

This manuscript reports measurements of NO and NO₂ concentrations at three heights above the snow in the Antarctic Plateau. The concentration gradient was used to estimate the NO_x fluxes by the flux-gradient approach. They report NO_x emissions similar in its dynamics but somehow larger than modelled NO₃⁻ photolysis rates. The dynamics of NO_x mixing ratios is shown to depend both on NO_x emissions and boundary layer height dynamics. This study reports new data of NO and NO₂ concentrations and flux measurements in the Antarctic Plateau. The experimental methods were well adapted and the cautiously analysed. The graphics and tables are clear (but could be improved though). The conclusions are correctly deduced from the results. The manuscript is quite well written and clear.

Reply: We thank referee No.3 for a very detailed review which helped to further improve the manuscript. Comments (in italic) are addressed below and we note corresponding changes in the revised version of the manuscript intended for submission to ACP.

1 General review comments

1) *The main concern is the fact that the gradient method was used between 0.01 m and 1 m. The lowest height (0.01 m above the snow) is very close to the ground and may well be in the roughness layer. In such conditions the gradient method which is based on the Monin and Obukhov similarity theory may not be adapted. The authors should estimate the dynamic roughness length at the site and check that 1 cm is well above z₀ (at least twice as large). I am not familiar with Antarctica and Dome C in particular. Probably the roughness length is very small (for ice z₀ is probably smaller than 1 mm). However, even if z₀ is small the uncertainty on the sampling height is also larger at the smallest height, and especially when sampling in very calm air (the air is drawn from a volume around the sampling line. Why the authors did not used the gradient between 1 and 4 m height? Why did they not, at least, compare the flux estimated based on 0.01 and 1 m and 1 and 4 m height? If 1 cm is above the roughness layer, the authors could also use the three heights together to estimate the NO_x flux by the aerodynamic gradient method. I therefore would like the authors to comment on these points and evaluate the flux at several heights.*

Reply: Using a lower inlet at 0.01 m and an upper inlet at 1.0 m was a good compromise to estimate flux based on the flux-gradient method at Dome C:

a) The lower inlet at 0.01 m was so positioned to be i) well above the roughness layer and ii) close to the surface.

i) We assume that the snow properties at Dome C are similar to those at Halley, being compacted, sintered firn with some sastrugi. The aerodynamic roughness length at Halley is $(5.6 \pm 0.6) \times 10^{-5}$ m, that is around 55 μ m (King and Anderson, 1994). A point inlet at 1 cm is therefore many scale lengths above this length. There is an unknown element of inlet capture, in that in perfectly calm wind conditions, air is drawn in from both above and below this height. This may have a biased effect due to the theoretical curvature of the concentration and indeed such bias may even exist during turbulence (assumed to be ubiquitous at this height at Dome C). We are assuming that such bias is small, however: typical 2 m/s winds at 4 m (see Figure 3) implies a 1 m/s wind at 0.01 m. The flow rate of 5 Litre/minute (p6, 20) at this speed gives a radius scale of 0.9 mm: that is, the air sample is an average of a disc of radius 0.9 mm around the sample level of 10 mm. The mean concentration C has curvature due to the gradient being (to a 1st approximation) proportional to 1/z. Hence the concentration changes proportionally to ln(z). The relative difference between a sample at exactly 10 mm and an average of 9 and 11 mm is therefore the difference between $(\ln(0.011) + \ln(0.009))/2$ and $\ln(0.01)$ which is a difference of < 0.2%.

ii) Getting values close to the surface does significantly enhance the signal in C, as seen below: again assuming constant flux, the signal between 1.00 m and 0.01 m is double that between 1.00 m and 0.10 m, whilst between 4 m and 1 m the difference is approximately 30% of that between 1.00 m and 0.01 m.

b) The upper inlet at 1.0 m was so positioned to be far enough from the lower inlet to yield a large number of statistically significant concentration gradients, but low enough to be most of the time within the surface layer as required by the application of scalar similarity theory. Model estimates used in this study and the vertical extension of ground fog observed occasionally indicate that the inlet at 4.0 m was frequently above the surface layer (i.e. 10% of the boundary layer height), especially in the early evening.

A summary of the above arguments is now included in the method section of the revised manuscript.

2) *Another concern is the fact that the NO₂ emission from the snow is evaluated based on the NO₃⁻ photolysis at the snow surface. However no NO₃⁻ measurements are reported in the manuscript and no mention is given on how it was constrained in the model. This should be detailed.*

Reply: Extensive measurements of NO₃⁻ profiles in surface snow done at Dome C during the measurement period, are described in detail in France et al. (2011), which we did not want to reiterate. For clarification, we

include now some detail on this in the method section of the revised manuscript.

3) *A general comment is that the manuscript should be a bit reorganised so that all methodological descriptions comes at once in the material and methods. In the present manuscript some methodological details are given in the results and even in the discussion section. See detailed comments in the attached document.*

Reply: Agreed, we followed these helpful suggestions as indicated below.

