Overview. The authors present a summer-long record of NO and NO2 measurements in the atmospheric boundary layer at Dome C along with snow-air NOx fluxes and associated micrometeorological parameters. The results show relatively high NO mixing ratios for such a pristine area, comparable to past measurements at South Pole, a result of significant snowpack emissions of NOx and some very low boundary layer heights in the late afternoon and evening. The manuscript does a good job of combining meteorology, snow photochemistry, and modeling to explain their results. There are several major issues that need to be addressed, but I am confident the authors can do this.

Reply: We thank referee No.1 for a constructive 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 Major comments

1) The manuscript is somewhat disjointed. One reason is that there are many figures and the text has the reader flipping back and forth between them. Part of this continuous figure hunting is due to the current order in which the figures are first called out; as best I can tell, this order is 1, 4, 2, 3, 7, 8, 5, 6, 9, 10. Of course this should be rectified so that theyre called out in order. But part of the issue is also that it seems many of the points are illustrated by multiple figures. Can the authors simplify this scheme to eliminate (or move to Supplemental Material) a figure or two?

Reply: As suggested we rectified figure order and simplified the data presentation by combining Fig.5 and Fig.7.

The other reason the manuscript is somewhat disjointed is that there is a very short (1 page) Results section that runs through some of the data and then a much longer (11 pages) Discussion section. Combining these would help the reader.

Reply: Done.

2) Page 9. The HONO interference calculation should be done with the Kerbrat et al. (2012) HONO data at Dome C in addition to (or instead of) the current calculation with the South Pole HONO data. Given that HONO appears to be much more significant based on the Kerbrat data, the authors should include a more sophisticated, statistical look at the likely HONO contribution to NO2, for example by looking at diel changes in the HONO contribution.

Reply: We included the suggested calculation.

Edited text: Median HONO mixing ratios from laser-induced fluorescence at South Pole in Summer were 5.8 pptv (maximum 18.2 pptv) (Liao et al., 2006) and would imply that the seasonal average NO2 at 1 m was overestimated by 1.3% (maximum 4.3%). Mean HONO mixing ratios measured with a wet chemical method at Dome C during December 2010 and January 2011 were 28 pptv and showed diurnal variability with morning (0600 LT) and evening (2100 LT) maxima (Kerbrat et al., 2012). A potential interference from HNO4 was stated to be small (Kerbrat et al., 2012). If HONO mixing ratios were similar at Dome C in summer 2009-10, then the seasonal mean of NO2 at 1.0 m would be overestimated by 6.7%. The overestimate can be up to ~13% from morning to noon if the median diurnal cycles of NO2 and HONO are taken into account. As no HONO measurements were available, we did not apply any correction to the NO2 data.

The authors qualify the Kerbrat measurements by suggesting they suffered from interferences. This is certainly possible, given past comparisons of mist chamber/ion chromatography results for HONO with more specific, gas-phase measurements. But if there are significant interferences in the Kerbrat HONO measurements (e.g., HOONO and HOONO2) it seems possible that the same species are also interfering with the NO2 signal in the CLD. Is this a reasonable supposition?

Reply: Note details in the method section (22317/10-15): "Interferents relevant for our system during polar day are bromine nitrate (BrONO2) and nitrous acid (HONO) (Ryerson et al., 2000), of which only the latter its expected to play a role on the East Antarctic Plateau." HOONO or pernitric acid HOONO2, both potentially interfering with LOPAP HONO measurements, do not absorb in the spectral region of the photolytic converter employed in our NOx instrument.

3) Page 13, lines 20-23. The authors state that . . . NOx variability on calm days lacks any correlation with UV irradiance. . . . It is not clear what they mean by variability. If this means variability in NOx mixing ratios, then I agree with the sentence. But if they mean the variability in NOx fluxes then I disagree (as does the text on page 19, lines 13-16, where they describe the close relationship between NOx flux and irradiance). This should be clarified.
Edited text: However, NOx mixing ratios lack on calm days any correlation with UV irradiance and show a peculiar asymmetry of the maximum with respect to solar noon.

