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Measurements of NO_X emissions from the Antarctic snowpack

A.E. Jones[1], R. Weller[2], P.S. Anderson[1], H.-W. Jacobi[2], E.W. Wolff[1], O. Schrems[2], H. Miller[2]

Abstract. It has been shown that NO_x is produced photochemically within the snowpack of polar regions. If emitted to the atmosphere, this process could be a major source of NO_x in remote snowcovered regions. We report here on measurements made at the German Antarctic station, Neumayer, during austral summer 1999, aimed at detecting and quantifying emissions of NO_x from the surface snow. Gradients of NO_x were measured, and fluxes calculated using local meteorology measurements. On the 2 days of flux measurements, the derived fluxes showed continual release from the snow surface, varying between ~0 and $3x10^8$ molecs/cm^2/s. When not subject to turbulence, the variation was coincident with the uv diurnal cycle, suggesting rapid release once photochemically produced. Scaling the diurnal average of Feb. 7th ($1.3x10^8$ molecs/cm^2/s) suggests an annual emission over Antarctica of the order 0.0076TgN.

Introduction

The chemistry of oxidised nitrogen species at high latitudes is proving to be surprisingly complex. Original polar studies were aimed at understanding the nitrate record in ice cores, which hold the potential to reconstruct concentrations of NO_x during past historic times [*Wolff*, 1995]. For this purpose it is necessary to understand both the background chemistry determining NO_x concentrations in the polar troposphere, and also any exchange processes between the snow and the air. Neither of these is currently fully understood.

Two recent studies have focussed on NO_x in the interstitial air within the snowpack of Greenland [*Honrath et al.*, 1999] and Antarctica [*Jones et al.*, 2000]. Several conclusions have been drawn from these studies: i) that in these locations, NO_x concentrations within the snowpack interstitial air are higher than those of the overlying atmosphere; ii) that this arises because of *in situ* production, possibly from the breakdown of nitrate impurities in the snow; iii) that this production is driven by photochemistry; and iv) that it appears that NO_2 rather than NO is the dominant product. Given that this has been observed in both polar regions, and that nitrate is a common impurity in snow and ice, it is likely that this process will occur in any snow-covered areas of the world. In snow-covered areas remote from anthropogenic emissions, such as Antarctica, this process could be the dominant source of NO_x to the regional atmosphere.

No study has yet attempted to directly identify nor quantify emissions of NO_x from snow, although there are observations which are in accord with such a process. *Weller et al.* [1999] report a diurnal variation of NO_y in the Antarctic troposphere which, although modulated by local meteorology, seemed to have a surface source. *Ridley et al.* [2000] reported diurnal cycle in both NO_x and NO_y at Alert, which they attribute to release of NO_x from the snow surface. In Greenland, *Dibb et al.* [1998] noted that gradients of HNO_3 could not explain fluxes of NO_y, either in magnitude or direction. *Munger et al.* [1999] suggested reversible adsorption of compounds such as PAN to ice surfaces as an explanation but emissions of NO_x could account for some of the NO_y fluxes.

We report here measurements made during the PEAN 1999 (Photochemical Experiment at Neumayer) summer campaign designed to detect and quantify NO_x emissions from the Antarctic snowpack, and to asses factors controlling the emissions

Experimental

1. Overview

The measurements were carried out from 5-7th February 1999 at the German Antarctic station, Neumayer (70°39'S, 8°15'W) [*Jones et al.*, 1999; *Weller et al.*, 1999]. The experiment required measurements of NO_x at two different heights. Because of instrument configuration, such a measurement is not straightforward and it was necessary to use two instrument systems. The first was an EcoPhysics PLC760, for photolytic conversion of NO_2 to NO, coupled to an EcoPhysics CLD780TR for chemiluminescent detection of NO. Automatic measurements with a PLC760/CLD780TR combination can either switch between NO_2 and NO measurement modes at a single location, or between measuring in one mode at two different heights. The system was therefore used to measure in the NO_2 mode at two different heights. This avoided a possible offset that might be present if each height level is sampled with a different detector. The measurement derived is not a direct value of NO_2, but represents the mixing ratio of NO plus the fraction of NO_2 that is photolytically converted to NO, and is referred to as NO.c. This conversion fraction was derived regularly throughout the 7 week measurement campaign from calibration tests and was $(0.65\pm0.06) \times NO_2$. The formula for derivation of NO_2 is therefore:

$$NO_2 = 1/0.65 \times (NO.c - NO) \quad (1)$$

In order to derive NO_2, and thereby NO_x, a measurement of NO is also required, so a second CLD780TR was employed to derive NO. This instrument was dedicated to a different experiment, however, and could therefore only measure at a single height. The influence of this on the derived gradients of NO_x is fully discussed below.

