8-1-2000

Release of NO(x) from sunlight-irradiated midlatitude snow

R E. Honrath
Michigan Technological University

Matthew C. Peterson
Michigan Technological University

M P. Dziobak
Michigan Technological University

Jack E. Dibb
University of New Hampshire, jack.dibb@unh.edu

Matthew Arsenault
University of New Hampshire - Main Campus

See next page for additional authors

Recommended Citation

R. E. Honrath, M. C. Peterson, M. P. Dziobak, J. E. Dibb, M. A. Arsenault, and S. A. Green, "Release of NOxfrom sunlight-irradiated midlatitude snow," Geophysical Research Letters, vol. 27, no. 15, pp. 2237–2240, Aug. 2000.

Authors

R E. Honrath, Matthew C. Peterson, M P. Dziobak, Jack E. Dibb, Matthew Arsenault, and S A. Green

Release of NO_x from Sunlight-irradiated Midlatitude Snow

R. E. Honrath, M. C. Peterson, M. P. Dziobak

Department of Civil and Environmental Engineering, Michigan Technological University, Houghton

J. E. Dibb and M. A. Arsenault

GRG/CCRC/EOS, University of New Hampshire, Durham

S. A. Green

Department of Chemistry, Michigan Technological University, Houghton

Abstract. Photochemical production and release of gas-phase NO_x ($NO + NO_2$) from the natural snowpack at a remote site in northern Michigan were investigated during the Snow Nitrogen and Oxidants in Winter study in January 1999. Snow was collected in an open 34 L chamber, which was then sealed with a transparent Teflon cover and used as an outdoor flow and reaction chamber. Significant increases in NO_x mixing ratio were observed in synthetic and ambient air pulled through the sunlit chamber. [NO_x] enhancements were correlated to ultraviolet sunlight intensity, reaching $\sim$300 pptv under partially overcast midday, midwinter conditions. These findings are consistent with NO_x production from photolysis of snowpack NO_3^-; the observed NO_x release implies production of significant amounts of OH within the snow. Snowpack NO_3^- photolysis may therefore significantly alter boundary layer levels of both NO_x and oxidized compounds over wide regions of the atmosphere.

Introduction

There is a growing body of evidence that snow surfaces are not inert reservoirs of adsorbed or absorbed compounds, but rather are active participants in photochemical reactions that alter the composition of both the snow and the overlying atmosphere. We have observed elevated levels of NO_x ($NO + NO_2$) in the interstitial air of the snowpack at Summit, central Greenland, and suggested that the NO_x was photochemically produced from nitrate [*Honrath et al.*, 1999]; confirming observations have been made in a study of Antarctic snowpack [*Jones et al.*, 2000]. Through wind pumping, snowpack interstitial air is mixed with the overlying atmosphere [*Albert*, 1996]. Recent measurements indicate that resulting impacts on ambient atmospheric composition are significant: a diurnal cycle in NO_x with amplitude as large as 30–40 pptv was observed at Alert, Nunavut, Canada, following polar sunrise [*Ridley et al.*, 2000], and NO levels in the range of 100 pptv were observed at South Pole, Antarctica [*Davis et al.*, 1999]; release from the snowpack was identified as the most likely cause in both cases.

Snow surfaces are present over large areas of midlatitude regions as well: as much as one-half of the land surface

north of 20°N is snow-covered during winter [*Frei and Robinson*, 1998]. Much of this region is remote from large anthropogenic emissions of NO_x. However, the photochemical release of NO_x from snowpack NO_3^- may effect the recycling of photochemically active nitrogen oxides (NO_x), extending the influence of NO_x emissions to more remote regions.

The Snow Nitrogen and Oxidants in Winter (SNOW99) study was organized to determine whether the photochemical processes observed in polar regions also occur in midlatitude snowpacks, and, through the simultaneous measurement of a variety of compounds, to begin to elucidate the mechanism and impacts of the process. Photochemical production of NO_x was investigated in two ways. In the first, snow was artificially produced from deionized water and from deionized water to which $NaNO_3$ was added. The results of those experiments demonstrate that the presence of NO_3^- alone is sufficient for the production of NO_x, and provide the basis for an analysis of the mechanism of NO_x production presented in a separate paper [*Honrath et al.*, 2000]. In the second set of experiments, natural snow was used. The results of these experiments demonstrate that significant photochemical NO_x production occurs in natural, midlatitude snow and are the subject of this paper.