4) *A question that arises from this work is: where does this nitrate in the snow come from? Does it come from precipitation mainly or also from deposition of HNO₃ which hence means a sort of cycling between NO₂ emissions from NO₃ in the snow which is deposited back to the snow. Could the authors comment on this.*

Reply: In Antarctica, primary NO₃⁻ sources are thought to be sedimentation of polar stratospheric clouds (PSCs) in late winter and a background tropospheric source from lightning, biomass burning and the ocean. The current thinking is that at polar sunrise vigorous photochemical cycling of reactive nitrogen species between surface snow and air is initiated (e.g. Frey et al., 2009; Davis et al., 2004a). A corresponding note and references are included in the revised manuscript.

2 Detailed comments

Minor comments from the review supplement are addressed below. Page and line numbers refer to the supplement, a manuscript version prior to final typesetting in ACPD.

p2, 13-15: *3-fold increase with decreasing BL height does not mean necessarily emissions. May be clarify*

Edited text: In particular, the NO_x emission flux estimated from atmospheric concentration gradients was during the measurement period on average ($\pm 1\sigma$) $6.9 (\pm 7.2) \times 10^{12}$ molecule m⁻² s⁻¹ and explains the 3-fold increase in mixing ratios in the early evening when the boundary layer becomes very shallow.

p2, 18: *Would not rather be "production"*

The quantity we compare is flux, i.e. number of molecules per area and time. The model yields a NO_x production rate from NO₃⁻ photolysis, i.e. molecules per volume and time, which is converted into flux by multiplying with snow depth in order to compare to measurements. We will clarify this throughout the text.

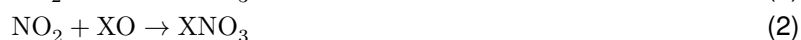
Edited text: The modelled mean NO₂ flux from nitrate (NO₃⁻) photolysis in snow is only about 62% of the observed NO_x flux and ...

p3, 2: *May be also give the product of the reaction; Unclear which latter it is if we may say so*

Edited text: This influence is achieved via photolysis of NO₂, the only source for in situ production of tropospheric ozone (O₃), through shifting HO_x radical partitioning towards the hydroxyl radical (OH) via the reaction NO + HO₂ → NO₂ + OH (R4), and finally through the latter reaction (R4) also controlling formation rates of peroxides (H₂O₂ and ROOH).

p4, 4: *As this reaction is the one retained as the only sink in the discussion section it should be also detailed here*

Edited text: NO₂ reacts further with hydroxyl or halogen radicals to form HNO₃ or XNO₃ which is then deposited to the snow surface:



p4, 5-6: *The authors may clarify where these reactions happens 'in snow' : surface, bulk, gas*

Edited text: The following simplified reaction scheme summarizes the main channels of NO_x production from NO₃⁻ photolysis taking place inside and on the surface of snow grains (Grannas et al., 2007): ...

p4, 7-11: *I wonder whether the reaction constants from each of these reactions should not be given in an appendix.*

Rate constants of the gas phase reactions can be found for example in Sander and Bottenheim (2012). For photolysis rates j we give a general expression in Section 4.2 as a function of quantum yield, absorption cross section and actinic flux. As an example relevant to this work we refer to France et al. (2011) where $j\text{-NO}_3^-$ is calculated for Dome C conditions.

Edited text: Reaction rate constants can be found for example in Sander and Bottenheim (2012). ... For example, photolysis rates of NO_3^- from reaction (R9) in the East Antarctic snow pack were derived previously as a function of solar zenith angle and snow depth (France et al., 2011).

p5, 22-23: *height of sonic and O_3 sensor*

Edited text: Measurements of the three-dimensional wind components (u , v , w) and temperature by a sonic anemometer (ATEC1-061101 at 7 m) mounted on a tower at 1.2 km distance were used to derive atmospheric turbulence parameters. Observations of ozone mixing ratios (Thermo Electron Corporation model 49I, Franklin, Massachusetts) at 15 m from Concordia station were also available (details in Legrand et al., 2009).

p6, section 2.1: *A scheme of the sampling system and the site would be good. It is hard to understand where the pump is and where mass-flow controller also.*

Figure 1 is now included in the revised version of the manuscript.

p6, 13: *This is very close to the ground. If you want to use the aerodynamic gradient method, you should ensure that the lowest measurement height is very high above the roughness height.*

See reply to general comment No.1.

p6, 14: *firn?*

Edited text: During selected time periods firn air (interstitial air) was sampled by inserting one inlet into pre-cored horizontal holes at 5–10 cm snow depth.

p6, 22: *Was the air drawn through the mass flow controller? If so wouldn't the NO be stuck there?*

Mass flow controllers and vacuum pump of the NO_x instrument were downstream of the reaction cell (see new Figure 1). It's NO_x production in the instrument rather than loss, which needs to be tested for (see note on artefacts below).

p7, 7-8: *Which quality, supplier etc...*

Edited text: The NO sensitivity of the CLDs was determined every 14 h by standard addition to the sample air matrix of a 1 ppmv NO/NO_2 mixture (UK National Physical Laboratory traceable BOC certified), which is further diluted to 4 ppbv of NO.

