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HONO emissions from snow surfaces

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Abstract
Photochemical production of NOₓ and HONO from surface snow can significantly impact the NOₓ, OH, and O₃ budgets in the overlying atmosphere. NOₓ production is driven by the solar photolysis of NO⁻ within or at the surface of snowpacks. HONO, however, is a secondary species that involves H-atom transfer between natural donors and photogenerated NO₂. Here we investigate the mechanism of HONO generation in snowpacks by exploring how its emissions respond to on-and-off illumination and temperature cycles, and to the addition of various snow dopants. The presence of humic substances within or at the surface of the snowpack significantly enhances, and may be an essential requisite for HONO production. Emission fluxes of NO, NO₂, and HONO from snow surfaces were measured under controlled temperature, ozone mixing ratio and actinic flux conditions. We used natural mid-latitude surface snow as the snow substrate. Their combined peak emission fluxes reached up to ∼3 × 10¹⁰ molecules cm⁻² s⁻¹, ∼10³ times larger than typical emissions from polar snowpacks. Less than 1% of available N was released in these experiments. We report significant post-irradiation HONO emissions from the snow. Present results indicate a strong, direct correlation between HONO emissions and the HULIS (humic-like substances) content of the snow surface.

Keywords: snow–atmosphere interactions, photochemistry, NOₓ, HONO

1. Introduction
Since emissions of nitrogen oxides from snow (Honrath et al 1999, Ridley et al 2000) were detected and their fluxes quantified for the first time (Zhou et al 2001, Beine et al 2002a, Honrath et al 2002) much work has been devoted to understanding the (photo)chemical mechanisms underlying NOₓ and HONO production from snow surfaces (Honrath et al 2000a, Jones et al 2000, Dibb et al 2002, Oncley et al 2004). It is well established that NOₓ formation originates from the photolysis of NO⁻ within or at the surface of snowpacks (Honrath et al 2000b, Cotter et al 2003). How HONO is produced, however, remains to be elucidated (Grannas et al 2007).

HONO is deemed to be a secondary species derived from NO₂, likely via a heterogeneous H-transfer pathway (Jacobi and Hilker 2007). Note that direct thermal H-atom abstraction by the NO₂ free radical from most stable organic substances is significantly endothermic (ONO–H bond energy = 78 kcal mol⁻¹ (Huie 1994)) and, hence, extremely slow at subfreezing temperatures. Alternative mechanisms involve H-atom abstraction by vibronically excited NO₂ (Li et al 2008), H-atom abstraction from persistent free radicals, (Stemmler et al 2006) or NO₂ addition to double bonds followed by intramolecular H-abstraction (Huie 1994). For example, Aubin and Abbatt (2007) observed the conversion of NO₂ to HONO on freshly made hydrocarbon soot surfaces that once depleted could not be reactivated with time or by exposure to humid air. The results of our snow experiments clearly suggest a similar (post-irradiation) dark pathway for HONO production in snow containing organic matter.
2. Experimental details

In our experiments, substrate snow was one of the nine (12° × 12° × 4′) slab samples collected at the Central Sierra Snow Laboratory (CSSL; 39° 19′N, 120° 22′W, 2100 m) on April 2, 2007. For each slab, five triplicate samples of adjacent snow were taken for subsequent ion analysis. Snow was sampled as described by Domine and Shipon (2002) and Domine et al (2004). Polyethylene gloves and full-body Tyvek suits were used to avoid contamination. Slabs were scooped up using virgin PTFE plates, and were stored in airtight custom-made PTFE bags, scrupulously avoiding contact with the (upper) faces of the slabs to be irradiated. All Teflon materials were rinsed with snow on-site prior to sampling. The samples were transported to Pasadena, CA in a refrigerated truck at a mean temperature of −10°C, and subsequently stored in a cold room at −25°C. The logistics of sampling and transport dictated the sampling time. On April 2, 6 days after the last major snow fall, air temperatures reached up to 13°C under sunny cloudless skies. Seasonally accumulated snow was 102 cm above the ground, with an average daily loss of 4.6 cm. Structural changes occurred in the snowpack surface due to partial melting during the day of sampling (and likely during prior warm days), possibly leading to the percolation of trace ions and other impurities into the snowpack bulk. The snowpack was essentially isothermal, without visual evidence of layering. The snow slabs refroze during transport and storage. Refreezing (during the night or during our transport) lead to the formation of larger rounded ice crystals, in which ion concentrations may have reached saturation. The remainder of trace ions and impurities would be located in interstitial liquid layers within the snow crystals (Domine et al 2008). Refreezing therefore created slabs having modified textures consisting of larger grains wetted by interstitial fluid films rich in trace ions and other species.