A mast was erected in a clean sector away from the observatory. Two 10 m PFA inlet lines (4mm i.d.) were attached at a height of 0.02 m and 2.5 m above the snow surface respectively. They were connected to the PLC760/CLD780TR system by a teflon switching valve, allowing the instrument to switch automatically between the inlet lines. Using a flow rate of 1500 cm^3 minute^{-1}, the residence time for samples in the inlet line was 5 seconds. A third inlet line at 1.5 m height connected to the CLD780TR for measurement of NO only.

2. Artefacts, accuracy and precision

Both detectors were calibrated according to the method described by *Weller and Schrems* [1996] the only exception being

[1] British Antarctic Survey, Natural Environment Research Council, Cambridge, UK

[2] Alfred-Wegener-Institute for Polar and Marine Research, Bremerhaven, Germany.

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that 1.03 (±5%) ppmv NO in N_2 (Messer Griesheim) was used for dynamic dilution to between 3 ppbv and 10 ppbv NO. NO_2 was generated by gas phase titration of the NO calibration mixtures. The potential artefact arising through production of NO_2 within the system from the reaction $NO+O_3$ [*Ridley et al.*, 1988] was assessed to be constant (due to constant ambient O_3 mixing ratios) and at worst 4% in the photolysis cell and less than 2.3% in the inlet lines. Both CLD780TRs were integrated for 200 secs and the data averaged to 20 minute means. The calculated accuracy, including all artefacts, was ±2 pptv NO and ±4 pptv NO_2 with an average detection limit for 20 minute means (2σ of background signal) of 2.0 pptv NO and 3.5 pptv NO_2 (see *Weller and Schrems* [1996] for details). Earlier laboratory tests showed that the instrument is capable of detecting spikes of less than 2 pptv NO/NO_2 mixtures on a 20 minute time base. Given that we are considering the difference between two measurements made with the same instrument, a key parameter is the precision of the instrument (see *Weller and Schrems* [1996] for details of derivation). The 2σ uncertainty of the 20 minute averages was 1.5 pptv NO_x, so that gradients greater than 2.1 pptv are significant on a 2σ level.

3. Error analysis for gradient measurements

To address the potential for instrumental bias, NO was measured in parallel with both detectors for 6 days prior to the flux measurements. The mean difference of the measured NO was 0.26 pptv (s.d. 2.2 pptv) ie. data from the two systems agree within the quoted error margin. The NO.c measurements were made with the same instrument and under the same conditions so the errors arise from the precision of the instrument (±15%) and the accuracy of the conversion fraction (±10%).

To derive gradients of NO_x it was necessary to assume that NO measured at 1.5 m height is representative of NO at both 0.02 m and 2.5 m, ie. that there was no gradient in NO. This assumption is unlikely to be correct and introduces a quantifiable bias into the derived gradients. We assess the limits on the size of the bias here.

$$\Delta NO_x = \frac{1}{0.65}\Delta NO.c - (\frac{1}{0.65} - 1)\Delta NO \quad (2)$$

The difference between the NO_x mixing ratios at 0.02 m height and 2.5 m height, given the conversion fraction of 0.65, and following the relationship in Eq'n 1 is:

$$\Delta NO_x^* = \frac{1}{0.65}\Delta NO.c \quad (3)$$

where Δ denotes the mixing ratio at 0.02 m height minus that at 2.5 m. Because we assume that NO is constant, we actually calculate: and our error is equal to 0.54ΔNO. If the true ΔNO is positive, assuming a zero gradient will lead to a positive bias in ΔNO_x, and vice versa.

