

This publication presents a nice data set resulting from gas measurements of nitrogen oxides conducted at Dome C, Antarctica. Air was sampled from within the firn, and from multiple heights on a tower. The tower gradient measurements were used to derive NO_x surface flux estimates. Measurements seem to be of good quality and the data interpretation was done in depth. However, in quite a number of places data processing and interpretation appears to be over-simplistic. The manuscript wanders off at times and seems to be overly lengthy for the amount of new findings that are presented. The writing could be improved to be more precise and concise. Overall, I think this manuscript is a good fit for this journal but it needs some substantial improvements for publication in ACP.

Reply: We thank referee No.2 for a constructive review which helped to further improve the manuscript. The comments regarding the flux calculations are very much appreciated. The length of the manuscript however seems justified given the amount of new material of some complexity, i.e. including NO₂ measurements and model/observation comparison of NO_x flux. Comments (in italic) are addressed below and we note corresponding changes in the revised version of the manuscript intended for submission to ACP.

1 Specific Comments

Page 22310/abstract: *Mention measurement period and overall number of days for which data were obtained.*

Edited text: Atmospheric nitrogen oxides (NO and NO₂) were observed at Dome C, East Antarctica (75.1° S, 123.3° E, 3233 m), for a total of 50 days, from 10 December 2009 to 28 January 2010.

Page 22310/13: *Please be very clear if data are reported as daytime averages, night-time averages, or 24-h averages given that Dome C does have a significant diurnal cycle, as seen in these data.*

Edited text: In particular, the average ($\pm 1\sigma$) NO_x emission flux from 22 December 2009 to 28 January 2010, estimated from atmospheric concentration gradients, was $6.9 (\pm 7.2) \times 10^{12}$ molecule m⁻² s⁻¹ ...

22310/24: *....NO and NO2 (NO + NO2 = NOx) play a*

Done.

22310/3-4: *Mention how/why halogens prevent elevated NOx levels.*

Edited text: Atmospheric NO_x concentrations in coastal Antarctica are small, with build up in part prevented by gas-phase formation of halogen nitrates (e.g. BrNO₃, INO₃) followed by their heterogeneous loss ...

22313/10: *Give dates of measurements.*

Edited text: Measurements of atmospheric NO_x for a total of 50 days, from 10 December 2009 to 28 January 2010, took place at Dome C ...

22313/17-22: *Provide sensor technical information.*

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). 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).

22315/23: *Instead of being speculative this effect should be quantified by laboratory tests.*

Lab tests under field conditions are not available. Instead we followed the recommendation of reviewer No.3 and estimated the pressure drop based on fluid dynamics.

Edited text: With CE_{Halley} of 0.55 and a ratio of τ_{DC}/τ_{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.

22316/2: *Please clarify what is meant by baseline. Is this the instrument background?*

See also reply to comment by reviewer No.3.

Edited text: Baseline count rates were determined by adding excess ozone to sample air in a pre-chamber so

that all electronically excited NO₂ has returned to ground state when reaching the reaction chamber.

22316/23-25: *Here and in other places where instrument performance and data are reported, be very clear what the averaging period for the reported results is.*

We clarified accordingly throughout the text.

Edited text: To remove pollution spikes a moving 1-min standard deviation filter was applied rejecting data when 1- σ of NO and NO₂ mixing ratios within the 1-min window exceeded 24 and 90 pptv, respectively.

22317/4: *Assuming that the background was determined properly and subtracted from measurements, then discarding of negative values would not be an appropriate method for data reduction. Due to statistical noise a certain fraction of data would be expected to be negative. Just eliminating these will bias the calculation of data averages.*

We agree with the argument of statistical bias, i.e. including negative NO₂, e.g. at 1m, leads to mean and median values \sim 4% lower than reported. Therefore, all data in the revised version of the manuscript are updated, accordingly (see also reply to comment by reviewer No.3).

22318/8: *I am not aware of any other flux study where turbulence and chemical gradient measurements were not co-located on the same tower. I understand the dilemma these researchers are facing here due to their sensor failure. This very unusual procedure raises questions about its applicability. This point needs to be evaluated and justified.*

We are aware that there is uncertainty in u_* due to the fact that turbulence was measured 1.2 km from the NO_x concentration measurement. We therefore included in the total uncertainty of NO_x flux an uncertainty in u_* of 3% (22319/23) determined previously at Halley and based on the relative difference of 10 minute averaged u_* measured at 4 m over a distance of 100 m (Bauguitte et al., 2012). This might be at the lower end of the true variability in u_* over 1 km distance, however given the very homogeneous and flat snow surface at Dome C we consider this a realistic estimate.

