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Speciation and Rate of Photochemical NO and NO_2 Production in Antarctic Snow

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Abstract. Measurements were made of NO and NO_2, in controlled experiments to investigate their production from snow. Throughout a diurnal cycle, measurements were made of ambient air and air from inside a snowblock. Enhanced concentrations of NO and NO_2 (up to 15 pptv and 32 pptv respectively) were measured inside the snowblock. The production rate inside the block varied with intensity of incident radiation, and reached a maximum of 1.1×10^6 molecs/cm^3/s for NO and 2.1×10^6 molecs/cm^3/s for NO_2. A second experiment, in which the snowblock was alternately exposed to sunlight and then shaded, confirmed that the diurnal production was driven by photochemistry rather than some other diurnally varying factor. Concentrations of nitrate in the snowblock did not change as a result of 50 hours of experiments, confirming that if nitrate is the source reservoir, it can not be rapidly depleted. Snowpack production may contribute significantly to NO_x concentrations in the Antarctic lower troposphere.

Introduction.

The existence of a diurnal variation in NO_y (= NO + NO_2 + HNO_3 + PAN + alkyl nitrates etc.) was observed in a measurement campaign at the German Antarctic research station, Neumayer (70°S, 8°W), in summer 1997 [*Weller et al.*, 1999]. A diurnal cycle in a tracer such as NO_y implies regular changes in either sources or sinks (or both) of one or more component family members. The NO_y data clearly showed an influence from local meteorology and some exchange of HNO_3 at the snow surface was also observed, but this could not account for the magnitude of the diurnal NO_y changes. Given that the Antarctic troposphere is remote from major pollution sources, any process which might influence concentrations of active chemicals, such as NO_x, clearly has important implications for regional tropospheric chemistry. It is potentially also an added complication in the quest to translate the ice core nitrate signal into one for past concentrations of NO_x [*Wolff*, 1995].

A recent paper reporting work from Summit, Greenland, suggested that photochemical reactions occurring within or upon surface snow produced NO_x from a N-reservoir compound within the snow [*Honrath et al.*, 1999]. There was some evidence in the reported measurements of a photochemical influence on NO_x production and the authors suggested that photolysis of nitrate, present in surface snow, may be a source of NO_2.

To investigate these findings further, we carried out controlled experiments during the PEAN 1999 (Photochemical Experiment at Neumayer) summer campaign, aimed at i) confirming the photochemical nature of the observed NO_x production, ii) determining whether NO or NO_2 was the dominant product, and iii) quantifying the source of both NO and NO_2. The experiments were based around comparing concentrations of both NO and NO_2 in ambient air, and in air that was sucked through a porous block of snow, supported so that all sides were exposed to the air and light. Any differences in concentration were thus a product of the snowblock activity. The experiments were carried out on days with a high incidence of solar radiation, and in a sheltered location to minimise any influence of varying wind speeds.

Experimental

Measurements were carried out at Neumayer's atmospheric observatory located 1.5 km upwind of the station [*Jones et al*, 1999]. An EcoPhysics PLC760, for photolytic conversion of NO_2 to NO, and an EcoPhysics CLD780TR, for chemiluminescent detection of NO, were used to measure NO and NO_2 [*Weller and Schrems*, 1996; *Jones et al.*, 1999]. The CLD780TR used either an integration time of 60 secs (later averaged into 5 minute means) or 200 secs (averaged into 20 minute means). The calculated accuracy of the NO and NO_2 measurements was ±2 pptv and ±4 pptv respectively, with an average detection limit for 20 minute averaging (2σ of background signal [*Weller and Schrems*, 1996]) of 2.0 pptv NO and 3.5 pptv NO_2.