A gradient in NO might arise from three causes:

i) if NO were deposited to the snow surface this would cause ΔNO to be negative (higher mixing ratio at 2.5 m). However, we currently have no reason to expect that such deposition occurs indeed we expect the opposite (see iii below).

ii) If NO_2 is emitted from snow and by 2.5 m height it has still not reached photochemical equilibrium with NO (through photolysis of NO_2 and the reaction of NO with O_3 or RO_2), then the ratio NO/NO_2 can be expected to increase with increasing height from the surface, making ΔNO negative. However, the timescale for vertical mixing at the site during the period of the measurements can be calculated as a few seconds (following *Garratt*, 1994) while the timescale for photolysis of NO_2 at noon in early February is around 1 minute. The NO/NO_2 ratio should therefore not be altered substantially from this cause.

iii) If NO is also emitted from the snow surface (perhaps some NO_2 is already photolysed before the air leaves the surface), and given the time required to reach photostationary state, then NO should decrease with height, ie. ΔNO would be positive. This seems to be the most likely scenario. From our previous work using a block of snow [*Jones et al.*, 2000], we found that during daylight when NO_x was being photochemically produced, the NO in the snow interstitial air was roughly 50% of the NO_2. Under these conditions, $\Delta NO \approx 0.5\Delta NO_2$. With our error of 0.54ΔNO it follows that:

$$\Delta NO_x^* = 1.2\Delta NO_x \quad (4)$$

In other words, under reasonable conditions we estimate that our assumption of constant NO causes our derived NO_x gradients to be up to 20% higher than the real ones.

Deriving fluxes

Various methods can be used to derive fluxes of chemical species depending on hardware available and the location of the flux measurements (eg. tree canopy, open water etc.) as is fully discussed by *Dabbert et al.* [1993]. For our work, fluxes of NO_x were derived from gradients in vertical NO_x concentrations and an eddy diffusivity as described by *Dabbert et al.* [1993].With this approach, the flux of a species and its vertical gradient are linked by a coefficient of proportionality, *K*. For fluxes of NO_x, the relationship can be written:

$$F(NO_x) = K_{NO_x}\frac{d(NO_x)}{dz} \quad (5)$$

K_{NOx} has not previously been measured, but following Monin-Obukhov surface layer similarity theory [*Stull*, 1988], it has a similar form to K_H, the transfer coefficient for heat. Following *King and Anderson* [1994], K_H can be derived from:

$$K_H = U_*.\kappa.z\left(\Pr + \alpha_T\frac{z}{L}\right) \quad (6)$$

where κ = von Kármán's constant (= 0.40); z = logarithmic mean of the measurement heights ($\ln^{-1}((\ln(2.5m) + \ln(0.02m))/2)$) (=0.22 m), U_* is the friction velocity. For neutral to moderate stability, as encountered in Antarctica during the summertime, $\alpha_T.z/L$ is negligible [*King and Anderson*, 1994]. The equivalent turbulent Prandtl number *Pr* for NO_x is unknown, but as similar numbers for heat and moisture are ≈1 [*King and Anderson*, 1994] it is reasonable to take *Pr* for $NO_x = 1$. Therefore, K_{NOx}, the transfer coefficient for NO_x, is derived:

$$K_{NO_x} = U_*.\kappa.z \quad (7)$$

U_* can be derived iteratively given a wind speed, temperature gradient and an assumed surface roughness [*King and Anderson*, 1994], parameters which are all available for Neumayer [e.g. *König*, 1985]. The mean error on U_* when $U_* > 0.2$ is 10%. Fluxes of NO_x, $F(NO_x)$, were then calculated from:

$$F(NO_x) = U_*.\kappa.z\frac{[NO_x]_{2.5m} - [NO_x]_{0.02m}}{\Delta z} \times LN \quad (8)$$

where *LN* = Loschmidt's number = number of molecules per cm^3 air (= 2.69×10^{19}) and Δz = 2.5 m - 0.02 m = 2.48 m. Positive fluxes represent release of NO_x from the snowpack to the atmosphere.