Experiments were carried out at Caltech’s Geology and Planetary Sciences’ cold room at −25°C. The snow slab was placed in a tight-fitting Teflon box with a 12.5′′ × 12.5′′ fused silica window. The box was custom made from virgin PTFE Teflon; it was not bonded, all seals had Viton O-rings. The fused silica glass was held in place by a stainless steel ring and sealed with Viton O-rings. Ultrapure air (Scott-Marrin Inc, Riverside) was supplied at 10 slm to the snow surface. A Teflon tube of ca 3 m length supplied this air flow from the Teflon box to the real time analyzers for HONO, NOx, and O3 that were located in an adjacent cold room. The temperature of the snow surface was measured using two thermocouples. These were painted white to reduce interference during irradiation experiments. The snow surface was irradiated using a 1000 W Xe-arc lamp (Oriel) through airmass filters (AM 0 and AM 1.5; Scientech, ON) to simulate a solar spectrum at a mid-latitude location, a dichroic mirror (2′′ Oriel) to eliminate IR radiation and a plano-concave lens (2′′ Thorlabs) to disperse the beam. An area of ca 16’’ in diameter was thus illuminated at the snow surface. Additionally two adjustable 100 W low-vis IR heat lamps (Zoo Med) were used to change the snow surface temperature independently of the UV irradiation. We did not expect the IR light to partake in NO3 photochemical reactions via IR overtones absorption; however, we do not discount the possibility that some unidentified metastable NOH species is produced in the photolysis of nitrate in ice, which could undergo further low-energy chemistry. Such reactions, however, are not discussed here.

The sweep air from the snow reaction chamber passed through ca 3 m of 1/8′′ (ID) Teflon tubing (0.14 s residence time at 10 slm airflow) and was analyzed for NOx, HONO, and O3. Measurements of NO2 were carried out using a custom-built two-channel chemiluminescence analyzer for NO (Sonoma Tech). NO2 was detected as NO following photodissociation by LED (Sonoma Tech); the conversion efficiency for NO2 was 51−55%. The instrument was calibrated using a NIST traceable NO standard (5.08 ppmv; Scott-Marrin). The 3σ d.l. for NO is below 0.5 pmol mol−1 (pptv) in a 1 min average. HONO was measured by quantitative trapping in a 10-turn coil sampler using 1 mM phosphate buffer, derivatization with sulfanilamide (SA)/N-(1-naphthyl)-ethylenediamine (NAD), and analysis using high-performance liquid chromatography (HPLC) and UV-vis absorption detection. The 3σ detection limit in a single HONO measurement was estimated as <0.8 pptv. The overall error at typical observed mixing ratios of 2 pptv was ca 40%. More details on this method can be found in Amoroso et al (2005). The HONO analyzer is calibrated using a nascent HONO standard generated from NaNO2 and HCl (Taira and Kanda 1990) that is checked against the NIST traceable NO standard through a thermal NOy converter as described by Amoroso et al (2008). Ozone was measured using a commercial UV photometric analyzer (Monitor Labs; detection limit 1 ppbv).

We tested the Teflon box for artifacts. The box was cleaned several times with MQ water and ethanol outside of the cold room. Blank experiments were performed in the cold by passing tank air through the empty chamber and analyzing the air for NOx and HONO. Two types of blank experiments were performed: (a) analyzing tank air with and without the empty chamber in line, and (b) analyzing tank air with the empty chamber in line turning the UV light on and off. The Ultrapure air (Scott-Marrin Inc, Riverside) contained on average less than 5 pptv NOx and no HONO (below detection limit); no changes were seen in this background with either blank test.

A total of ca 1 mg humic acid (IHSS Suwannee River National Organic Material 1R101N) was deposited onto the snow surface using AGSCO #1250 Novaculite as inert carrier material. The powders were ground together and then placed in a glass tube that was positioned in-line with the air flow that entered the reaction chamber. Humic acids were loaded twice on the snow slab; for the first addition the powder was kept in the inlet air flow for only a couple of minutes. For the second addition the powder was kept in the airstream for about 10 min.