A snowblock, roughly 20 cm x 20 cm x 20 cm, was cut from surface snow using cleaned equipment to avoid contamination. The block dimensions were then measured accurately. In the middle of the uppermost face, a hole (diameter=3 cm, depth=9 cm) was cut into the block. The block was then supported on two horizontal poles 1 m above the snow surface. All sides were thus exposed to the air and sunlight. A teflon filter holder with diameter slightly greater than 3cm was inserted into the hole to a depth of 2.5 cm so that the hole was sealed from outside ambient air. Two 10 m long PFA inlet lines (4 mm id) were connected to the CLD780TR *via* a 3-way teflon valve. One line was attached to the teflon filter holder in the snowblock such that any air entering this line would have passed through the snowblock from the air outside. The other line sampled ambient air 1 m above the ground adjacent to the snowblock. The flow rate to the CLD780TR was 1500 cm^3/min such that the residence time of air in the inlet lines was 5 seconds. The volume of the snowblock was 10.14 dm^3. Assuming 50% of the volume was air (ie. a snow density of 0.45g.cm^{-3}), and an equal flow of air

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through the block from all directions, the residence time of air in the snowblock was 3.4 minutes. Two specific experiments were carried out. Furthermore, snow samples taken from the snowblock, and from the pit from which it was dug, were analysed for nitrate (NO_3^-).

1. Diurnal measurement.

Measurements of NO and NO_2 were made continually throughout a day/night cycle, from 14:00 on February 22nd to 16:00 on February 23rd. The inlet line switched between sampling ambient air and the snowblock air roughly every 1 to 2 hours, allowing representative NO and NO_2 averages to be calculated. The results are shown in Figure 1. Figure 1a) shows the variation in NO, with a clear diurnal variation in ambient air, with zero NO during the night, and a maximum of roughly 9 pptv around noon. The concentrations of NO in air that has passed through the snowblock follow a similar cycle, but the concentrations during the daylight hours are substantially larger than those in ambient air, with an average of 22 pptv around noon on the first day. During nighttime, concentrations of NO in both ambient air and snowblock air drop to zero. Figure 1b) shows the variation in NO_2. The diurnal variation in ambient air has a minimum around midday and a maximum (roughly 16 pptv) around midnight. However, air that has passed through the snowblock shows a totally different diurnal cycle, with maximum NO_2 mixing ratios around noon and minimum during the night. During the day, mixing ratios of NO_2 in snowblock air are consistently higher than in ambient air, reaching around 35 pptv on both days. During the night, the mixing ratios effectively track those of ambient air.