p7, 11: *This term was not defined previously. How is it measured?*

Edited text: The instrument artefact originating from NO_x producing surface reactions in inlets and reaction cells was determined by overflowing the instrument inlet with scrubbed ambient air supplied by an Eco-Physics Pure Air Generator (PAG003). The artefact was measured every 14 h, offset by 7 h to the calibration runs.

p8, 2: *It would be easy to estimate the pressure drop in the lines, knowing the flow rate, the line diameter the pressure and temperature. This is a standard estimation in fluid mechanics.*

Edited text: With $\text{CE}_{\text{Halley}}$ of 0.55 and a ratio of $\tau_{\text{DC}}/\tau_{\text{Halley}}$ of 0.72 one obtains a CE_{DC} of 0.44. Contrary to Halley long sample intake lines were used continuously at Dome C causing a pressure drop inside the photolytic cell of ~ 110 mb estimated from flow rates, temperature and inlet diameter. This further reduces the theoretical CE_{DC} to 0.38. Thus most of the difference in CE can be attributed to a shorter residence time of sample air in the photolytic cell.

p8, 5-11: *This is unclear: what is the baseline level? is that the count rate when zero air was sampled in each line? Clarify*

Edited text: Baseline count rates were determined by adding excess ozone to sample air in a pre-chamber so that all electronically excited NO_2 has returned to ground state when reaching the reaction chamber.

p9, 4-6: *Although there are physical reasons to discard negative values, there is no statistical argument. Moreover, by doing so one may actually bias the overall statistic of the concentration. Can the authors provide an estimate of the change in mean and median that is introduced by discarding these negative data.*

We agree with the argument of statistical bias, i.e. including negative NO_2 , e.g. at 1m, leads to mean and median values $\sim 4\%$ lower than reported. The revised version of the manuscript includes now $\text{NO}_2 < 0$ and all statistics are updated, accordingly.

p10, 16: *Usually to apply this flux gradient relationship to gradient measurements. The change in variable $z \rightarrow (\ln(z) - \Psi_h(z/L))$ is made which then leads to a more applicable form (somehow integrated). See for example eq. (1) and (2) in Stella, P., Loubet, B., Laville, P., Lamaud, E., Cazaunau, M., Laufs, S., Bernard, F., Grosselin, B., Mascher, N., Kurtenbach, R., Mellouki, A., Kleffmann, J. and Cellier, P., 2012. Comparison of methods for*

the determination of NO-O3-NO2 fluxes and chemical interactions over a bare soil. *Atmospheric Measurement and Techniques*(5): 12411257.

This is what we did, indeed: integration of equation 4 yields equation 5, a more general but equivalent form of the cited equations in Stella et al. (2012). Stability functions Φ_h appropriate for Antarctica were chosen, of which the integrated forms can be found in many micrometeorology text books, e.g. Jacobson (1999).

Edited text: Integrated forms of Φ_h can be found in Jacobson (1999).

p10, 20-21: *In this section the information is missing on what heights were used for estimating the flux : 0.01 and 1, 1 and 4 or the three of them? This is a critical point as 0.01 m may be too close to the ground. Indeed, the Obukhov similarity only works at heights much larger than z_0 . You should hence also give estimates of the roughness height z_0 . It can be estimated from wind speed and u^* inverting the logarithmic profile: $u(z)=u^*/k \ln(z/z_0)-Psim(z/L)$. Or from wind speed profiles if they exist. See e.g. Kaimal, J.C. and Finnigan, J.J., 1994. *Atmospheric Boundary Layer Flows, Their structure and measurement*. Oxford University Press., New York, 289 pp.*

See reply to general comment No.1.

p10, 20: *Since three measurement heights were done, either you can use the three heights (if they are sufficiently high above z_0 , or you only use two heights). If the three heights can be used, you should rather do a linear regression*

For the flux estimates NO_x measurements from two inlets (0.01 and 1.0 m) were used. See reply to general comment No.1.

p11, 3-6: *This information should be given at once. It is the third time that this anemometer is quoted but we only learn now which anemometer and what height it was placed at.*

Agreed, see reply to comment on p5, 22-23

p11, 8-11: *Although necessary, this 5 minutes measurements would probably imply slight underestimation of u^* due to highpath filtering. Did the author check this with other datasets?*

We include a minor correction as the instrument in fact alternated between 10 minutes of measurements and 10 minutes of heating. We therefore assume that the 10 minute averages of u^* are not biased.

Edited text: The instrument alternated between 10 min of measurements and 10 min of heating to prevent frost build up on the sensors.

p11, 17: *u^* is not a diffusion velocity. The turbulent time scale should better be estimated as $z_2 * Ra(z_2) = z_2 * u(z_2)/u_*^2$ See e.g. Stella, P., Loubet, B., Laville, P., Lamaud, E., Cazaunau, M., Laufs, S., Bernard, F., Grosselin, B., Mascher, N., Kurtenbach, R., Mellouki, A., Kleffmann, J. and Cellier, P., 2012. *Comparison of methods for the determination of NO-O3-NO2 fluxes and chemical interactions over a bare soil. Atmospheric Measurement and Techniques*(5): 12411257.*

Calculating a turbulent transport time scale τ_{mix} as z_2/u_* , sometimes referred to as a surface layer time scale (e.g. Stull, 1988), probably underestimates real values. Following the suggestion we use instead the product of surface layer thickness and aerodynamic resistance R_a , and estimate R_a for a gas from similarity theory after Jacobson (1999).