3. Results

The natural snow slabs were sampled at the end of the winter season, after they had been extensively processed under intense sunlight. Refreezing during transport and storage may have partially transformed the snow surface into icy patches. Insignificant NOx or HONO emissions were detected.
in initial photochemical experiments either at \(-25^\circ\text{C}\) or at higher, subfreezing temperatures. Average \(\text{NO}_3^-\) and \(\text{NO}_2^-\) concentrations in all snow samples were 32.6 and 2.7 ppbw, respectively. These values are significantly lower than in fresh snow from Arctic sites (e.g. Beine et al 2002b). The inorganic ion balance was consistent with alkaline snow, from which HONO (\(pK_a = 3.25\)) could not be released into the gas-phase. Therefore, our pre-processed snow samples should be exclusively considered as realistic, inert substrates that retained the mesoscopic morphology of actual snow. First, by grinding the icy snowblocks against each other the slabs were turned mechanically into loose crystals of varying size (ca 1–3 mm), thus increasing the surface area significantly. Second, we added acids (HCl, HNO3) and humic acids to the surfaces to acidify our substrate, provide reactants, and investigate the role of natural organic substances in the mechanism of HONO production, respectively. The inorganic acids were added by continuously spraying a solution directly into the loose snow while grinding the icy snowblocks. The snow used on 6/1 was doped with 100 ml of 20 mM HCl, the snow used on and after 6/2 was doped with 290 ml solution containing both 20 mM HCl and 20 mM HNO3. Since the spray froze fairly quickly at \(-25^\circ\text{C}\), frozen acid droplets initially were located on the surface of the individual snow crystal aggregates; however, they were distributed fairly homogeneous over the entire snow sample volume. This procedure attempted to generate realistic snow samples, in which layers of fresh and older snow of different morphology, crystal structure, pH, and ionic content often are co-located and exchange properties through physical and chemical processes (e.g. heating, metamorphism, diffusion) (Domine et al 2008). It should be contrasted with the production of ‘snow samples’ by freezing acidic nitrate solutions, as reported elsewhere.

Figure 1 shows timeseries for NO, \(\text{NO}_2\) and HONO mixing ratios released from the snow surfaces during a day-long experiment. NO and \(\text{NO}_2\) were released in response to exposure to UV light, as expected from snow surfaces rendered acidic by the addition of both HNO3 and HCl. Similar timeseries were observed for both NO and \(\text{NO}_2\) in all experiments. NO is immediately emitted upon irradiation, as expected from a primary photochemical product promptly released from the snow surface. In contrast, \(\text{NO}_2\) emissions responded more slowly to the onset of irradiation, implying that they are largely controlled by secondary processes such as outward transport and/or diffusion from the snow lattice, photolysis, or chemical reactions. The NO/\(\text{NO}_2\) ratio of the emissions changed as expected as a function of UV light, surface temperature and \(\text{O}_3\) addition. Substantial NO background levels of 10–50 pptv were, however, detected in the dark (before and after irradiation). This background NO was released from all samples, even from alkaline snow or at lower temperatures. We verified, however, that the empty cold chamber did not release NO in the dark or under irradiation. It is conceivable that HONO, which is trapped in the cold alkaline snow as nitrite reacts to form \(\text{N}_2\text{O}_3\) (and water), which in turn disproportionates to NO and \(\text{NO}_2\). The more volatile, chemically inert NO would be emitted at cold temperatures, while \(\text{NO}_2\) is hydrolyzed and/or adsorbed on the alkaline snow.

