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Deposition of atmospheric nitrous acid on alkaline snow surfaces

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[1] The photolysis of atmospheric nitrous acid (HONO) is a significant source of OH radicals in remote and Polar Regions. HONO is produced in/on snow surfaces in a photochemical reaction from nitrate ions. In an attempt to quantify the production of HONO at a snow covered mid-latitude location we made measurements of HONO fluxes for a 10-day period at the Mt. Cimone (MTC) research station in the Italian northern Apennines (2165 m asl) during March 2004. Production fluxes under normal background conditions were small, and reached maximum values of $20 \text{ nmol m}^{-2} \text{ h}^{-1}$ on only two occasions. However, during a transport event of Saharan dust to MTC we observed deposition fluxes of up to $-120 \text{ nmol m}^{-2} \text{ h}^{-1}$ of HONO on to the snow surface. The deposited Sahara dust had rendered the surface snow alkaline, so that large amounts of acids could be absorbed from the atmosphere. **Citation:** Beine, H. J., A. Amoroso, G. Esposito, R. Sparapani, A. Ianniello, T. Georgiadis, M. Nardino, P. Bonasoni, P. Cristofanelli, and F. Dominé (2005), Deposition of atmospheric nitrous acid on alkaline snow surfaces, *Geophys. Res. Lett.*, *32*, L10808, doi:10.1029/2005GL022589.

1. Introduction

[2] The photolysis of atmospheric nitrous acid (HONO) is believed to be a significant source of OH radicals in remote and Polar Regions [Yang *et al.*, 2002]. HONO, together with NO_x, is produced in/on snow surfaces in a photochemical reaction from nitrate ions [Beine *et al.*, 2002; Zhou *et al.*, 2001]. As snow cover extent changes with global change, HONO may be a link between atmospheric chemistry, the oxidative capacity of the troposphere, and global climate change.

[3] The production and atmospheric chemistry of HONO in urban and rural areas is well documented [Febo *et al.*, 1996; Kleffmann *et al.*, 2003]. Further, while production fluxes of NO_x were observed in mid-latitude snow covered locations [Honrath *et al.*, 2000] no such observations exist for HONO. Additionally, the deposition of nitric acid is well known, while the deposition of HONO was so far observed only in rural/urban environments [Stutz *et al.*, 2002, and references therein].

[4] In preparation for an Arctic spring campaign we measured HONO fluxes and chemical surface snow properties for a 10-day period in the Italian northern Apennines during March 2004. Our objective was to observe HONO fluxes at a reasonably remote mid-latitude location that only occasionally receives atmospheric pollution [Bonasoni *et al.*, 2000].

2. Experimental

[5] Measurements were carried out at the research station "O. Vittori" at Mt. Cimone (MTC; 44°11'N, 10°42'E, 2165 m asl; <http://www.isac.cnr.it/cimone/>) in the Apennine mountains between Mar 8 (DOY 68) and Mar 17 (DOY 77), 2004. Several scientific programs were established at MTC to study climatology and the chemical-physical characteristics of the Mediterranean free troposphere, the most relevant of which, in the context of the present study, was MINATROC [Fischer *et al.*, 2003]. MTC is part of the WMO-GAW program for O₃ and CO₂. Surface O₃ is measured by UV-absorption (Dasibi 1108), particle concentration and size distribution are measured by optical particle counter (Particle Size Analyzer Grimm Mod. 1.108). For this work we discuss only the relevant coarse aerosol fraction ($1 \mu\text{m} \leq D_p \leq 20 \mu\text{m}$) range. Frequent increases of coarse particle concentration at MTC are attributed to transport of Saharan air masses rich in mineral dust [Bonasoni *et al.*, 2004].

[6] Standard meteorological parameters (air temperature, relative humidity, atmospheric pressure, wind direction and intensity) were continuously observed at 1-min resolution at this baseline station at a height of 4 m above the ground. 6-day back-trajectories were calculated every three hours using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPPLIT) driven by FNL wind fields [Draxler and Rolph, 2003].

[7] We derived HONO fluxes from independent chemical measurements of HONO at two sampling heights above the snow surface and simultaneous temperature and wind speed measurements at the same locations. MTC is located on a slope near the mountaintop; the site is characterized by complex orography. Below the station, however, a plateau gave enough space for the flux measurements with a radius of ca. 10 m near-level undisturbed area around our sampling site.