Experimental Methods

Measurement Site: The measurements were made in a small clearing in a mixed hardwood and conifer forest in a remote region of northern Michigan (see Figure 1). The region between the field site and Lake Superior was devoid of combustion sources, and the region across Lake Superior to the west and northwest of the site is sparsely populated. As a result, during periods when winds were from the prevailing westerly/northwesterly direction, NO_x levels were relatively low and stable, allowing us to observe incremental effects of snow chemistry upon ambient air composition. Convection over Lake Superior and orographic lifting as air flowed eastward over the Keweenaw Peninsula resulted in frequent lake-effect snow during the study period and provided large amounts of relatively clean snow for analysis.

Snow Photochemistry Chamber: A PFA Teflon-coated high-cross-section aluminum flow chamber (53 cm width by 10 cm height) was used, to allow sampling by multiple investigators during other SNOW99 experiments. Chamber length was 67 cm; perforated TFE

Table 1. Summary of Observed $[NO_x]$ Enhancements

Experiment	$d[NO_x]/dJ_{NO_2}$, 10^3 pptv s^{-1}	Method[a]	$[NO_3^-]$, μM	Q,[b] sLpm	$\dfrac{d[NO_x]/dJ \cdot Q}{[NO_3^-]}$
Jan. 28 (Fig.2)	55 ± 0.1	Regression	15.00 ± 0.80	9	33
Jan. 12 (Fig.3a)	33–76	$\Delta[NO_x]/J$	10.56 ± 0.07	9	28–65
Jan. 11 (Fig.3b)	26 ± 5	$\Delta[NO_x]/J$	10.60 ± 0.22	20	36
Artifically created snow[c]	234	Regression	100	9	21

[a]Regression: slope from regression analysis. Uncertainty in column 2 reflects ±1 standard error of the slope. $\Delta[NO_x]/J$: J_{NO_2}-normalized difference between $[NO_x]$ exiting the flow chamber when exposed to sunlight and that exiting the flow chamber when darkened. Range presented in column 2 for Jan. 12 reflects range of covered and uncovered NO_x levels shown in Figure 3(a). Uncertainty presented in column 2 for Jan. 11 reflects ±1 standard error of the difference between the mean covered and uncovered NO_x levels.

[b]Q, volumetric flow rate.

[c]Snow produced using deionized water with 100 μM NaNO$_3$ added. Regression slope is taken from Figure 4 of *Honrath et al.*, 2000.

Teflon dividers held the snow in the center 62 cm. Spaces at the inlet and outlet were provided for pressure equalization. The top was sealed with transparent FEP Teflon film; transmittance smoothly increased with wavelength, and ranged from 75% at 290 nm to 90% at approximately 430 nm. Time-response experiments using addition of NO at the inlet indicate that flow through the snow-filled chamber was not uniform: at 9 standard liters per minute (sLpm), a concentration pulse resulting from the initiation of standard addition of $\sim$600 pptv NO traveled through the chamber in 10–20 s, rather than ≥170 s as expected for uniform flow through snow of typical densities in the 34 L chamber. In addition, a time constant of 70–130 s was observed in response to the step-function increase in inlet concentration; this is interpreted as the characteristic time for mixing between the main flow and the full chamber volume. It is expected that measured NO_x production rates would have been similar to or higher than those reported here had flow through the chamber been more ideal. The effect of the chamber walls was investigated by flowing air through the chamber while empty. In both ambient and synthetic air, increases in $[NO_x]$ upon flowing through the chamber were ≤ 50 pptv and were not correlated to sunlight intensity.

The flow chamber was left uncovered in an untraveled region between experiments, to allow snow to fall directly inside. During the night prior to the Jan. 11 experiment, 3.5 cm of new snow filled the chamber; the remainder of the chamber was filled by gently transferring fresh snow from the surrounding region into the flow chamber, using a clean scoop. For the Jan. 12 experiment, day-old snow from the same snowfall was used to fill the chamber. Fresh snowfall filled the chamber to overflowing during the 36 hr prior to the Jan. 28 measurements.

