Programma Nazionale di Ricerche in Antartide (PNRA)

Final project report

Project ID:	2004/6.02
Title:	Climatic Effects of Snow Interstitial Photochemistry (CESIP)
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Activities and results

The chemistry of snow and ice controls aspects of boundary layer chemistry over large regions of world. Findings of NO_x production in snow interstitial air show that photochemical NO_x production in or above snow surfaces from nitrates (NO_3^-) is sufficient to alter the composition of the overlying atmosphere. The production of gas phase HONO from snow surfaces is also generally understood to proceed through a mechanism similar to that of NO_x starting by the photolysis of NO_3^- in the snow surface analogous to reactions in liquid phase. Fluxes were quantified above snow surfaces at Alert (Nunavut, Canada), at Summit (Greenland), at ny-Alesund (Norway). Simple calculations show that this species is responsible for the formation of OH radicals in the polar troposphere, surpassing OH production from ozone photolysis. Very high OH concentrations were observed in Antarctica.
Climate and Global change may affect many aspects of these mechanisms (changes in UV radiation, in snow cover, in temperature and in concentrations of pollutants).
The aim of this project is to understand the snow-atmosphere interaction better, and to investigate the various links with global change issues.
During the first year of this project, measurements were carried out at Browning Pass (74°36.915'S, 163°56.487'E), which is located 10.1 km from the Italian coastal Antarctic station "Mario Zucchelli" (formerly Terra Nova Bay). The site does not receive direct sea spray, and is, during the rare katabatic flow from the Boomerang and Campbell glaciers somewhat removed meteorologically from marine influences by the Northern Foothills (up to 1000m altitude); however, the marine influence is prevailing. At this field site, which was accessed by helicopter daily, we measured HONO fluxes, chemical and optical snow properties between 9 and 28 November 2004.
Fluxes of HONO were derived from independent chemical measurements of HONO at two sampling heights above the snow surface (25 and 150 cm) and simultaneous temperature and wind speed measurements at the same heights. We sampled HONO at 25 and 150 cm above the snow surface, using two independent 2.5 cm (I.D.) light-shielded inlet lines of 20m length at flow rates of 38 L $min^{□1}$ to feed the sample into the container where the instrument was placed. HONO was trapped quantitatively in a 10-turn glass coil sampler using 1 mM phosphate buffer (pH 7). The scrubbing solution was then derivatized with sulfanilamine (SA)/ N-(1-naphtyl)-ethylendiamine (NED), subsequently analyzed using highperformance liquid chromatography (HPLC), and detected by uv-vis absorption.
To characterize the surface-atmosphere interaction and to determine the turbulent fluxes we used a UVW tri-propeller anemometer (Gill, model 200-27005), which measured the three orthogonal wind vectors at 1 Hz sampling frequency. Fluxes were computed using the eddy covariance technique in the post processing. Additionally, profile measurements of air temperatures and wind speeds were performed to be able to compute fluxes of chemical species. The instrument was set up ca. 10m from the chemical measurements.
The 3□ detection limit for the individual HONO measurement was <0.5 pmol $mol^{□1}$. Taking into account the difference between the eddy covariance and gradient flux techniques, our HONO fluxes generated by the gradient flux theory have a (mean) total error on the order of 50%.
The optical properties (scattering and absorption cross sections) of the Antarctica snowpacks found at Browning Pass were determined by an experimental and modeling method we have used previously in mid-latitude snowpacks and sea ice. Briefly, the optical properties of a snowpack can be defined and constrained by measuring the wavelength-resolved albedo and the wavelengthresolved transmission of light through