[8] HONO was measured using a new instrument constructed at C.N.R. – IIA following the design by X. Zhou [Zhou *et al.*, 1999; Huang *et al.*, 2002]. We sampled HONO at 25 and 150 cm above the snow surface, using two independent 3/4" (I.D.) light-shielded inlet lines of 15 m length at flow rates of 12 L min^{-1} to feed the sample into the building where the instrument was placed. The samples

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were taken from this flow through ca. 50 cm of 1/16" (I.D.) tubing at 3 L min⁻¹. The total residence time in the inlet lines was 22 s. Gaseous HONO was trapped quantitatively in a 10-turn coil sampler using 1-mM phosphate buffer. The scrubbing solution was derivatized with sulfanilamine (SA)/N-(1-naphthyl)-ethylendiamine (NAD), subsequently analyzed using high-performance liquid chromatography (HPLC), and detected by UV-Vis absorption. Typical operating conditions were; sample flow rate: 3 L min⁻¹, solution flow rate: 0.2 mL min⁻¹, derivatization conditions: 5 min at 45°C; HPLC: loop: 300 mL C18 reverse phase column (Varian), eluent: 20% acetonitrile in 15 mM HCl. Calibrations of the HONO instrument were carried out feeding a liquid standard into the sampling trap (while sampling ultrapure N₂). The 3σ detection limit in a single measurement was estimated as <0.5 pmol mol⁻¹. The overall error at typical mixing ratios of 2 pmol mol⁻¹ was on the order of 30%, at 10 pmol mol⁻¹ the error was reduced to ≤15%. This error included the effect of possible interferences by NO₂, which were independently assessed in the lab and in ambient urban air near Rome, Italy (using the inlets described above). Data below the detection limit are shown with their numerical value.

[9] HONO samples were taken simultaneously at the two sampling heights and analyzed over the next 10 min. We made profile measurements of air temperature and wind speed at the two HONO sampling locations (at 25 cm and 150 cm height), and averaged over a 10-min. envelope around the chemical measurements to determine the HONO fluxes. The derivation of HONO fluxes from the gradient technique [Sozzi *et al.*, 1998] is fully described by Beine *et al.* [2003]. Because 3D wind speed measurements were not available at the site, the vertical wind speed component was parameterized utilizing a similarity procedure. Considering that under neutral atmospheric stability conditions the sensible heat flux is zero, turbulence is generated by the mechanical interaction of the mean flow with the surface by means of momentum exchange alone. The resulting eddy dimensions are consequently a direct function of the height from the surface and of the surface roughness.

[10] 3D measurements previously conducted for a 25-day period in late spring at the same heights and over the same surface type at Ny-Ålesund, Svalbard [Beine *et al.*, 2003] allowed to parameterize the vertical wind speed as a function of the friction velocity under near-neutral atmospheric stability.¹ Thus, at MTC, the Monin Obukhov length (L), required to calculate HONO fluxes, was not measured directly but obtained through iterative computation. Assessing an overall error with this method is difficult; however, the largest contribution to the overall error in the chemical fluxes should be the chemical measurements themselves.

[11] We took daily triplicate measurements of surface snow close to the atmospheric sampling site. During the first 6 days these samples were analyzed within a few hours at MTC by ion chromatography. Samples from the last three days were not analyzed until ca. 2 weeks later at our lab in

Rome. Unfortunately, NO₂⁻ is labile in solution and could no longer be detected in these samples.

3. Results

[12] We will focus in the following on the effects of Saharan dust transport on snow surface chemical composition and related HONO exchange processes. Although we observed during the initial 6 days of our campaign various synoptic situations, the recorded HONO mixing ratios were fairly small and invariable (median HONO at the lower and upper inlet were 2.7 and 2.9 pmol mol⁻¹, respectively). No diurnal variation was observed. The HONO emission fluxes were minute and well below the uncertainty of the methods involved; on only two occasions emission fluxes of up to 20 nmol m⁻² h⁻¹ from the snow surface were seen for up to 6 hours length. We will not further discuss the emission fluxes, since we believe that two small events do not warrant extensive discussion, and that the basic photochemical emission mechanism seems to be understood [Beine *et al.*, 2003].