4) There are a number of assumptions that the authors make in their NOx budget for the purposes of modeling. The assumptions are reasonable, but they also limit the extent to which the disagreement between modeled and measured quantities can be used to infer problems with model inputs (e.g., the quantum yield for NO2 formation from nitrate photolysis). One assumption is that OH is the dominant sink for NO2. This is a good assumption, but does this sink represent 90% of NO2 loss? 80%? Is NO2 + HO2 (or RO2) significant given the high peroxyl radical concentrations inferred from the NO2:NO ratios? Of course it is difficult to quantify the NO2 sink based on the available data, but any missing sink will propagate through the calculations to bias the results, making it appear that the modeled NOx flux from the snowpack is too small. Similarly, the assumption of a constant OH concentration of 2E6 mlc cm-3 based on South Pole data is reasonable, but certainly the actual average value during this study was different from this. If actual OH concentrations were higher, then this would appear as a missing NOx source in the model.

Reply: To clarify: in this work we compared (a) observed NOx concentrations changes with calculated NOx changes from Equation 7 and (b) observed NOx flux with modeled NOx production from nitrate photolysis in snow (France et al., 2011, with more detail provided now in response to Reviewer No.3). Regarding (a) we limit ourselves to the assumption that OH is the dominant sink for NO2, but note that NO2 + HO2 (or RO2) might play a role (see reply to the following comment). A detailed discussion of the hydroxyl budget and the NOx sink strength is part of ongoing work. Regarding (b), the model is simplistic and does not include important processes such as transport and chemical reactions, i.e. no assumptions on hydroxyl levels and NOx sink reactions were made. Indeed, including any sink reaction would decrease the modelled flux and thus further increase the difference to observations. We apply this simple model, as it is often used to estimate upper limits of NOx production from snow. Thus a comparison to observations will tell if this is good practise.

Overall, the median NO2 flux from the model was 30% lower than the measured median NO2 flux. This difference seems well within the uncertainties inherent in the model assumptions. Similarly, the NOx flux measurements must have absolute uncertainties that are close to this difference. The model-observation comparison is important and should remain in the manuscript. But it should be qualified with an assessment of the uncertainties in both the model assumptions and flux measurements. The bottom line: is the 30% measurement-model difference statistically different from zero?

Reply: In the manuscript the uncertainty from systematic errors in observed NOx flux was estimated to be 31% for the 10-min values and 13% for the 1-hr averages (22319/25-26). The uncertainty in the median cycle of observed NOx flux over the entire period is even smaller and is estimated to be on the order of ~6% (see new Fig. 1). Thus, a 30% difference to modelled NO2 flux is significant and as suspected the use of a such a simple model, i.e. considering only NOx production from nitrate photolysis, is not warranted.

We agree with the reviewer that model assumptions have considerable uncertainties. For example, including transport and gas phase sink reactions of NOx will further decrease modelled NOx flux, whereas taking into account uncertainties regarding quantum yield of nitrate photolysis, the contribution of nitrite photolysis or spatial variability of nitrate concentrations can increase modelled NOx flux. Since snow concentrations were measured, we further evaluated model sensitivities to nitrite photolysis and variability of nitrate concentrations in snow (see reply to comment 7 and new Fig. 1). Including the uncertainties, we still find that NOx flux during night time is larger than model predictions. More detailed air-snow modelling will need to be done to elucidate relative roles of gas phase transport, NOx sinks and quantum yield in determining NOx emission flux. One difficulty is that quantum yield is possibly a large source of uncertainty: more recent data on quantum yield for 308 nm photolysis of nitric acid on ice films (Zhu et al., 2010) would potentially increase the NO2 production by a factor of ~400 (France et al., 2011).

5) Page 20, lines17-19: More details are needed about the model-measurement comparison at night. The modeled NOx production rate is . . . of the order of magnitude needed to explain the evening rise of NOx concentrations. . . . Is the modeled production rate too small to match observations? Is the BL height uncertainty so large that it prevents useful information from the model-measurement comparison?