In contrast, HONO was released only under certain conditions. Figure 2 shows the results of experiments performed on four successive days. The same snow sample was used for the latter three days. On 6/1 only background HONO levels (10–20 pptv) were detected under constant illumination, after the slab was sprayed with HCl and warmed up to \(-6^\circ\text{C}\). If the added acid (100 ml of 20 mM HCl) were all distributed evenly in the bulk of the snow the resulting pH would have been 3.37. On 6/2, after HNO3 and further HCl additions HONO background signals were significantly larger. Additionally, \(\sim 10\%\) larger than dark background levels were detected upon irradiation. This marginal photochemical enhancement suggests that nitrite was present in the original snow samples, and released as HONO upon acidification. These photochemical HONO emissions were found to increase at higher surface snow temperatures, but did not correlate with photochemical production of NO or \(\text{NO}_2\). The next series of
Figure 2. Box-and-whisker plot of HONO mixing ratios during 4 days of snow experiments. The center vertical line marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall, with the box edges (hinges) at the first and third quartile. The whiskers show the range of values that fall within the inner fences. Values between the inner and outer fences are plotted with asterisks. Values outside the outer fence are plotted with circles (SPSS, Inc. 1999). On June 1 no HONO was emitted from snow that was still largely alkaline on the surface. On June 2, HONO was emitted upon acidifying the snow; UV light had a marginal effect on HONO emissions. On June 3, the dispersal of humic acids onto the snow led to a prompt and significant increase of HONO emissions; it is not clear, however, whether UV light induced further enhancement. Finally, on June 4, after an overnight cooling-and-warming cycle UV light had a clear-cut, positive effect on HONO emissions.

Experiments on 6/3 involved spreading humic acid onto the snow as described above. The first addition, which covered a small fraction of the snow surface (ca 10%) with humic acid, nearly doubled HONO emissions. The second addition, which was performed using a larger airflow, led to the rather uniform dispersal of humic acid over the entire snow surface. This action brought out a prompt, significant but transient increase in HONO emissions in the dark (figure 3, after 12:30). Subsequent irradiation weakly enhanced the HONO emissions. These observations demonstrate that HONO is produced in a dark reaction between nascent or preformed, persistently trapped NO₂ and humic substances. It should be emphasized that the second addition of humic acid was made on snow surfaces at −8°C, above that temperature a +11.5 pptv HONO/°C temperature dependence of HONO emissions is suggested by our data (figure 4). The increase in HONO mixing ratios between 12:45 and 13:15 is related to temperature, which rose in this time by 4°C.

We also tested the effect of O₃ additions to our system. A pen-ray UV lamp was used to generate ca 28–35 ppb O₃ in the 10 slm air flown over the snow samples. Whereas the empty reaction chamber rapidly equilibrated with O₃, it took several hours for the input and output O₃ concentrations to equalize over snow samples, particularly in the presence of NO. HONO emissions decreased to some extent at higher O₃ concentrations. This inverse correlation has already been noted by Amoroso et al (2005) on Arctic snow surfaces at Ny-Ålesund during boundary layer O₃ depletion events.

The experiments on June 4 released less HONO than on the previous day, pointing to partial reactant depletion. However, HONO emissions increased by 50–100% upon irradiation, an effect that was further enhanced by higher snow surface temperatures (figure 5). Overnight cooling and re-heating may have conceivably modified the snow surface as reaction medium. Ozone input to the system was varied between 0 and 35 ppbv on June 4, without discernible effect on HONO emissions.

In summary, nitrite, which accumulates in alkaline snow, is released as HONO upon acidification. Minimal photochemical HONO production is observed in snow samples containing natural levels of humic acids. Spreading snow surfaces with humic acids led to enhanced HONO dark emissions, which were not stimulated by further irradiation, and were only weakly dependent on temperature or O₃ addition. However, these samples, after being subjected to partial melting and refreezing, i.e., to the incorporation of humic acids deeper into the snowpack, are able to sustain significant photochemical HONO production having a positive temperature coefficient (figure 5).

4. Discussion

Some HONO is released once the snow surface is rendered acidic; NO₂ stored in an alkaline ice matrix might be released
as the pH changes. The mean NO$_3^-$ concentration in the snow was only 2.7 ppbw; if all this NO$_3^-$ had been released as HONO into the circulating gas during 3 days, a mean mixing ratio of 250–380 pptv would have resulted (depending on the actual snow density) versus the actual 10–20 pptv background levels actually detected. The experiments of June 2, 3, and 4 were carried out on the same snow after doping its surface with 3.5 × 10$^{11}$ NO$_3^-$ ions, or ~20 ppmw N, which is far larger than the amount originally present in the collected samples. Polar snow typically contains ~100 s ppbw NO$_3^-$ (Beine et al 2002b, 2006). The maximum emissions from this surface were on the order of 2.5–3 × 10$^{10}$ N molecules cm$^{-2}$ s$^{-1}$ in the form of NO, NO$_2$ or HONO (figure 6). Figure 6 also shows that emissions gradually fell off along the experiments. A total of 7 × 10$^{17}$ N-containing molecules, or about 0.02% of the available nitrogen returned to the gas-phase through acid release, photochemistry or organic secondary reactions. These findings are consistent with previous observations from Arctic field experiments (e.g. Beine et al 2002a). They indicate that only surface nitrogen is available for release, whereas deeper NO$_3^-$ does not react, or reaction products are retained by the ice matrix.