Edited text: In this study, we used sonic anemometer measurements of atmospheric turbulence available from a tower at 1.2 km distance, since in situ observations were compromised due to instrument malfunctioning. The impact of using turbulence measurements not co-located with NO_x observations is taken into account in the estimate of total uncertainty further below. ... The total uncertainty of the 10-min NO_x flux due to random error in $\Delta[\text{NO}_x]$ (31%), u_* (3% after Bauguitte et al. (2012)) and measurement height (error in $\ln z_2/z_1$ of \sim 7%) amounts to 32%. This reduces to 13% when considering 1-hr flux averages. Note that the uncertainty in u_* was determined previously at Halley based on the relative difference of 10 minute averaged u_* measured at 4 m over a distance of 100 m (Bauguitte et al., 2012). This might be at the lower end of the true variability in u_* over 1 km distance, however given the very homogeneous and flat snow surface at Dome C it is considered a realistic estimate.

22319/5: *Or 0.8 km?*

Edited text: In this study, we used sonic anemometer measurements of atmospheric turbulence available from a tower at 1.2 km distance, since in situ observations were compromised due to instrument malfunctioning.

22319/8-10: *Revisit sentence structure.*

Edited text: Eq. (5) implies that a positive flux is in upward direction, equivalent to snow pack emissions and a negative flux is in downward direction, equivalent to deposition.

22319/20-22: *This explanation does not seem reasonable. Please provide more detail. How is the 1- σ s standard error defined here? Is this the error for the gradient? How was it determined? Or is this a measure of the variability of the gradient?*

Reading the entire section 2.2 does indeed answer the above comment: throughout the text the standard error is calculated as defined in 22317/4-6. The uncertainty in the concentration difference $\Delta[\text{NO}_x]$ is determined using the standard error in concentration measurement and applying standard error propagation. For further clarification:

Edited text: 22317/4-6 The uncertainty in the 1-minute averages due to random errors was estimated as the 1- σ standard error $\bar{\sigma} = \sigma/\sqrt{N}$, with standard deviation σ and number of samples N .

22319/20-22 It should be noted that application of the flux-gradient method is only possible, when concentration differences $\Delta[\text{NO}_x]$ can be detected. 10-min averages of $\Delta[\text{NO}_x]$ not significantly different from zero, i.e. smaller than their respective 1- σ standard error were therefore not included in the flux estimates. The 1- σ standard error in $\Delta[\text{NO}_x]$ was determined by error propagation of the 1- σ standard error of NO_x observations.

22319: *Despite the fact that the authors try to be detailed in their description of methods and analysis procedures, there are some significant shortcomings of the flux data processing. Flux gradient determination is*

compromised by a number of environmental conditions. For instance, these relationships lose applicability under stable conditions or/and when boundary layers become so shallow that measurements are above the surface layer (lowest 10% of boundary layer). The flux calculations should be revisited with closer consideration of these limitations (see for instance (Cullen and Steffen, 2001), (Cohen et al., 2007), (Bocquet et al., 2011)).

Agreed. The calculated 10-minute average flux values (1602 values) are now filtered as follows to take into account limitations of the flux gradient method: a) flux values are removed when the concentration difference ΔNO_x is not significantly different from zero, i.e. within $\pm 1\text{-}\sigma$ standard error (removal of 210 values) and b) flux values are removed when boundary layer height estimates $Z_{\text{mix}} < 10$ m (after Pollard et al. (1973) or after Zilitinkevitch et al. (2002)) indicating that the upper inlet at 1.0 m is likely above the surface layer & similarity theory cannot be applied (removal of 369 values). Both filters remove a total of 36% of available flux values. Statistics are updated in the revised manuscript, accordingly, i.e. the average NO_x flux is now slightly higher at $8.2 (\pm 7.4) \times 10^{12} \text{ molecule m}^{-2} \text{ s}^{-1}$.

22319: *It would also be desirable to see an uncertainty estimate of the flux estimation.*

The total flux uncertainty was given on 22319/22-25. See update of text provided in reply to comment on 22318/8.

22320/18: *Are these really enough data to deduce seasonal trends?*

The term 'trend' is now omitted.

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).

22320/28: *What was the threshold for significant and how was it determined?*

See reply above to comment on 22319/20-22.