Measurements: NO, NO$_2$, and NO$_y$ were determined using a system described previously [*Peterson and Honrath*, 1999]. NO and NO$_2$ measurements were made in ambient air, in air exiting the flow chamber while it was darkened, and in air exiting the flow chamber while it was sunlit. NO$_y$ (total reactive nitrogen oxides) was determined simultaneously in the ambient air and is used as an indicator of the presence or absence of variations in ambient NO_x levels. The photodissociation method used to determine NO$_2$ has a known $\sim$12–30% interference from HONO [*Kley and McFarland*, 1980; *Ridley et al.*, 2000], which may be released

from sunlit snow. However, our measurements of HONO and NO_x release rates during SNOW99 and at Summit, Greenland, indicate that [HONO] is generally less than [NO$_2$], so this interference has a minimal impact on the results presented here. Excluding any impact from HONO interference, measurement accuracy is estimated to be 6%, with precision <12 pptv. Nitrate in melted samples was determined by ion chromatography [*Dibb et al.*, 1994], and total organic carbon (TOC) was determined by high-temperature persulfate oxidation.

A 2-π St J_{NO_2} radiometer (Metcon USA) adjacent to the flow chamber was used to monitor the downwelling component of the NO$_2$ photolysis rate constant, as a measure of ultraviolet radiation. Calibration was provided by the manufacturer; no corrections were applied. J_{NO_2} values reported in this paper reflect only the downwelling component determined above the snow surface. Although the absorption cross-section for NO$_2$ extends further into the red than does that of NO$_3^-$ [*Meyerstein and Treinin*, 1961], J_{NO_2} is used here as the best indicator of ultraviolet actinic flux available during the present study.

Experiments: Two experiments were conducted using ambient air during periods when variability in ambient NO_x levels was low enough to allow detection of changes in mixing ratio of $\sim$<100 pptv. On January 12, the effect of snow photochemistry was investigated by uncovering the
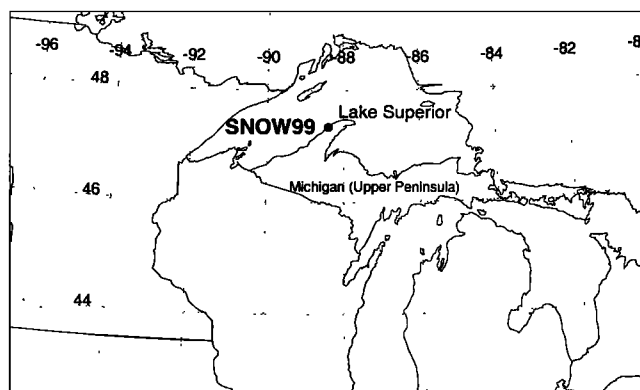

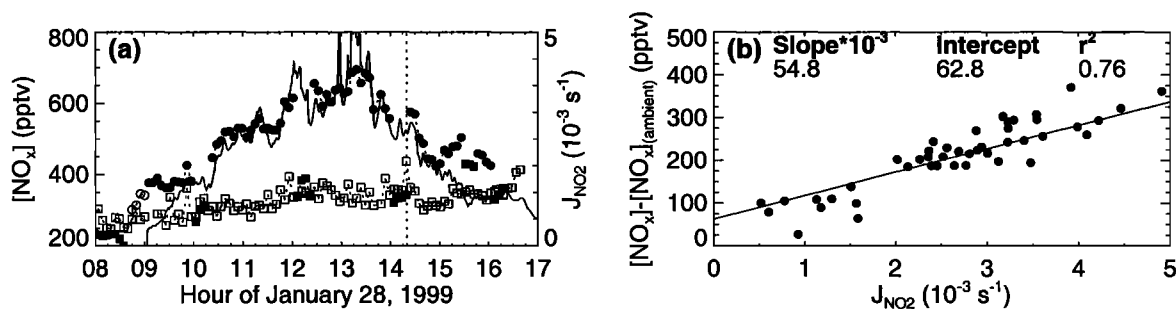**Figure 1.** The location of the SNOW99 field site in northern Michigan.