snowpack. The albedos of the snowpack were measured using a GER1500 spectrometer (□=300–1000 nm) and measured relative to a reflectance standard under identical light conditions. The aim of the optical measurements of the snowpack was to calculate the photolysis rate, $J(NO)_3^-$ of nitrate in the snowpack and to estimate the expected molecular fluxes of gas phase NO_2 and HONO from the snowpack.
Snow and ice samples were also collected at various distances from the coast for chemical and physical measurements to understand the HONO emissions from the snow. The snow precipitation was also examined during the measurement period. Thus, the influence of sea salt on the snow composition was studied because its deposition makes basic snow preventing atmospheric HONO emissions. Melted snow samples were analyzed in situ by ion chromatography (Dionex IC mod. DX120 and DX100) using Dionex AS12 and CS12 columns for anions and cations, respectively.
The median positive HONO flux was 1.66 $nmolm^{□2}$ $h^{□1}$; the median negative HONO flux was –1.74 $nmolm^{□2}$ $h^{□1}$. Compared to typical Arctic values of HONO and NOx emissions of around 40 $nmolm^{□2}$ $h^{□1}$ these values are very small.
The snow surface at Browning pass is shaped by wind. In late October, it consisted of hard windpacks with a positive relief and of softer layers in hollows, each type covering roughly half of the surface. As observed during our stay, snow layers are formed by wind events that remobilize recent precipitation and exposed layers, and are always discontinuous. As a result, the apparently similar-looking windpacks that outcropped were in fact outcrops of different layers (perhaps 2 to 5) formed at different times, so that spatially variable snow chemistry and physics can be expected. The snow stratigraphy is composed of alternating hard windpacks formed of small rounded grains, including an incredibly hard layer of density 0.61 (no melting visible) 40 cm down in the deep pit we dug, and softer layers composed of larger crystals showing some variable degrees of faceting, of density as low as 0.3.
We analyzed 148 triplicate snow samples from Browning Pass, almost all taken within 2 km from our air sampling site, and >70% taken within 100 m. It is clear that sea salt has a major influence on snow composition, as most major ions are correlated to $[Na^+]$. $Cl^□$ and Mg^{2+} show ion/Na^+ ratios very close to those of sea water. $[K^+]$ shows the best correlation with $[Na^+]$, but surprisingly the ratio, $[K^+]/[Na^+]$ is 50% greater than that of sea water. Furthermore, $Cl^□$ and Na^+ were usually the most abundant ions on a molar basis, sometimes exceeding 1000 □eq, while Ca^{2+}, $SO_4^{2□}$ and Mg^{2+} were also abundant, reaching 200 □eq. Concentrations of $NO_3^□$ and K^+ reached 50 and 40 □eq, respectively. The sea is just a few km from our site, so the trends and the predominance of Na^+ and $Cl^□$ were expected. $SO_4^{2□}$ has a source other than sea salt, and this is presumably the oxidation of dimethyl sulfide, with a possible volcanic contribution from Mount Melbourne, some 40 km away. Ca^{2+} also has an extra source, most likely terrigeneous particles, as a lot of rock outcrops are present nearby.
We are found the excellent correlation between the concentrations of $NO_3^□$ and Na^+ in aged snows. The most likely explanation is that gas phase nitric acid reacted with sea salt to release HCl and form $NaNO_3$. Na^+ concentrations are a function of sea salt mass, while the rate of sea salt reaction depends on aerosol surface area. The existence of this excellent correlation suggests that the size distribution of sea salt aerosol varies little at Browning Pass. The ion balance of almost all fresh samples is acidic, with corresponding pH values in the range 5–6. The ionic concentrations are also much lower than for many aged snows Our interpretation is that the source of $NO_3^□$ in these snows is gas phase HNO_3 that dissolved in the ice to form a solid solution may also contribute to the $NO_3^□$ signal. Thus, the snow results show that the snow is mostly basic due to the dominant presence of sea salt composed primarily by sodium and chloride. Then nitrate in the snow is present as sodium nitrate ($NaNO_3$), which does not allow the photolysis products to be emitted into the atmosphere.
Our monitoring of snow layers showed that fresh snow always had low ionic concentrations. Most of the mineral ion loading came from dry deposition due to wind pumping or while snow was airborne. The same mechanisms that deposit soluble mineral ions probably also deposit organic compounds. Both Arctic and Antarctic measurements cited above involved aged snows and the conclusion that they had a significant organic loading may thus not apply to our fresh snows, that may well have been depleted in organic compounds. We therefore suggest that the concentration of organic compounds was too low to support production of detectable HONO fluxes. This is consistent with our back trajectory calculations that showed that air masses generating fresh precipitation came from the continent.
In summary; HONO production from nitrate does strongly depend on its physical (surface or volume) and chemical (ice or salt) environment. It is clear that HONO production could follow several pathways, the prevalence of one over the other depending on several aspects of snow chemistry, such as the chemical form of $NO_3^□$, the concentration of organic photosensitizer, etc. Well designed laboratory experiments, with different chemistry of the (natural) ice substrate and ideally a control over the location of $NO_3^□$ in the substrate, seem necessary to solve the puzzle.