[13] Between DOY 74 and 77 air mass characteristics changed several times at MTC, suggesting that air masses with different origins influenced the trace gas and particle concentrations at the measurement site (Figure 1). The analysis of the 850 hPa surface showed a trough extending from UK to north-eastern Africa on DOY 73. From this trough a low developed over Algeria on DOY 74 accompanied by a cold front. The 6-day HYSPLIT 3D back-trajectories indicated for DOY 74 – 76 air masses reaching MTC from the Sahara. This flow was favored by a high pressure system over the central Mediterranean which lead air masses rich in Sahara dust (mobilized by the cold front) to move toward MTC from the African coastline. On DOY 75, the low O₃ concentrations (45 nmol mol⁻¹) were caused by an intrusion of Saharan dust with very high coarse particle number concentrations (>12 N/cm³). Following the dust transport, the air masses at MTC were characterized by 10 hours of high O₃ (up to 70 nmol mol⁻¹), low coarse particle number concentration (0.4 N/cm³) and RH decrease (to 50%). On DOY 75.5 a new input of mineral dust (up to 9.8 N/cm³) reached the measurement site, consequently a new O₃ minimum (46 nmol mol⁻¹) was recorded at MTC on DOY 76.1. The decrease of O₃ in the presence of mineral dust may be explained by heterogeneous ozone destruction on mineral particle surfaces due to decomposition, catalytic destruction or absorption on mineral oxides [Hanisch and Crowley, 2003]. Following the dust transport, air masses poor in mineral dust (mean value: 0.1 N/cm³) and rich in O₃ (mean value: 65 nmol mol⁻¹) affected the measurement site until the end of our campaign.

[14] After an initial spike at DOY 75.0 the HONO background level underwent a marked increase: previously the median HONO mole fraction was ca. 2.8 pmol mol⁻¹, while during the Sahara dust event it was 9.5 (median at lower inlet) and 13.5 pmol mol⁻¹ (median at upper inlet). These higher mixing ratios persisted until the end of the HONO measurements. Significantly, the observed HONO fluxes during this period indicated deposition onto the surface. Since the fluxes rule out HONO production at the snow surface, we speculate that surface reactions on the crustal particles (possibly during transport) led to the increased

¹Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2005GL022589.

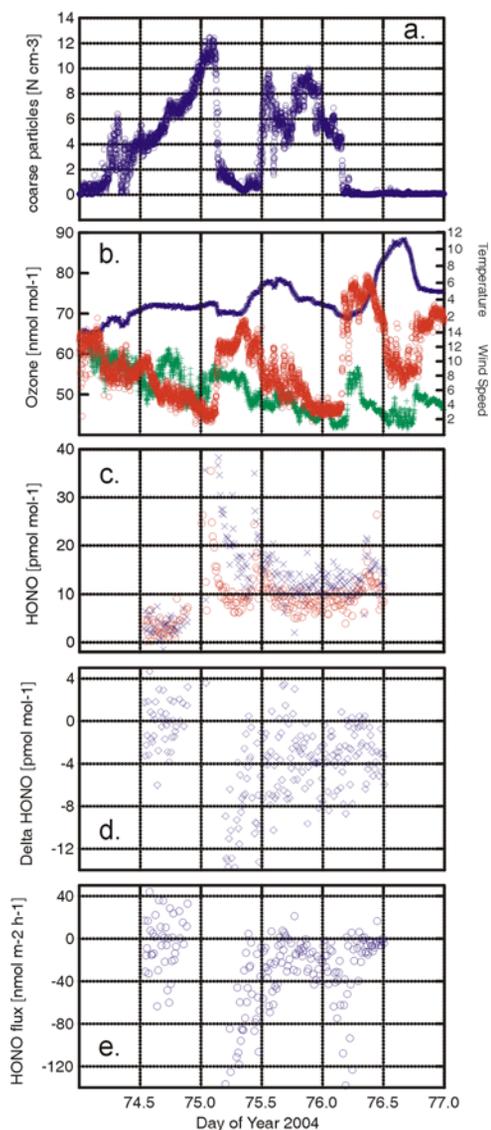


Figure 1. (a) Coarse aerosol particle number concentration [N cm^{-3}]; (b) ozone mole fraction (red symbols, left scale), air temperature [$^{\circ}\text{C}$] (blue symbols, upper right scale), and wind speed [ms^{-1}] (green symbols, lower right scale) (all 3 measurements from MTC); (c) HONO mixing ratios (red symbols, lower inlet, blue symbols upper inlet); (d) Measured $\Delta_{\text{HONO}} (= \text{HONO}_{\text{lower inlet}} - \text{HONO}_{\text{upper inlet}})$ [pmol mol^{-1}]; (e) HONO flux [$\text{nmol m}^{-2} \text{h}^{-1}$] during the Sahara dust event.

HONO mixing ratios. We made no measurements of NO_2 during our short campaign; however, surface reactions of NO_2 are well documented to produce HONO [e.g., Vogel *et al.*, 2003] through the heterogeneous, apparently non-photoenhanced hydrolysis of NO_2 [e.g., Ramazan *et al.*, 2004], and may thus well explain these elevated HONO mixing ratios.