Figure 2. NO$_x$ production in ambient air on January 28, 1999. (a) Time series of [NO$_x$] determined in ambient air (solid squares), the effluent of the flow chamber while covered (open circles), and the effluent of the flow chamber while exposed to sunlight (solid circles). Open squares indicate ambient [NO$_x$] estimated as 0.60 times ambient [NO$_y$]. The downwelling component of J$_{NO_2}$ measured above the snow surface is indicated by the solid line (J$_{NO_2}$ is set to zero during the period when the flow chamber was covered prior to 9 am). The vertical dotted line indicates the end of the period used in the regression analysis of (b); ambient [NO$_x$] measurements after this time diverged from those estimated from ambient [NO$_y$]. (b) Relationship between the [NO$_x$] enhancement resulting from production within the flow chamber and J$_{NO_2}$. [NO$_x$] enhancement is calculated as the difference between [NO$_x$] in the effluent of the sunlit chamber (solid circles in [a]) and ambient [NO$_x$] (estimated; open squares in [a]).

darkened flow chamber for two periods of approximately 1 hr duration while monitoring the effluent composition. On January 28, the chamber was uncovered in the morning and remained uncovered for the 7-hour experiment; ambient NO$_x$ levels were monitored periodically during this period. An additional experiment using breathing-air-quality synthetic air was conducted on January 11. The protocol on this day was similar to that used on January 12, except that the chamber was uncovered only once, for a 1.5 hr period. Temperatures during the experiments on Jan. 28, Jan. 12, and Jan. 11 were −6 to −2, −13 to −12, and −18 to −12 °C, respectively. TOC levels in the snow used in the experiments on these days were 0.04–0.07, 0.27, and 0.4 ppm, respectively.

Results and Discussion

Results from the January 28 experiment are shown in Figure 2a. Ambient NO$_x$ levels varied by $\lesssim$150 pptv during the first 6 hours, and the variation present is captured adequately by scaling ambient NO$_y$ levels. NO$_x$ levels exiting the darkened chamber were approximately 50 pptv higher than ambient when flow through the chamber was initiated at 0830. [NO$_x$] rose when the chamber was uncovered at

0900, and variations in NO$_x$ levels exiting the uncovered chamber followed variations in solar radiation for the remainder of the day. The correlation between the NO$_x$ enhancement above ambient and solar radiation, as indicated by J$_{NO_2}$, is shown in Figure 2b.

Results from the other two, more limited experiments are shown in Figure 3. On both days, NO$_x$ levels in the effluent of the covered chamber were initially much higher than those in the air entering the chamber. This apparently resulted from exposure of the snow in the chamber to sunlight without flow, prior to covering the chamber. NO$_x$ levels exiting the covered chamber declined over time, eventually approaching those in the ambient air (Figure 3a) and synthetic air (Figure 3b) entering the chamber. The process governing the rate of NO$_x$ decline in the dark is not known. On both days, NO$_x$ levels in the flow chamber effluent increased when the chamber was uncovered.

These results indicate that NO$_x$ production occurred within the snow, at a rate directly related to the sunlight intensity. Table 1 summarizes results from the three experiments, in terms of the observed increase in [NO$_x$], normalized by ultraviolet intensity. It would be preferable to use J$_{NO_3^-}$ to normalize the observations. However, as the nec-
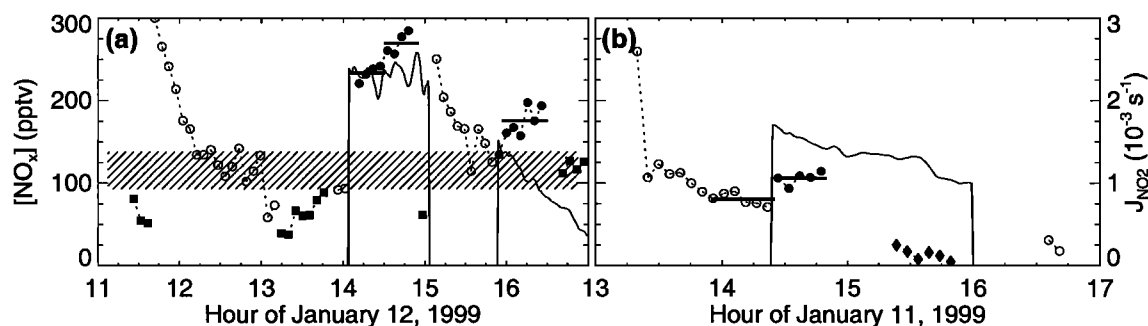