Products

A – papers in scientific magazines

1. M.D. King, J.L. France, F.N. Fisher, H.J. Beine (2005). Measurement and modelling of UV radiation penetration and photolysis rates of nitrate and hydrogen peroxide in Antarctic sea ice: An estimate of the production rate of hydroxyl radicals in first-year sea ice. Journal of Photochemistry and Photobiology A: Chemistry, 176, 39–49.
2. H. J. Beine, A. Amoroso, F. Dominé, M. D. King, M. Nardino, A. Ianniello, J. L. France (2006). Surprisingly small HONO emissions from snow surfaces at Browning Pass, Antarctica. Atmospheric Chemistry and Physic, 6, 2569-2580.
3. H. J. Beine, A. Amoroso, G. Esposito, M. Nardino, M. Montagnoli, A. Ianniello (2007). Relantionship between NO, NO2, HONO, and HNO3 fluxes above snow surfaces at Ny-Alesund, Svalbard (Arctic). Geophysical Research Abstracts, Vol. 9, 07406. ISSN: 1607-7962.
4. A. Amoroso, F. Domine, G. Esposito, S. Morin, J. Savarino, M. Nardino, M. Montagnoli, J.-M. Bonneville, J.-C. Clement, A. Ianniello, H. J. Beine (2010). Microorganisms in Dry Polar Snow Are Involved in the Exchanges of Reactive Nitrogen Species with the Atmosphere. Environmental Science and Technology, 44, 714-719.

B – book chapters

1. I. Allegrini, A. Ianniello (2005). La ricerca ambientale in aree estreme: sfide e prospettive. Il K^2 Cinquant'anni dopo, la ricerca scientifica negli ambienti estremi, Il Veltro Editrice, Editorial Board: Virginia Cappelletti, Franco Tagliarini della Rivista "Il Veltro" e Maria Rosaria Valensise del CNR, pp. 213-219. ISSN 0042-3254
2. A. Ianniello, I. Allegrini (2007). Determinazione delle specie gassose e particellari nella troposfera polare mediante i denuders di diffusione. Clima e Cambiamenti Climatici – le attività di ricerca del CNR (CNR – Dipartimento Terra e Amnbiente Editrice, Edito da Bruno Carli, Giuseppe Cavarretta, Michele Colacino, Sandro Fuzzi, CNR Editore), pp. 315-318. ISBN 978-88-8080-075-0.315.

C - proceedings of international conferences

1. H. J. Beine, A. Amoroso, F. Dominé, A. Ianniello, T. Georgiadis, M. Nardino, M. King (2004). Fluxes of nitrous acid from snow surfaces in Antarctica. Eos Trans. AGU, 85(46), Fall Meet. San Francisco, CA, Suppl., Abstract A11B-0035.
2. H.J. Beine, A. Amoroso, A. Ianniello, F. Dominé, M. King, M. Nardino (2005). Surprisingly Small HONO Emissions Fluxes From Snow Surfaces at Browning Pass, Antarctica. Eos Trans. AGU, 85(52), Fall Meet. Suppl., A24A-04.
3. A. Amoroso, H.J. Beine, M. Nardino, A. Ianniello, G. Esposito (2005) Significant Emission of Nitrous Acid from Arctic Snow Surfaces During Ozone Depletion. Eos Trans. AGU, 85(52), Fall Meet. Suppl., A21C-0867.
4. A. Amoroso, H.J. Beine, G. Esposito, M. Nardino, F. Dominé, A. Ianniello (2007). Three Events of Nitrogen Emission From Snow Surfaces at Ny-Alesund, Svalbard (Arctic). Eos Trans. AGU, 88(52), Fall Meet. Suppl., A53B-1142.

D - proceedings of national meetings and conferences

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E – thematic maps

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F – patents, prototypes and data bases

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G - exbitis, organization of conferences, editing and similar

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H - formation (PhD thesis, research fellowships, etc.)

1. CNR Research fellowship on "Reattività diffusionale ed analisi di inquinanti atmosferici contenenti azoto".
2. PhD thesys on "Interstitial snow photochemistry in polar zones" of University of Siena (2008).

Research units

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Note