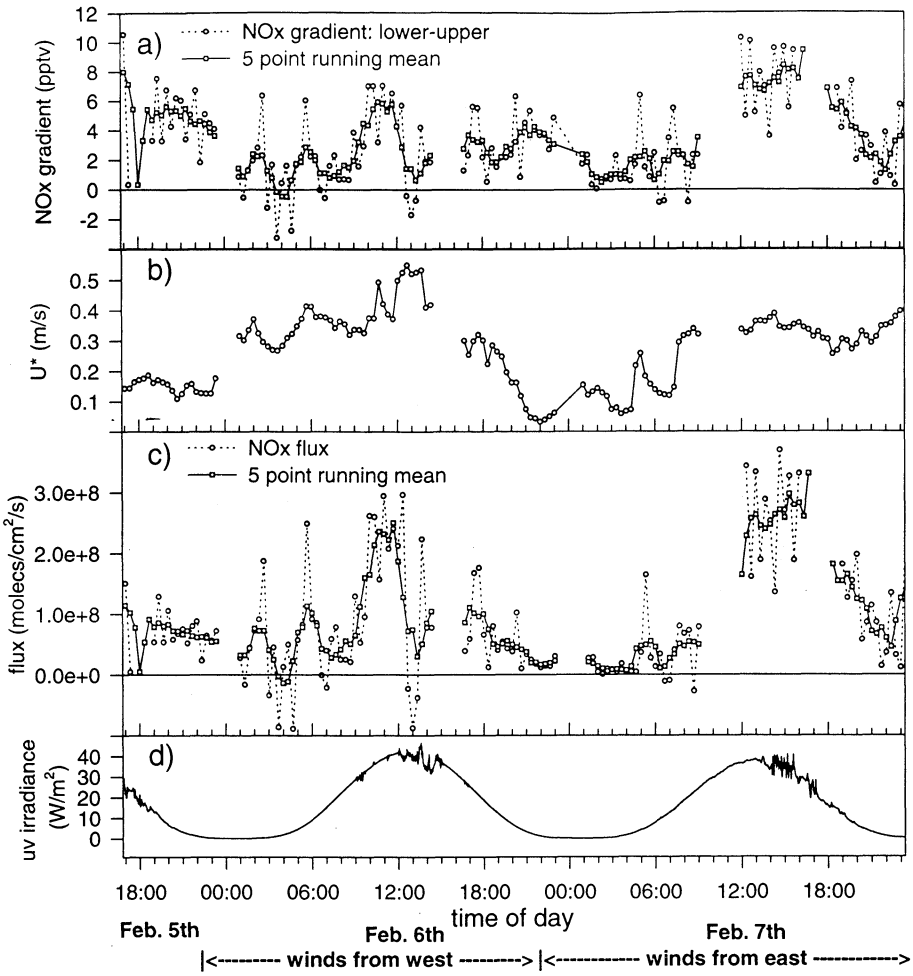

Figure 1. a) Gradients of NO_x derived from measurements at 2 cm - 2.5 m. Based upon considerations of instrument precision, gradients greater than 1.5 pptv are significant at the 2σ level; b) Variation in the friction velocity, U_*, which governs turbulent transfer, on the days of gradient measurements; c) Fluxes of NO_x derived from the measured gradients and U_*. Note that those measured during westerly winds are subject to turbulence. During easterly winds, the measurements are not influenced by turbulence; d) Diurnal variation in ultra violet irradiance (290 to 385 nm) on the days of measurements.

Combined errors from uncertainties in gradients and in U_* can thus be quoted as +10%/-30%.

Results

Figure 1a shows the gradient in NO_x (0.02 m - 2.5 m) measured on all days of the experiment. Gradients are generally positive and greater than the 2σ uncertainty. The magnitude varies between 0 and 9 pptv, based on a 5 point running mean. However, from 21:00 on Feb. 5th until 21:30 on Feb. 6th, winds were from the west and the inlets prone to turbulence from a nearby container. These data should thus be treated with appropriate caution. On Feb. 7th, with consistent easterly winds all day and no issues of turbulence, a noticeable diurnal cycle is evident. Figure 1b shows the variation of U_*, the friction velocity, during the same measurement period. U_* was smaller during the night (of the order 0 to 0.1 m/s) and with a tendency for larger U_* (up to 0.5 m/s) during the day. As a result, the transfer coefficient for NO_x, K_{NOx} (Eq'n 7), also varies in a similar way during the period of measurements. The NO_x flux, $F(NO_x)$, derived from the gradients and U_* is shown in Figure 1c. The calculated fluxes show significant variability, with essentially zero flux during the night, but reaching noon maxima of up to ~3 (+0.3/-0.9) x 10^8 molecs/cm²/s. NO_x is thus clearly being emitted from the snow to the overlying atmosphere throughout the majority of the day. Figure 1d shows the measured uv irradiance (290 to 385 nm) over these days, which also shows regular maxima at noon and nighttime minima.