Edited text: The application of MOST and the assumption of constant flux both require a chemical lifetime (τ_{chem}) much longer than the turbulent mixing time scale (τ_{mix}) of the respective tracer. A typical τ_{mix} is calculated as the product of layer thickness, i.e. distance between the surface roughness height for heat ($z_{0,h}$) and reference height z_r (here 1 m), and aerodynamic resistance R_a .

$$\tau_{mix} = (z_r - z_{0,h})R_a \quad (3)$$

R_a of a gas is estimated from similarity theory as the inverse of the turbulent diffusivity for heat $K_h = \frac{\kappa u_* z}{\Phi_h(\frac{z}{L})}$ (Equation 4) integrated over the layer thickness (Jacobson, 1999):

$$\tau_{mix} = (z_r - z_{0,h}) \int_{z_{0,h}}^{z_r} \frac{\partial z}{K_h} = (z_r - z_{0,h}) \frac{\int_{z_{0,h}}^{z_r} \Phi_h(\frac{z}{L}) \frac{\partial z}{z}}{\kappa u_*} \quad (4)$$

During the study period τ_{mix} was on average on the order of ~ 10 min assuming $z_{0,h} \sim z_{0,m}$. τ_{chem} of NO and NO₂ is short due to rapid interconversion on the order of seconds. However, in the case of NO_x previous estimates of τ_{chem} range between 6.4 h (daily mean) at Halley (Bauguitte et al., 2012) and 8 h (median) at South Pole (Davis et al., 2004a). τ_{chem} of NO_x is ~ 40 times larger than τ_{mix} and NO_x flux estimates based on MOST are therefore justified.

p12, 5-6: *But not in Table 3 for 16-31 dec. Can you explain why?*

The NO median values in ambient air calculated for 2-week periods include variable numbers of data points because the 4 m inlet was used frequently to sample firn air. During Dec 16 -31 the total sampling time at 4 m was only half that at 1 m and predominantly during times when NO was higher leading to a higher median value at 4 m than at 1 m. To clarify the representativeness of the median values the total sample time (sum of all 1-minute intervals) are now included in Table 3 (similar to Table 2).

p12, 9-10: *Actually it rather decreases already at 0.01 m height to a value non significantly different from that at 4 m. From these data I would be cautious to conclude that it decreases with height...*

Agreed. Only examination of the median diurnal cycle of NO₂:NO ratios shows in fact a significant difference between 0.01 and 1.0 m during daytime, as discussed in section 4.3 (Fig.10).

Edited text: Furthermore, examination of the median NO₂:NO ratio reveals a strong decreases from 1.5 in firn air to 0.7–0.8 in air above the snow surface (Figs. 2, 3, Table 2).

p12, 13: *It is a bit confusing to go to Figure 7 already. Reconsider Figure order*

Agreed, adjusted in revised manuscript.

p12, 20-22: *Where do these number come from? It is difficult to make the link with Figures and tables there. Clarify*

Edited text: On a seasonal time scale the two-week medians of atmospheric mixing ratios of NO at 1 m are with 120 pptv highest before the summer solstice (1–15 December) and decrease in the second half of December and January to lower values ranging between 75 and 81 pptv (Table 3). Previously, at South Pole maximum atmospheric mixing ratios of NO were also observed in early summer, i.e. in the second half of November (Table 3).

p12, 24: *In Table 3 I do not see values for Dome C in November*

Clarified in reply to previous comment.

p12, 25: *It is only here that the reader see that the flux was estimated from differences between 0.01 and 1 m heights. This should have been explained before. Moreover an estimate of z₀ should be provided to compare with the lowest height*

See reply to general comment No.1.

p13, 11: *high? or elevated?*

Edited text: A first look at absolute atmospheric concentrations shows that the NO_x mixing ratios observed at Dome C are enhanced.

p15, 2-3: *Yes but if it is strongly stratified it means also that turbulence generated by wind shear is destroyed. Under stable conditions the turbulent exchange is diminished.*

Edited text: Noon maxima of u_* and K_h suggest that mixing is strongest around solar noon and has contributions from turbulence due to buoyancy (free convection) since $z/L < 0$, whereas during late afternoon to morning (16:00–07:00 LT) the atmosphere is stably stratified ($z/L > 0$) and any turbulence present is due to wind shear (forced convection) as the sole driver of mixing.

p15, 14-17: *This is true if there is no sinks at night.*

Here we demonstrate that mixing ratios follow a behaviour expected when mixing of snow emissions dominates atmospheric sources/sinks.