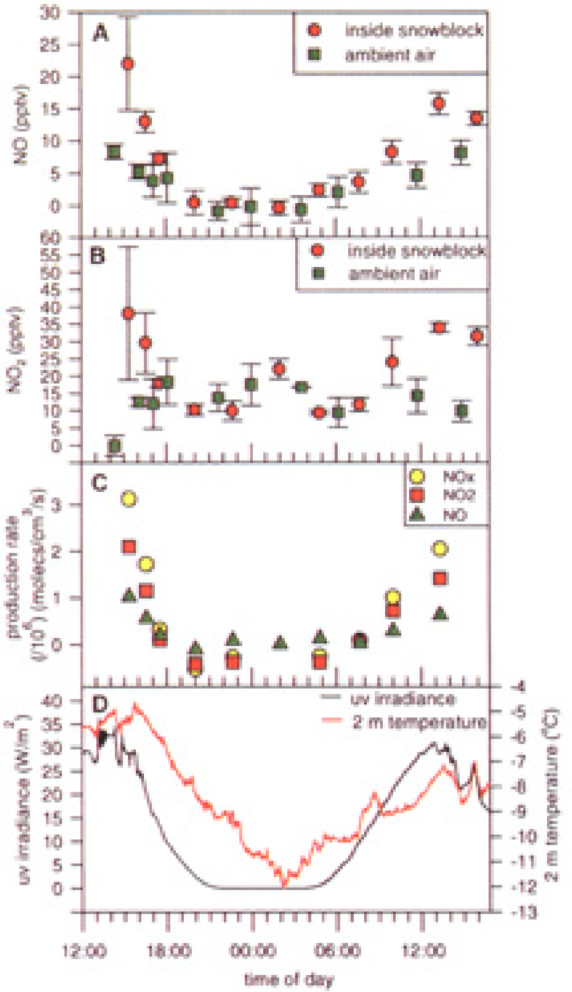

Figure 1. Measurements of a) NO and b) NO_2, both in ambient air and from air within the snowblock. The "snowblock air" has recently been ambient, the change in NO and NO_2 concentration is caused by processes within the snowblock. Measurements are for a complete diurnal cycle, and each data point shown is the average of between 30 minutes and 2 ½ hours of sampling. Error bars are the standard deviation of the individual measurements. c) Production rate of NO, NO_2, and therefore NO_x from the snowblock, over a diurnal cycle. d) Variation in ultraviolet irradiance (290 to 385 nm), and ambient air temperature at 2m height, during the period of the experiment.

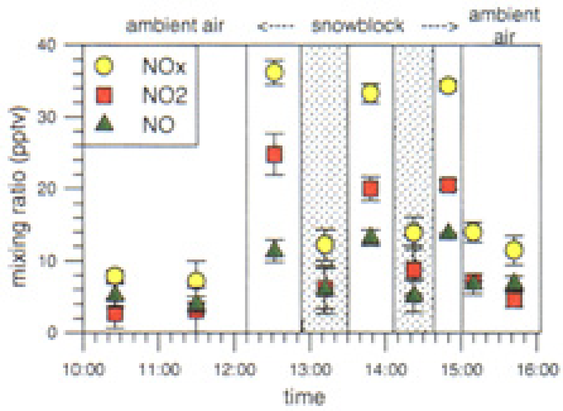

Figure 2. Measurements of NO, NO_2, and NO_x in the "shading experiment". The first and final sections (1 and 7) are measurements made in ambient air. Middle sections are measurements made within the snowblock, alternatively fully exposed to sunlight and fully shaded to eliminate any photochemical activity. Periods of shading are indicated by stipling.

It is now possible to calculate production rates of NO and NO_2 over the day. This was done by interpolating the data from Figures 1a) and b) onto a common time axis and deriving the magnitude of NO, NO_2 and thereby NO_x produced. The production rate per unit volume of the block (ie. snow + air) is calculated from:

$$\underset{(molecs/cm^3/s)}{production} = \frac{\Delta NO,\ \Delta NO_2\ or\ \Delta NO_x\ (pptv) * LN * FR}{volume\ of\ block\ (cm^3)}$$

where $\Delta NO = (NO_{snowblock} - NO_{ambient\ air})$, $\Delta NO_2 = (NO_{2\,snowblock} - NO_{2\ ambient\ air})$, $\Delta NO_x = (NO_{x\ snowblock} - NO_{x\ ambient\ air})$, LN = Loschmidt's number = 2.69×10^{19} molecules/cm^3, FR = flow rate (cm^3/s). The result is shown in Figure 1c). The production rates of NO and NO_2 reached a maximum of 1.1×10^6 molecs/cm^3/s and 2.1×10^6 molecs/cm^3/s respectively, and fell to essentially zero between 19:00 and 07:00 on these days. In terms of mixing ratio, an increase of 47 pptv of NO_x was measured early afternoon on Feb 22nd. Figure 1d) shows the variation in ultra violet irradiance (290 to 385 nm) measured with an Eppley TUVR radiometer, and ambient air temperature at 2 m height, during the experiment.