22322/4: *Why do the authors not use the observations from this study?*

In general observations and model estimates (e.g. of boundary layer height) are compared to findings of King et al. (2006) during December 1999 to January 2000, but not used in calculations to be as close as possible to conditions during December 2009 to January 2010.

22323/20: *The authors use the term diffusion as a surrogate for atmospheric turbulence or transport. This is probably not appropriate. Diffusion is one, and the weakest/slowest of the processes driving atmospheric transport (Neff et al., 2008). I recommend that the entire paper be revisited with a stricter adherence to the definition of atmospheric transfer terms.*

As described in section 2.3, atmospheric transport occurs via molecular and turbulent (or eddy) diffusion (see for example Neff et al., 2008). The latter overwhelms in most boundary layer applications the former, i.e. the eddy diffusivity is typically orders of magnitude larger than the molecular diffusivity, except very close to the snow surface or in firn interstitial air. Any ambiguities are modified accordingly.

Edited text: Thirdly, the mixing height Z_{mix} of the boundary layer is another parameter, important for chemical budget calculations, as it determines the available air volume into which snow emissions are transported.

22323/21: *For boundary layer height estimation two approaches, i.e. the Pollard et al. and the Zilitinkevitch equation were used. Unfortunately there is no discussion under what stability range these were applied the estimating BLH. It almost seems that these equations were applied regardless of conditions (i.e. were any stability conditions filtered out in the BLH estimates?). As far as I understand, in the literature these two diagnostic equations only provided good comparisons to observations for stable to weakly stable conditions - so there is no support for using these models outside of that range, for instance at night (based on the scaling estimates used to derive these equations it doesn't seem to make sense to apply them outside of the stable to weakly stable range). I suggest that the authors clarify what range and filters they used for the BLH estimation.*

Limitations of the parameterizations used are indeed highlighted in the text (22323/21-26), including their applicability only for stable to weakly unstable conditions. The equation after Pollard et al. (1973) was applied only for cases with positive vertical gradients of potential temperature and the equation after Zilitinkevitch et al. (2002) only for cases with Monin-Obukhov length $L > 0$. This information is now included in the text.

Edited text: For Dome C the parameterization after Pollard et al. (1973) was applied only for cases with positive vertical gradients of potential temperature and the parameterization after Zilitinkevitch et al. (2002) only for cases with Monin-Obukhov length $L > 0$.

22325/22: *This is a very large error for an atmospheric temperature determination?*

Agreed, replaced with $\sim 0.1^\circ\text{C}$, according to manufacturer specifications.

22328/13-15: *One should be very careful in applying South Pole data, resulting from conditions without diurnal cycle and boundary layer turnover, to conditions at Dome C. How were the diurnal changes in T, BLH, radiation, WS at Dome C considered for estimating diurnal OH cycles?*

In the simple model of NO_x production rates OH was set to a constant value corresponding to the December mean measured at South Pole (22328/12). We added a sensitivity estimate of the calculated NO_x production rates assuming a simple diurnal cycle in OH.

Edited text: These results are sensitive to the assumed values of Z_{mix} and OH. For example, chemical loss rates from the right hand term in Eq. (11) were 3 pptvhr^{-1} at noon and 13 pptvhr^{-1} at midnight. These change to 5 pptvhr^{-1} at noon and 6 pptvhr^{-1} at midnight, if one assumes the same daily average OH, but the presence of a diurnal cycle with a noontime maximum of $3.0 \times 10^6 \text{ molecule cm}^{-3}$ and a midnight minimum of $1.0 \times 10^6 \text{ molecule cm}^{-3}$.

22329: . . . *vary considerably between sites* . . .

Changed.

22333/16-29: *This section needs improvement in its writing. Furthermore, can these statements indeed be supported by valid flux data, given the limitations of the flux gradient technique under strong radiative cooling and low BLH conditions?*

Limitations of the flux gradient technique are discussed now in more detail (see above) and these statements remain valid.

2 Figures

I recommend using a consistent format for labeling times/dates in all figures. All abbreviated axis labels and legends should be explained in the figure caption.

Done.

Fig. 4 caption line 4: *Again, this procedure seems questionable, but is hard to fully evaluate without having a more concrete explanation how the standard error was determined.*

See reply to comment on 22319/20-22.

Fig. 5d: *The same vertical axis scale should be used for displaying the two boundary layer estimates, otherwise this graph is misleading.*

We disagree. The point of this figure is to show asymmetry in the various diurnal cycles. And to avoid confusion it is noted that the vertical axis scale is different.

References

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