Edited text: The dominant role of mixing for NO_x mixing ratios is illustrated by the inverse relationship with K_h ($R^2 = 0.54$ for binned data), and therefore u_* : NO_x mixing ratios are small around local noon when efficient convective mixing takes place and increase during the night, when K_h is small (Fig. 6a).

p15, 16: *There was no demonstration so far that the relationship was non linear in this study, just that there was a relationship.*

An inverse relationship is observed, similar to South Pole ($R^2 = 0.54$ for binned data in Fig. 6a). The term 'non-linear' is omitted.

p15, 18: *I would suggest to use another symbol for H as it is often the sensible heat flux which is also discussed in this manuscript.*

Symbol for mixing height of the boundary layer replaced by Z_{mix} .

p16, 15-17: *This is not completely true: the sensible heat flux is also controlling the boundary layer height.*

Edited text: This implies that the turbulent diffusivity of the atmosphere controls not only concentration gradients but also, with contributions from sensible heat flux, the magnitude of Z_{mix} .

p16, 24-26: *Well, from the data I can see here I disagree on the interpretation: 1) the NO_x concentrations basically increase at night (Fig 3) when H is lower and when Kh is also lower. 2) They decrease during the day when Kh increases and H increases. This is also what Fig. 6 shows. I do not see the reason why we should observe a peak in the morning?? The basic conservation equation for the boundary layer could be applied to interpret these data: $d\text{Mass}/dt = \text{emissions} + \text{production} - \text{destruction}$, then $\text{Mass} = \text{Concentration} * \text{boundary layer height}$.*

The NO_x production rate from photolysis of NO₃⁻ in surface snow is symmetrical around solar noon and always larger than zero since the sun never sets. One would therefore expect a morning peak, as seen for example at Summit/Greenland, when the atmosphere has low Kh, but photolytic NO_x emissions are non-zero. As suggested, a full mass balance model would be desirable, but was not employed in this study due to lack of measurements to constrain atmospheric NO_x sink rates and Z_{mix} .

p16, 26: *Do you mean wind speed profiles? I do not recall it was mentioned in the material and method; This profile (temperature) measurement was not presented in the material and method section. It should be added. Temperature profiles are mentioned under methods, whereas only wind speed from 3.3 m was available.*

Edited text: Examination of temperature profiles and wind speed ...

p17, 5-14: *I would suggest to put this part in the material and method section. Rib should be defined before it is shown in Figures: Figure 3 has been shown already a few paragraphs before.*

Done.

p17, 22: *This is a large error indeed. But I do not see any description of the temperature profile in the material and method. All these measurements should have been presented in the material and method section.*

Clarified under methods.

Edited text: Ancillary data collected were standard meteorology from an automatic weather station (AWS) at 0.5 km distance, including air temperature (Vaisala PT100 DTS12 at 1.6 m), relative humidity at 1.6 m, wind speed and direction (Vaisala WAA 15A at 3.3 m), as well as in situ measurements of temperature of air (PT100 class 1/10 mounted in a passively ventilated radiation shield at 1 m) and of the snow surface (Campbell Scientific infrared radiometer IRR-P), and broadband UV-A radiation (Kipp & Zonen UVA CUV4 at 1 m).

p18, 2-4: *This sentence is more important than it looks like. The authors should explain in more details why NO should decrease more quickly than NO₂ during night. And looking at the NO_x dynamics would be very helpful for that: Indeed if only NO₂ photolysis was diminished, then NO₂ should increase, apart if the mixing height increased in the exact amount to compensate this increase It may be so but it needs stronger arguments.*

Indeed, the above is simply rephrasing our assumption, i.e. the increase in mixing height offsets in part the increase in NO₂ expected from reduced photolytic loss. We clarify this.

Edited text: NO mixing ratios decrease sooner and at a quicker rate than mixing ratios of NO₂ (Figs. 3,7) leading to maximum NO₂:NO ratios during night time (Fig. 10). Differences in dynamics likely reflect that NO₂:NO ratio shift to a new equilibrium, i.e. NO₂ dilution from mixing is in part offset by a reduction in its photolytic sink (Reaction R1), whereas NO dilution is further enhanced by a reduction in its photolytic source (Reaction R1).

p18, 13: *What is a "snow heat flux"? Please clarify...*

Snowpack heat flux is a component in the surface energy balance above snow, equivalent to soil heat flux above other surface types.

Edited text: This is confirmed by the asymmetry in the average diurnal cycle of snowpack heat flux, i.e. the energy flux across the air-snow boundary, which shows ...

p18, 5-17: *The preceding paragraph lacks from a a figure of sensible heat flux to illustrate it.*

The characteristics of average diurnal cycles of sensible and snowpack heat flux at Dome C important to this discussion are given in the text, thus in our opinion no need to reproduce Fig.9a in King et al. (2006), to which the interested reader is referred to.

p18, 24: *and sources and sinks*

The snowpack source will be discussed in section 4.2.