2. Shading experiment.

Measuring over a diurnal cycle is clearly a good start when looking for photochemical effects, but other parameters, such as temperature, also vary on a diurnal timescale (as shown by Figure 1d). Care is therefore needed when interpreting diurnal variations. With this in mind, an experiment was carried out on Feb 24th to directly control the amount of sunlight reaching the snowblock over short time intervals. Initially, measurements of NO and NO_2 were made in ambient air, to provide a reference. The inlet line was then connected to the snowblock as previously described, and a measurement integration time of 60 seconds selected. Measurements of NO and NO_2 were then made from air that had passed through the snowblock which was exposed to full sun. This was done for 40 minutes, such that a representative number of measurements were made and meaningful averages could be calculated. The snowblock was then "shaded" by carefully wrapping aluminium foil around all sides of the block to shade it from the sun, while ensuring that the foil was loose enough not to restrict the air flow. The air from the snowblock was then measured for a further 40 minutes. The shading was then removed so that the sequence of measuring the snowblock "unshaded" and "shaded" could be repeated. After several cycles, measurements of NO and NO_2 were repeated in the ambient air for reference.

The results from this experiment are shown in Figure 2. The dramatic increase in both NO and NO_2 mixing ratios during the "sunlit" phases as opposed to the "shaded" phases is immediately obvious. Mixing ratios of NO and NO_2 during the "shaded" phases are essentially the same as in the ambient air measured at the start and end of the experiment, at ~6 pptv and ~5 pptv respectively. However, during the "sunlit" phases, mixing ratios of NO rose to an average of 13 pptv, and those of NO_2 rose to 22 pptv. Furthermore, the changes in concentration between the "sunlit" and the "shaded" modes were extremely rapid in both directions, and evident in the first measurement made after the change in light intensity. This experiment demonstrates conclusively that the source of NO_x is dominated by photochemistry in the snow.

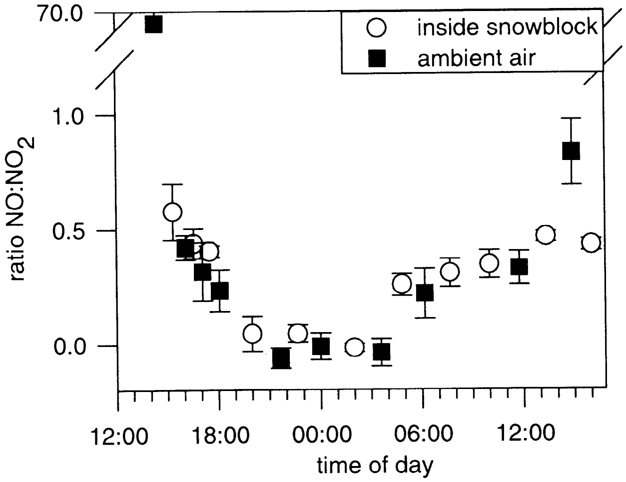

Figure 3. Ratio of NO:NO_2 in both ambient air and in the snowblock, from February 22nd to 23rd. The ratio is derived from the data of Figure 1. Error bars are based around standard error of the mean; for the first point they are out of range of the plot, at ±65.9, ie. ratio range from 3.4 to 135.5.

3. Snow analysis.

Duplicate snow samples were taken both from the snowpit at the time of cutting the snowblock, and from the snowblock itself at the end of the experiment. The samples were analysed while at Neumayer using an ion chromatograph to measure concentrations of NO_3^-. The upper 4 cm of the snowblock comprised of freshly deposited wind-blown snow with relatively low concentrations of nitrate (~30 ng/g). Concentrations increased with depth to a smooth profile of roughly 50 ng/g throughout the rest of the block. The profile from the aged snowblock was essentially the same as that of the snow pit from which it was dug: no significant change in nitrate concentration in the snowblock occurred between the time the snowblock was dug, and the time that the experiments ended (~50 hours).