Substantial HONO emissions required the presence of organic/humic material. According to Aubin and Abbatt (2007) thermal H-abstraction from fresh soot can convert primary photochemical NO$_2$ into secondary HONO. It appears that the requisite conditions were not met initially for the photochemical production of HONO via the process envisioned by Stemmler et al (2006); the organic/humic material present was either inadequate, or improperly located (Domine et al 2008). However, after the snowpack was annealed overnight, the redistribution of solutes within the snowpack led to significant photochemical HONO production, which was further enhanced at higher temperatures. It is conceivable that the humic acids thawed into the snow surface and refroze, thus changing the surface and favoring the photochemical over the dark mechanism. In addition, since humic acids are supramolecular aggregates (Sutton and Sposito 2005) it is unlikely that they retain their structure and properties throughout the experiment. The denaturated species may become more reactive toward vibronically excited NO$_2$ than the original material. Note that the longer-lived electronically excited NO$_2$ states have a radiative lifetime of ~50 μs, and are efficiently quenched by H$_2$O (Li et al 2008). Even at high emissions, only less than 1% of total N available in the snow was released from the surface. The system behaves as if there were a pool of NO$_x$ species in the snow that could be reduced by HULIS (humic-like substances) in the dark at low temperatures. This NO$_x$ pool gets partially depleted, and the system reacts to light as if it were replenished of NO$_x$ at the right sites. This suggests a rapid H-atom transfer in NO$_x$/HULIS encounters.

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**References**

Amoroso A, Beine H J, Sparapani R and Nardino M 2005 Observation of coinciding Arctic boundary layer ozone depletion and snow surface emissions of nitrous acid Atmos. Environ. 40 1949–56

Amoroso A, Beine H J, Domíné F, Esposito G, Nardino M, Ianniello A, Montagnoli M and Allegrini I 2008 Photochemical emissions of NO$_3$ and HONO from the snow surface during snowfalls in the marine high Arctic, in preparation

Beine H J, Honrath R E, Domine F, Simpson W R and Fuentes J D 2002a NOx during background and ozone depletion periods at Alert: fluxes above the snow surface J. Geophys. Res. 107 4584
Cotter E S N, Jones A E, Wolff E W and Baugitte S J-B 2003 What controls photochemical NO and NO2 production from Antarctic snow? Laboratory investigation assessing the wavelength and temperature dependence J. Geophys. Res. 108 4147
Domine F and Shepson P B 2002 Air–snow interactions and atmospheric chemistry Science 297 1506–10
Domine F, Sparapani R, Ianniello A and Beine H J 2004 The origin of sea salt in snow on Arctic sea ice and in coastal regions Atmos. Chem. Phys. 4 2259–71
Honrath R E et al 2000a Release of NOx from sunlight-irradiated midlatitude snow Geophys. Res. Lett. 27 2237–40
Honrath R E, Guo S, Peterson M C, Dziobak M P, Dibb J E and Arsenault M A 2000b Photochemical production of gas phase NOx from ice crystal NO3 J. Geophys. Res. 105 24183–90
Huie R E 1994 The reaction kinetics of NO3 Toxicology 89 193–216
Li S, Matthews J and Sinha A 2008 Atmospheric hydroxyl radical production from electronically excited NO2 and H2O Science 319 1657–60
Ridley B et al 2000 Is the Arctic surface layer a source and sink of NOx in winter/spring? J. Atmos. Chem. 36 1–22
SPSS, Inc 1999 Systat 9, Chicago, IL
Taira M and Kanda Y 1990 Continuous generation system for low-concentration gaseous nitrous acid Anal. Chem. 82 630–3