Edited text: Despite of these shortcomings both direct and profile methods suggest that at Dome C the diurnal change in atmospheric stability is an important factor to explain the diurnal cycle of atmospheric NO_x mixing ratios.

p19, 10: *Why is it not present in Dome C. Please comment*

Edited text: Atmospheric halogens in coastal Antarctica are thought to originate from the sea ice zone and are therefore expected to play a much less important role further inland.

p19, 16-18: *It would be more convincing to show an average NO_x mixing ratio in the firn and UV over the entire period rather than three days as in Fig.8*

A subplot c) is added to the figure (here Fig.2) showing the mean diurnal cycle of UV-A and NO_x in firn air from the 11 days, when firn air was monitored.

p19, 20: *It is rather "the fate of the produced NO_x"*

Edited text: However, the fate of NO_x from nitrate photolysis in snow is strongly controlled by boundary layer diffusivity once released from the snowpack.

p19, 24-25: *But then where is the NO_x coming from if there is no NO_x production at that time? I would rather formulate something like "which reflects the release of the NO_x produced in the firn to the atmosphere by wind shear generated turbulence"*

Since the sun never goes below the horizon during the measurement period nitrate photolysis and, therefore, NO_x production in firn air do not shut down during night time.

Edited text: The median NO_x reveals a small secondary flux maximum during the night, which reflects the release of NO_x produced in the upper snowpack to the atmosphere by wind shear generated turbulence (Fig. 9).

p20, 1: *This reaction was not presented in the introduction. It should have been. Also the reason for retaining this reaction as the main NO_x sink should be further developed.*

See reply to comment on p4, 4.

Edited text: Assuming that NO_x snow emissions are uniformly mixed throughout the boundary layer and that in continental Antarctica, away from potential halogen sources, the main NO_x sink is the reaction with hydroxyl radicals (Reaction R8), one can calculate ...

p20, 3: *NO_x should be [NO_x] and [NO₂]+[OH] should be [NO₂].[OH]. kNO₂ should be kNO₂+OH*

Corrected. Thanks for noting this.

p20, 12-14: *Where do these estimates come from? Is that the "snow emission" model? It should have been presented before*

From the above model equation (Eq.7).

p21, 20-29: *Here there is no mention of how, when and where NO₃⁻ was measured. Was it assumed a given concentration in the snow? Moreover I would suggest to put this section in the material and method section to make sure all methods are given prior to commenting on graphs.*

Agreed. A brief summary of the nitrate photolysis model and nitrate measurements during this study described in France et al. (2011) is added to the method section.

Edited text: Modelling nitrate photolysis in snow. Potential NO₂ production rates from the main NO₃⁻ photolysis channel in snow (Reaction R10) for Dome C conditions are modelled as described in detail in France et al. (2011). Briefly, the radiation transfer model TUV-snow (Lee-Taylor and Madronich, 2002) is used to calculate photolysis rates of nitrate in snow $j_{\text{NO}_3^-}$ as a function of solar zenith angle and snow depth:

$$j_{\text{NO}_3^-} = \int_{\lambda_1}^{\lambda_2} \sigma_a(\lambda, T) \phi(\lambda, T) I(\lambda, \theta, z) d\lambda \quad (5)$$

Where σ_a is the absorption cross sections of aqueous nitrate (from Chu and Anastasio, 2003), λ is the wavelength, T is the temperature, ϕ is the quantum yield for nitrate photolysis on ice (from Chu and Anastasio, 2003), I is the actinic flux, θ is the solar zenith angle and z is the depth into the snowpack. The snow depth dependency of I was measured at Dome C during this study (France et al., 2011). A depth integrated NO₂ flux F_{NO_2} is computed with

$$F_{\text{NO}_2} = \int_{z=0m}^{z=1m} [\text{NO}_3^-] j_{\text{NO}_3^-} d\lambda \quad (6)$$

where $[\text{NO}_3^-]$ is the nitrate concentration in snow. Several snow profiles of NO₃⁻ were measured within the clean-air sector during this study, and further details on snow sample collection and chemical analysis are given in France et al. (2011).

p22, 22-29: *Since no indication was given on how the NO₃- concentration was constrained, it is still to be considered as a source of error.*

This source of uncertainty was constrained by measurements during this study. See reply to comment on p21, 20-29.

p24, 6-7: *Not easy to understand. Rephrase*

Edited text: With the extended Leighton ratio we calculate a season mean for [OX] of 7.4×10^8 molecule m⁻³ (38 pptv), a value about 9 times the [HO₂] + [RO₂] observed at South Pole (ref) and 3 times of [HO₂] + [RO₂] seen at Summit (ref) ...

p24, 22: *Explicit this term*

East Antarctic Ice Sheet.

p25, 7: *unclear*

See reply to comment on p16, 24-26.

p25, 17-18: *This is highly hypothetical and also not propos here. I suggest deleting or moving to another section*

Moved to Section 4.1.

p25, 23-24: *Unclear could be replaced by: "with the former controlling the vertical mixing of emitted NO_x".*

Edited text: In summary, a strong diurnal cycle of atmospheric mixing ratios of NO_x and likely any other chemical tracer with a surface source is driven by the diffusivity and mixing height of the boundary layer, with the former controlling the vertical mixing of emitted NO_x.

p26, 14-21: *but no NO₃- concentration in the snow was reported in this study. It is therefore hard to determine whether the NO₃- concentration may also be a source of uncertainty: its spatial variability, etc.*

It is a source of uncertainty but was constrained during this study by measurements. See reply to comment on p21, 20-29.

p35, Table 3: *How to explain this lower value?*

See reply to comment on p12, 5-6.

p36, caption Fig. 1: *In this Figure AU is not defined. Please define all abbreviations in Figures*

We now omit use of AU for arbitrary units. All definitions included now.

