Nitrous acid (HONO) was measured every 9 min by two-channel system with derivatization and analysis by HPLC equipped with UV-Vis absorption detector. The 3σ detection limit for HONO was 0.5 ppt (Spataro et al. 2016).

Measurements of HNO_3 , and fine ($< 2.5 \mu\text{m}$) and coarse ($2.5 > \mu\text{m}$) particulate NO_3^- were carried out with 12 h and 24 h sampling times at two heights above the snow by two independent annular denuder lines (Ianniello et al. 2007; 2016).

In addition, determination of O_3 and chemical and physical properties of snow (ionic composition, pH, temperature, specific surface area) were carried out. The specific surface area (SSA) was determined by short-wave infrared (SWIR) method (Dominé et al. 2006; Salzano et al. 2016).

All snow and denuder samples were analysed on site by ion chromatography for major anions and cations within 24 h of sampling.

Further, measurements of NO_x and O_3 were performed every 1 min using automatic and commercial analysers from 18 May to 8 October 2015 at the Gruvebadet station.

Results

Both NO and NO_2 showed clear diurnal cycles with noontime maxima and nighttime minima during spring time 2010 and 2011 (Figure 1). Significant emission fluxes of NO and NO_2 were observed, reaching noontime values up to 19.42 and 25.20 $\text{pmol/m}^2 \text{ s}$, respectively (Figure 2). The snow surface was the source of NO and NO_2 but these observed releases were small due to almost alkaline snow environment and chemical forms of snow NO_3^- . Nitrate concentrations in the snowpack were variable with the highest values during the snowfall events and were related to the specific surface area of the snow indicating that NO_3^- was located on surface snow. In fresh and acid snows, NO_3^- was present as dissolved or adsorbed HNO_3 taken up from the gas phase. This suggested that snow NO_3^- was available for photochemical reactions and for physical exchanges, that led to NO and NO_2 emissions at Ny-Ålesund. However, the presence of sea salt and crustal particles in this marine environment made also the snow alkaline. Indeed, the ionic composition of snow revealed that NO_3^- in aged snows was associated with heavier cations such as Na^+ , and, then, was not always reactive regard to physical exchanges with the atmosphere, resulting in low NO and NO_2 emissions.

No clear diurnal cycle for the HONO concentrations was observed. Emission of HONO from the snow surface was only a minor HONO source in the atmosphere at Ny-Ålesund.

Significant deposition fluxes of HNO₃, fine and coarse particulate NO₃⁻ were also observed, reaching peak values up to -18.00, -37.80 and -12.50 pmol/m² s, respectively, during snowfall events and contributed up to 24 % of the NO₃⁻ (-N) budget in the snow. However, these dry depositions were not large at Ny-Ålesund, so that the main NO₃⁻ source for snow was wet deposition in falling snow. In addition, emissions of HNO₃ were also observed during windy periods and were related to a decrease in snow nitrate concentration.

Furthermore, during the time period 2015 the measurement results showed that long-range transport and local air pollution impact on the NO and NO₂ concentrations as observed during spring season 2010 and 2011. Air coming from NW and NE directions had higher values of NO_x during spring and summer periods. The highest mean concentration observed when wind was from northerly direction is consistent with the influence of local pollution sources on NO_x measurements.

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