Discussion

We have provided clear evidence that photochemical activity in surface snow in Antarctica can significantly increase concentrations of both NO and NO_2 in firn air. An important question is what is the mechanism supplying the additional NO_x, and what is the reservoir species. These are likely to be the same as those responsible for the observed NO_x production at Summit [*Honrath et al.*, 1999]. Having measured both NO and NO_2, we looked at the ratio NO:NO_2 for clues. The ratio of NO:NO_2 in both ambient air and the snowblock has a clear diurnal variation, with minimum during the night rising to a noon maximum (Figure 3). The difference occurs in the early afternoon, when the ratio in ambient air rises sharply to a high maximum (due to the decline in NO_2 - see Figure 1b), while the ratio within the snowblock declines due to the relatively much greater concentrations of NO_2. Unless radically different chemistry occurs inside the snowblock to that outside (ie. for the drivers of the NO:NO_2 partitioning: $j(NO_2)$, O_3 and RO_2), this strongly suggests a source of NO_2 within the firn. If nitrate is the reservoir for this production, its erosion appears to be slow. Taking even the lowest snow nitrate concentration in the block (30 ng/g) and the highest production rate shown in Figure 1c), the nitrate reservoir in the snowblock would be sufficient for 2 years of NO_x production, so it is not surprising that we see no loss in snow nitrate over a few days.

Although the production is within the firn, and the calculated production rates do not immediately translate into an atmospheric source strength, some exchange between firn and atmosphere will undoubtably occur and influence local photochemistry. *Dibb et al.* [1998] reported air/snow fluxes of NO_y at Summit that were not accounted for by HNO_3 exchange. The production rate per unit area receiving sunlight can be estimated assuming a surface area of 1450 cm^2 (=3 sides of the block, since not all sides were receiving full sunlight). The average production rate of NO_x for the day in Figure 1) would be $9x10^6$ molecs/cm^2/s, which if fully vented would be enough to replenish a 50 m thick inversion layer by ~5 pptv of NO_x per day. Assuming a concentration of OH of

4×10^5 molecs/cm^3 [*Crutzen*, 1994] and with the main sink of NO_x being reaction with OH, the lifetime of NO_x is of the order of 24hours. The calculated NO_x source from the snowpack could therefore make a significant contribution.

The implications of this study are numerous and significant. Firstly, a key goal of studying ice core nitrate is to reconstruct past levels of NO_x [*Wolff*, 1995]. This study suggests a significant influence of local variables (particularly uv irradiance and concentration of nitrate in snow) on tropospheric NO_x concentrations over Antarctica. Reconstructing past tropospheric NO_x in polar regions from the local ice core nitrate signal could therefore be possible. However, the ultimate goal is the global picture, and for this, the complete derivation (sources and deposition mechanisms as well as re-cycling) of snowpack (and hence ice core) nitrate must be known. Secondly, at low accumulation sites concentrations of nitrate in ice cores drop off rapidly with depth [*Wagnon et al.*, 1999] and although remobilisation and re-emission are suggested as causes, the mechanism is not fully understood. Photolytic decay is a potential contributor to this observed loss. Finally, the influence on polar tropospheric chemistry must be considered. The annual cycle of surface ozone measured at South Pole [*Schnell et al.*, 1991] shows a secondary maximum in late spring coincident with the current annual maximum in uv-B radiation [*Booth et al.*, 1994]. Based on the competition between the reactions HO_2 + NO and HO_2 + O_3 , the balance between production and destruction of ozone at South Pole in springtime (30 ppbv O_3, -30°C) is of the order 5 pptv NO, ie. the pivotal concentration of NO is of the order reported for coastal Antarctica [*Jefferson et al.*, 1998; *Jones et al.*, in press]. The growing intensity of uv radiation arising from growth of the Antarctic ozone hole [*Farman et al*, 1985, *Jones and Shanklin*, 1995] might have provided an increased source for NO_x, switching this clean air regime to ozone production during late spring. Photochemical activity in polar snow has recently been proposed as a source of HCHO [*Sumner and Shepson,* 1999], although another study attributed elevated HCHO to temperature-dependent degassing of HCHO deposited with snowfall [*Hutterli et al.*, 1999]. If there is a photochemical source, and considering the increase in uv radiation, the snowpack could increasingly have become an important source for peroxy radicals, and hence OH, to the troposphere. It is evident from these observations that the chemistry of the polar regions, although "clean", is nonetheless extremely complex. The role of the snow surface in influencing a range of chemical reactions could be extremely significant.