Edited text: The potential interference of HONO in the detection of NO₂ was estimated using **(a)** the scaled intensity I_v of the photolytic converter (200-W high pressure arc mercury lamp, USHIO-200DP), the respective quantum yield ϕ , total transmittance \mathcal{T} of the optical filters, including a Pyrex window (Oriol, Part No. 60127) and a KBr filter (KG3, Oriol Part No. 51960), **(b)** the respective absorption cross sections σ_a (ref) and **(c)** scaled ($\phi\sigma_a I_v$) in order to calculate respective photolysis rates $j = \int \phi\sigma_a I_v d\lambda$ and their ratio. λ is wavelength and note different scale of x -axis in **(c)**.

p37, caption Fig. 2: *Again, wspd and T are not defined. Please define all symbols. Should mixing ratio not be under brackets? Please use smaller dots in order to be able to distinguish between heights. I also suggest to enlarge the graphs so that we could better see the dynamics. May be a graph giving NO and NO₂ at 1m on the same plot and then three plots showing the difference between 0.01 and 1 and 1 and 4 m may be easier to read and provides more insight. Please consider this option.*

Definitions will be included as well as figure size increased. However we think that the dynamics are well shown on a seasonal time scale (Fig.2) and on a time scale of a few days to highlight differences between the three intakes (Fig.3).

p38, caption Fig. 3: *I would like to see NO_x concentrations there to see whether it follows Rib or not. See comments in the text on negative NO₂.*

NO_x mixing ratios do follow also Ri_b , as can be easily extrapolated from Fig.3, we do not see the benefit of an extra panel to this plot. For negative NO₂ see reply to comment on p9, 4-6.

p39, caption Fig. 4: *I am getting a bit confused now: Was the flux only calculated with heights 0.01 and 1 m. It may be too close to the ground to apply the Obukhov similarity Also delete interpolated values on Kh in the graph. A "molecular flux" may be misunderstood as "molecular diffusion flux" just delete "molecular". Also give the height at which the flux was estimated.*

As the caption states, only heights 0.01 and 1 m were used for the flux calculation (see reply to general com-

ment 1). The interpolated values on K_h in panel b) are deleted now. The height of the flux estimate follows indeed from (a) the heights of concentration measurements used and (b) the constant flux assumption (see Section 2.3).

Edited text: 10-min averages of NO_x flux at Dome C in summer 2009–2010 between 1.0 and 0.01 m: **(a)** difference in NO_x mixing ratios (ΔNO_x) between 1.0 and 0.01 m (blue symbols); values within $\pm 1\text{-}\sigma$ standard error were excluded from the flux calculation (red symbols), **(b)** turbulent diffusion coefficient of heat (K_h) at 1 m and wind speed (w_{spd}) at 3 m, and **(c)** NO_x flux ($F\text{-NO}_x$).

p40, caption Fig. 5: *It may be more interesting to look at the stability factor z/L (where z can be the height at which the sonic anemometer is placed). This would probably give a graph easier to interpret*
As suggested, we present now in panel b both stability parameters analysed in this work, i.e. z/L and Ri_b .

p41, caption Fig. 6: *The mean in this graph is probably a bit misleading. the median and 5-95 percentile would better render the reality of K_h values.*

As suggested median values with error bars indicating the 5-95 percentile range of NO_x and K_h are plotted, showing the same trends as discussed.

Why is there no grey symbol for the lowest two values of NO_x ? Please clarify
Missing data points are now included.

p42, caption Fig. 7: *Heights 0.01 and 1.0 m are difficult to distinguish. Change symbols.*
Done.

The stability parameter (z/L) may also be shown there as it scales well with Ri_b
Agreed. z/L and Ri_b are both shown now in Fig.5b, whereas Fig.7 is left as is, since Ri_b tracks NO_x better.