Figure 3. NO$_x$ production in ambient air on January 12 and in synthetic air on January 11, 1999. Symbols are as described for Figure 2. (a) January 12: The range of [NO$_x$] exiting the covered chamber and the levels of NO$_x$ exiting the sunlit chamber, used to estimate the NO$_x$ enhancements listed in Table 1, are indicated by the shaded region and the horizontal solid lines, repectively. (b) January 11: the average levels of NO$_x$ exiting the covered and uncovered chamber, used to estimate the NO$_x$ enhancement listed in Table 1, are indicated by solid lines. The mixing ratio of NO$_x$ in the synthetic air entering the flow chamber is indicated with solid diamonds. Missing data on January 11 reflect periods when ambient air was sampled to allow other compounds to be determined in the chamber effluent.

essary spectral actinic flux measurements were not possible during SNOW99, we use J$_{NO_2}$.

The J-normalized NO$_x$ production rates shown in the second column of Table 1 vary by a factor of 2.1 to 3. As the observed NO$_x$ production is attributed to photodissociation of NO$_3^-$ [Honrath et al., 2000], NO$_x$ production should be related to NO$_3^-$ concentration within the snow. Relative molar NO$_x$ release rates (the enhancements in NO$_x$ mixing ratio, normalized by both J$_{NO_2}$ and NO$_3^-$ concentration, times the flow rate) during each experiment are shown in the last column of Table 1. These values are more tightly clustered than the J-normalized release rates in column 2, consistent with the expectation that NO$_x$ release in these experiments was the result of nitrate photolysis. However, the number of experiments is insufficient to determine the functional relationship between NO$_x$ release, actinic flux, and nitrate concentration. For comparison, the NO$_x$ enhancement observed in synthetic air during an experiment using artificially created snow [Honrath et al., 2000] is shown in the bottom row of Table 1. Although the increase in NO$_x$ mixing ratio observed in that experiment reached 600 pptv, twice the maximum observed in natural snow, this difference appears to be largely or entirely attributable to the higher NO$_3^-$ level in the snow.

In all experiments, the observed NO$_x$ enhancement was the result of an increase in NO$_2$, not NO. For example, on Jan. 28, [NO$_2$] exiting the chamber was significantly greater than [NO$_2$] in ambient air, while [NO] exiting the chamber was lower than that in ambient air. Oxidation of NO to NO$_2$ cannot explain this observation. Based on the apparent mixing period observed for flow through the chamber (discussed above) and measured ozone mixing ratios (30–35 ppbv), oxidation of <60% of NO is expected within the flow chamber. Therefore, we conclude that NO$_x$ production occurred primarily in the form of NO$_2$. This is consistent with findings based on experiments with artificially produced snow and synthetic air, in which NO$_2$ production in NaNO$_3^-$-containing snow exceeded that of NO by a factor of at least 8 [Honrath et al., 2000]. We attribute this to direct NO$_2$ formation through the overall reaction NO$_3^-$ + $h\nu$ + H$^+$ → NO$_2$ + OH on snowpack ice grains, followed by volatilization of NO$_2$.

Implications

The impact of the observed NO$_x$ production on the ambient atmosphere may be significant. NO$_x$ released into the interstitial air of surface snow will be released to the atmosphere through wind pumping: wind driven advection is known to ventilate polar snowpacks to a depth of ≥1 m [Albert, 1996; Davis et al., 1996]. Thus, in remote regions, nitrate "recycling" to NO$_x$ may form a significant component of the boundary layer NO$_x$ budget. In addition, co-production of OH from NO$_3^-$ photolysis should lead to oxidation of organic compounds present within the snow or snow interstitial air and, through release of photolabile oxidized compounds, to enhancement of ambient HO$_x$ (OH + HO$_2$) levels.