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References

Booth, C.R., T.B. Lucas, J.H. Morrow, C.S. Weiler, P.A. Penhale, The US NSF/Antarctic Program's Network for Monitoring Ultraviolet Radiation, in *Ultraviolet Radiation in Antarctica: Measurements and Biological research*, (C.S. Weiler and P.A. Penhale, eds.), AGU Antarctic Research Series, vol. 62, AGU, Washington, D.C., 17-37, 1994.

Crutzen, P., Global tropospheric chemistry, in *Low-temperature chemistry of the atmosphere*, NATO ASI Series I, vol. 21 (editor G.K. Moortgat et al.), *465-498,* Springer-Verlag, New York, N.Y., 1994.

Dibb, J.E., R.W. Talbot, J.W. Munger, D.J. Jacob, S.-M. Fan, Air-snow exchange of HNO_3 and NO_y at Summit, Greenland, *J. Geophys. Res., 103*, 3475-3486, 1998.

Farman, J.C., B.G. Gardiner, and J.D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction, *Nature, 315,* 207-210, 1985.

Honrath, R.E., M.C. Peterson, S. Guo, J.E. Dibb, P.B. Shelson, B. Cambell, Evidence of NO_x production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett., 26*, 695-698, 1999.

Hutterli, M.A., R. Röthlisberger, R.C. Bales, Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland, *Geophys. Res. Lett., 26*, 1691-1694, 1999.

Jefferson, A., D.J. Tanner, F.L. Eisele, D.D. Davis, G. Chen, J. Crawford, J.W. Huey, A.L. Torres, H. Berresheim, OH photochemistry and methane sulfonic acid formation in the coastal Antarctic boundary layer, *J. Geophys. Res., 103,* 1647-1656, 1998.

Jones, A.E., R. Weller, A. Minikin, E.W. Wolff, W.T. Sturges, H.P. McIntyre, S.R. Leonard, O. Schrems, S. Bauguitte, Oxidised Nitrogen Chemistry and Speciation in the Antarctic Troposphere, *J. Geophys. Res.*, 1999.

Jones, A.E. and J.D. Shanklin, Continued decline of total ozone over Halley, Antarctica, since 1985, *Nature, 376,* 409-411, 1995.

Schnell, R.C., S.C. Liu, S. J. Oltmans, R.S. Stone, D.J. Hofmann, E.G. Hutton, T. Deshler, W.T. Sturges, J.W. Harder, S.D. Sewell, M. Trainer, J.M Harris, Decrease of summer tropospheric ozone concentrations in Antarctica, *Nature, 351*, 726-729, 1991.

Sumner, A.M. and P.B. Shepson, Snowpack production of formaldehyde and its effect on the Arctic troposphere, *Nature, 398*, 230-233, 1999.

Wagnon, P., R.J. Delmas, and M.Legrand, Loss of volatile acidic species from upper firn layers at Vostok, Antarctica, *J. Geophys. Res., 104*, 3423-3431, 1999.

Weller, R. and O. Schrems, Photooxidants in the marine arctic troposphere in summer, *J. Geophys. Res., 101*, 9139-9147, 1996.

Weller, R., A.E. Jones, E.W. Wolff, A.Minikin, P.S. Anderson, G. König-Langlo, O. Schrems, Investigating possible causes of the observed diurnal variability in Antarctic NO_y, *Geophys. Res. Lett.*, 1999.

Wolff, E., Nitrate in polar ice, in *Ice core studies of global biogeochemical cycles,* NATO ASI Series I, vol. 30 (editor R.J. Delmas), *195-224,* Springer-Verlag, New York, N.Y., 1995.

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