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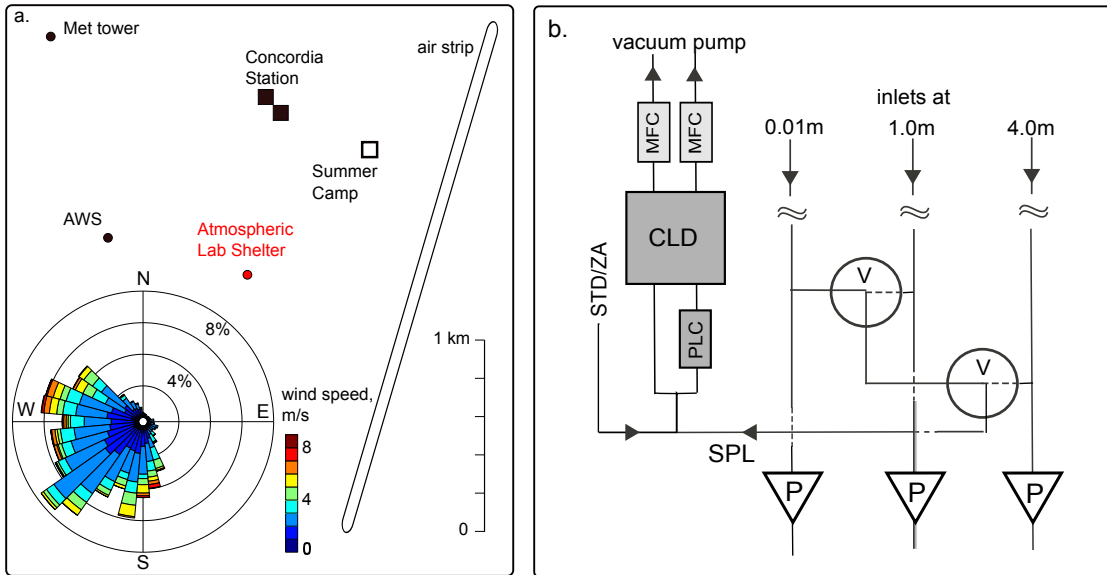


Figure 1: (a) The wind rose for Dome C during December 2009 to January 2010 and location map of the atmospheric lab shelter, air strip, Concordia station, automatic weather station (AWS) and meteorology tower with sonic anemometer. (b) Schematic of the NO_x sampling set up: sample air (SPL) is drawn continuously by vacuum pumps (P) from 3 inlet heights which are sampled by automatic switching of two 3-way valves (V). Sample flow into the chemiluminescence detector (CLD) through two channels, one with photolytic converter (PLC), is regulated by mass flow controllers (MFC). For calibration NO gas standard (STD) and for artefact tests zero air (ZA) are added upstream of the PLC. Triangles indicate flow direction (details in text).

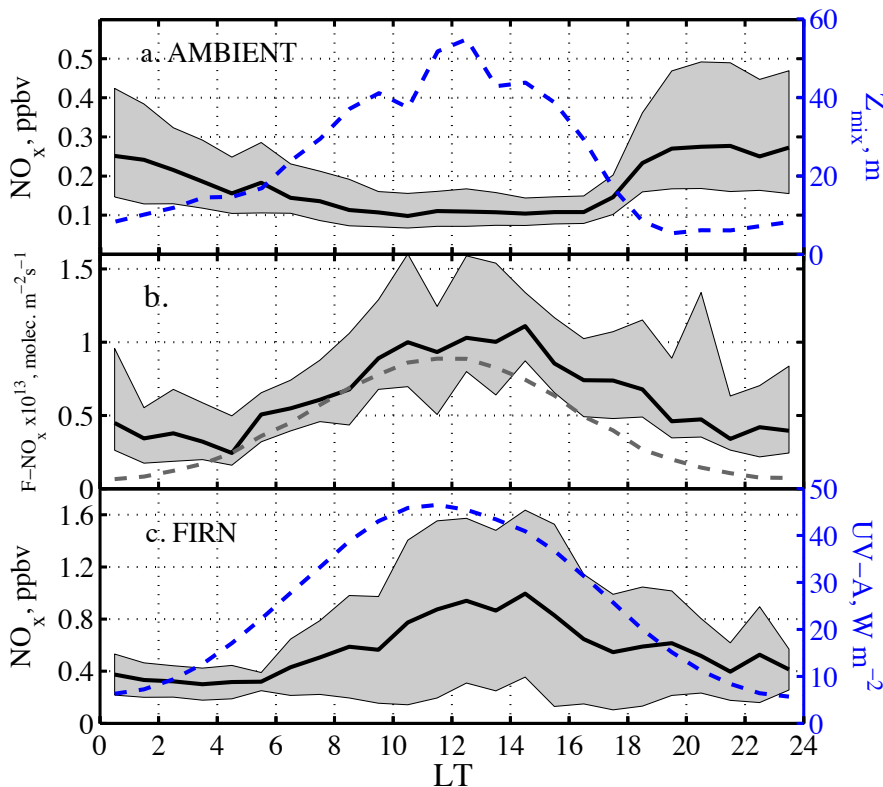


Figure 2: The diurnal cycle of atmospheric mixing ratios and flux from 22 December 2009 to 28 January 2010: **(a)** NO_x mixing ratios at 1 m with boundary layer height Z_{mix} estimated after Pollard (1973), **(b)** observed NO_x flux ($F\text{-NO}_x$) between 0.01 and 1 m compared to modeled potential NO_2 flux from nitrate photolysis in snow (grey dashed line) and **(c)** NO_x mixing ratios in firn air from occasional sampling (Table 2) and UV-A radiation at 1 m. All lines are median values and shaded areas the 25-75 percentile range of 1-hourly bins; except NO_x in firn air is average $\pm 1\sigma$.