[15] The occurrence of transport from the Sahara is supported by our snow surface ionic measurements. During our campaign the concentrations of most trace ions on the snow surface showed a declining trend. We speculate that due to the high temperatures surface melting with percolation was induced, which washed impurities to lower layers.

The most relevant feature of snow chemistry at our site was the increase of ions of crustal origin, Ca^{2+} , and to a lesser extent Mg^{2+} on DOY 74, due to Saharan dust deposition (Figure 2). This led to a radical change in the snow ion balance from acidic to alkaline. Assuming simply that the observed ion balances require only H^+ or OH^- to establish neutrality, a pH value for the samples may be calculated. The tentative pH value after DOY 75 was ca. 8.6. We must caution, however, that from our ion measurements of the melted snow we cannot a priori say where the alkalinity in the snow is; there are scenarios imaginable where the bulk snow is alkaline even though the surface is acidic. The localization of acidity/alkalinity in snow is not within the scope of this work, even though the discussion below suggests that the snow surface was alkaline. An alkaline surface is expected to react with gaseous acids; this principle in fact is used to quantitatively strip atmospheric HONO in a number of analytical techniques.

4. Discussion

[16] Because of missing data around DOY 75.0 no clear correlation between particle concentrations, air masses, and HONO surface fluxes can be tested. Fluxes were negative throughout the period after DOY 75.0 (median $-28.5 \text{ nmol m}^{-2} \text{ hr}^{-1}$), however, the highest deposition fluxes (ca. $-120 \text{ nmol m}^{-2} \text{ hr}^{-1}$ around DOY 75.2 and 76.2) occurred when there was a change in air mass and therefore in air chemistry, wind speeds were highest, and temperatures were coldest. It is difficult to determine a priori which of these variables were actually responsible for the enhanced deposition. Chemical factors appear unlikely. The first replacement of a Saharan air mass by a colder air mass (DOY 75.2) is accompanied by a significant rise in atmospheric HONO, while the second one (DOY 76.2) results in no detectable change. Yet, both replacements resulted in the large deposition fluxes; thus the chemistry of the air mass appears to have no effect. On the contrary, physical factors seem to have been similar during both elevated deposition events and are more likely to explain the observations. Days 74 and 75 were both warm ($T_{\text{max}} > 8^{\circ}\text{C}$ at 25 cm above the snow surface) and produced significant melting of the snow. Clear nights (75 and 76) favored rapid radiative cooling which was further enhanced by the arrival of a colder air mass. However, air temperatures remained above freezing at 25 cm above the snow surface, and while the very surface

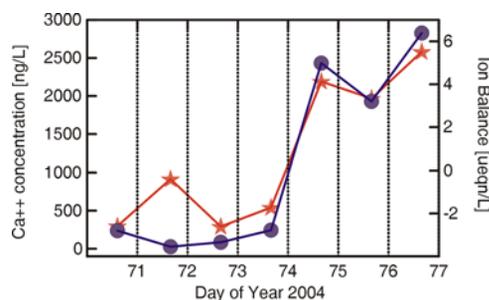


Figure 2. Concentration of Ca^{2+} ions in the snow surface [ng L^{-1}] (left scale, blue symbols), and ion balance in the snow samples [$\mu\text{eqn L}^{-1}$] (right scale, red symbols).

of the snow probably froze, it is very unlikely that all the liquid water generated during these warm days re-froze. This cold water, which was probably alkaline, then was able to take up large amounts of HONO because of the enhanced solubility of HONO at colder temperatures [Park and Lee, 1988; Becker et al., 1996]. This process was enhanced by the high winds, which efficiently ventilated the snowpack down to a depth of many centimeters [Albert et al., 2002], i.e. throughout the alkaline wet layer so that its uptake capacity was maximized. In summary, our favorite interpretation is that the presence of cold alkaline liquid water at the surface of the snow crystals, together with efficient snowpack ventilation, are responsible for the enhanced HONO uptake. Obviously, we only have one observable (HONO uptake) and several changes in physical variables that affect it. More observations with different combinations of these variables are necessary before the role of each one is established. We nevertheless speculate that in coastal Arctic regions affected by sea salt input, the resulting alkaline surfaces [Dominé et al., 2004] may be strong HONO absorbers, given the appropriate meteorological conditions (note that high winds are frequent in coastal regions and that with global warming, melting is expected to be more frequent). This may inhibit the emission of OH radicals from Arctic snow surfaces, and thus may have significant effects for the oxidative capacity of the atmosphere.

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