The degree to which snow photochemistry is active under more polluted conditions is not known. Further investigation is called for, as snow surfaces are seasonally present in many urban and industrial regions, and release of oxidants or oxidized organics could potentially play a significant role in springtime urban photochemistry in such regions.

The results presented here are based on a limited number of experiments. While they clearly demonstrate the occurrence of significant photochemical NO$_x$ production in natural mid-latitude snow, additional experiments are necessary to more precisely determine the relationship between the rate of production and snow properties, spectral actinic flux, and snow composition, and the magnitude of the resulting emission of NO$_x$ to the overlying atmosphere.

References

Albert, M. R., Modeling heat, mass, and species transport in polar firn, *Ann. Glaciology*, *23*, 138–143, 1996.

Davis, R. E., E.M. Arons, and M.R. Albert, Metamorphism of polar firn: Significance of microstructure in mass, energy, and chemical species transfer, In Wolff, E. W., and R. C. Bales, editors, *Chemical Exchange between the Atmosphere and Polar Snow, NATO ASI Ser. I*, volume 43, pp. 379–402, New York, 1996, Springer-Verlag.

Davis, D. D., M. Buhr, J. Nowak, G. Chen, R. Mauldin, F. Eisele, and D. Tanner, Unexpected high levels of NO at South Pole: Observations and chemical consequences, *Eos Trans. AGU*, *80*, F190, 1999.

Dibb, J. E., R. W. Talbot, and M. H. Bergin, Soluble acidic species in air and snow at Summit, Greenland, *Geophys. Res. Lett.*, *21*, 1627–1630, 1994.

Frei, A., and David A. Robinson, Evaluation of snow extent and its variability in the Atmospheric Model Intercomparison Project, *J. Geophys. Res.*, *103*, 8859–8871, 1998.

Honrath, R. E., M. C. Peterson, S. Guo, J. E. Dibb, P. B. Shepson, and B. Campbell, Evidence of NO$_x$ production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, *26*(6), 695–698, 1999.

Honrath, R. E., S. Guo, M. C. Peterson, M. P. Dziobak, J. E. Dibb, and M. Arsenault, Photochemical production of gas-phase NO$_x$ from sunlight irradiation of ice-crystal NO$_3^-$, *J. Geophys. Res.*, in press, 2000.

Jones, A. E., R. Weller, and H.-W. Jacobi, Speciation and rate of photochemical NO and NO$_2$ production in Antarctic snow, *Geophys. Res. Lett.*, *27*, 345–348, 2000.

Kley, D., and M. McFarland, Chemiluminescence detector for NO and NO$_2$, *Atmos. Tech.*, *12*, 63–69, 1980.

Meyerstein, D., and A. Treinin, Absorption spectra of NO$_3^-$ in solution, *Trans. Faraday Soc.*, *57*, 2104–2112, 1961.

Peterson, M. C., and R. E. Honrath, NO$_x$ and NO$_y$ over the northwestern North Atlantic: Measurements and measurement accuracy, *J. Geophys. Res.*, *104*, 11,695–11,707, 1999.

Ridley, B., J. Walega, D. Montzka, F. Grahek, E. Atlas, F. Flocke, V. Stroud, J. Deary, A. Gallant, H. Boudries, J. Bottenheim, K. Anlauf, D. Worthy, A. L. Sumner, and P. Shepson, Is the arctic surface layer a source and sink of NO$_x$ in winter/spring?, *J. Atmos. Chem.*, *36*, 1–22, 2000.

M. P. Dziobak, R. E. Honrath, and M. C. Peterson, Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI 49931, U.S.A. (e-mail: reh@mtu.edu)

S. A. Green, Department of Chemistry, Michigan Technological University, Houghton, MI 49931, U.S.A. (e-mail: sgreen@mtu.edu)

M. A. Arsenault and J. E. Dibb, GRG/CCRC/EOS, Morse Hall, 39 College Road, University of New Hampshire, Durham, NH 03824, U.S.A. (e-mail: jack.dibb@unh.edu)