Discussion and conclusions

When measurements were not disrupted by turbulence, the fluxes of NO_x varied in a regular manner with minima during the night and maxima around noon. Although U_*, driven by wind speed and temperature, clearly has an influence on NO_x fluxes, from ~02:00 to 22:00 on Feb. 7th, U_* is relatively constant but the flux of NO_x shows a marked diurnal variation. Given that we know NO_x is produced photochemically within the snowpack [*Jones et al.*, 2000], this strongly suggests that changes in uv irradiance is driving the flux. Furthermore, the NO_x flux decreases at the same time as the uv irradiance declines suggesting that photochemically-produced NO_x does not accumulate within the snowpack. We note that the measurements of *Honrath et al.* [1999] showed elevated concentrations of NO_x at 10 cm depth within the snowpack during daylight which also declined when the intensity of uv irradiance

dropped. With a diffusivity of around 10^{-5} m^2s^{-1} [Schwander et al., 1988], the venting timescale for this depth is 16 minutes, suggesting venting of photochemically produced NO_x on this timescale.

The impact of the NO_x flux on the overlying atmosphere will vary throughout the year according to production rate and seasonally-varying chemistry. For Neumayer on Feb. 7th, the mean daytime (i.e. from 06:00 to 21:00) NO_x flux, $F(NO_x)$, was $1.7x10^8$ molec/cm^2/s. Assuming the dominant NO_x loss occurs from reaction of NO_2 with OH (even at twilight the calculated photolysis rate of NO_3 is an order of magnitude greater than reaction with DMS, so that the latter does not provide an alternative sink for NO_x during this part of the day) and that photochemical equilibrium between NO and NO_2 is reached within a minute, the increase in the NO_x mixing ratio within a uniformly mixed layer of height z can be estimated from:

$$\frac{d[NO_x]}{dt} \approx \frac{F(NO_x)}{z} - k[OH][NO_2] \qquad (9)$$

With $k=2.4x10^{-11}(T/300)^{-1.3}$ cm^3 s^{-1} [*DeMore et al.*, 1994], a daily averaged $[OH]\approx 2x10^5$ molec cm^{-3} [*Jefferson et al.*, 1998] and a mixed layer height of 300m, the calculated NO_x increase between 06:00 and 21:00 is 9.6 pptv, close to the observed NO_x increase of ~10 pptv. Clearly this calculation is sensitive to the mixed layer height, and further the profile shape of NO_x emitted from the snow surface will be strongly influenced by the stability of the overlying boundary layer so will not always be uniformly mixed.

On a regional scale, if the source of NO_x is photolysis of nitrate impurities in the firn [*Honrath et al.*, 1999], and given the high concentrations of nitrate in polar snow [*Wolff*, 1995] we can assume that this production is occuring throughout the Antarctic continent. An average annual NO_x flux can be derived by scaling the Feb. 7th flux ($1.3x10^8$ molecs/cm^2/s) according to the relative uv irradiance (15.4 W/m^2 on Feb. 7th cf. 8.97 W/m^2 for the year). With an ice-covered surface of Antarctica of 13,340,000 km^2 [*Bartholomew*, 1985], an annual emission rate of 0.0076 TgN can be derived. Any tropospheric NO_x deposited as HNO_3 can potentially be recycled, but additionally, any nitrate deposited more directly to the snowpack can provide a source of new NO_x to the Antarctic troposphere. The source of NO_x from the snowpack is potentially very significant to Antarctica which is remote from most anthropogenic and biogenic sources. With regards the quest to derive atmospheric NO_x mixing ratios from concentrations of nitrate in ice cores, the findings presented here add a further twist and highlight an additional important factor that must be considered. Further measurements are clearly needed to derive a representative flux throughout the year and for different snow types.

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A.E. Jones, E.W. Wolff, P.S. Anderson, British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge, CB3 0ET, UK. (e-mail: a.jones@bas.ac.uk)

R. Weller, H.-W. Jacobi, O. Schrems, H. Miller, Alfred-Wegener Institut für Polar- und Meeresforschung, 27570 Bremerhaven, Germany. (e-mail: r.weller@awi-bremerhaven.de)

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