Reply: See above clarification regarding comparison of observations with calculations. Case (a): Comparing observed NOx concentrations changes with calculated NOx changes from Equation 7 we find that on average calculations are similar to the observations in the early evening and confirm the importance of the NOx snow source for BL concentrations. This calculation depends mostly on the assumed boundary layer height and to some degree on hydroxyl radical (OH) concentrations, provided NO2+OH is the main sink. This is now explained in more detail (see below and reply to comment on 22328/13-15 by Reviewer No.2). Case (b): comparing fluxes we find a difference between observed and modelled flux, but the snow photolysis model does not include any chemistry or assumptions on BL height.
6) More information about the model inputs and outputs are needed. It would be useful to have Supplemental plots of: (a) the measured nitrate concentrations and modeled \( j(\text{NO}_3^-) \) values as a function of depth (see Page 21, line 27) and (b) modeled NOx production rates over the course of a median day compared to the flux measurements.

Reply: (a) During this study surface snow profiles of \( \text{NO}_3^- \) were measured within the clean-air sector and are reported in France et al. (2011). They were typical of what has been observed at Dome C in the past by others (e.g. Frey et al., 2009b). Modeled \( j(\text{NO}_3^-) \) values as a function of depth are also published in France et al. (2011). In order not to duplicate we briefly summarise and refer to France et al. (2011) for details. (b) This has been done in the current manuscript: modeled NO\(_2\) production rates over the course of a median day are compared to flux measurements in Figure 9b (see also updates in Fig. 1 for the revised manuscript).

7) Credit goes to the authors for trying to measure nitrite in their snow. Concentrations were below their method detection limit, so the authors dropped any consideration of nitrite as a source of NO\(_x\). But these low concentrations don't preclude a significant contribution of nitrite to the NO\(_x\) flux. The 0.5 ppbw NO\(_2\)- detection limit corresponds to 11 nM of nitrite in the melted snow sample. Based on Chu and Anastasio (2007), \( j(\text{NO}_2^- \text{ to NO})/j(\text{NO}_3^- \text{ to NO2}) \) is approximately 200 at South Pole on 12/21, midday; values at Dome C are likely to be higher. Therefore 11 nM of NO\(_2\)- is the NO\(_x\)-producing equivalent of approximately 2 uM of nitrate. This nitrate-equivalent concentration is probably lower than the (unspecified) measured concentrations of nitrate at the surface (5 - 10 uM, typically?), but large enough that nitrite could be a significant component of the NO\(_x\) flux budget. Furthermore, NO\(_3^-\) concentrations at depth are probably at, or lower than, 2 uM, suggesting that nitrite could be the dominant source of NO\(_x\) below the surface. A set of reasonable assumptions of nitrite concentration should be put into the model and the resulting impact on NO\(_x\) fluxes should be described. The nitrite contribution likely is at least as large as the missing 30% of NO\(_x\) flux inferred from the model-measurement comparison.

Reply: Agreed. We estimated maximum contributions to the modelled NO\(_x\) flux from nitrite photolysis (Reaction R10) in surface snow (Fig. 1). To do this the same model was run to obtain depth-integrated photolysis rates of nitrite \( j_{\text{NO}_2^-} \), which were then multiplied with a constant NO\(_2^-\) snow concentration based on an upper limit of 0.5 ppbw (Fig. 1). In addition, the impact of the observed variability in snow nitrate concentrations at Dome C on flux calculations is assessed as well (Fig. 1). We find that the presence of nitrate can increase modelled NO\(_x\) flux (1800-0400 LT) to match or even exceed observations during day time (0400-1800 LT), but not at night (Fig. 1). Spatial variability of nitrate concentrations contributes as well to the model uncertainty. Considering these uncertainties observed night time NO\(_x\) flux still exceeds model predictions. Using larger quantum yields of photolysis in combination with a daytime sink of NO\(_x\) may resolve this discrepancy. However, more detailed field measurements and air-snow modelling are needed to test this (subject of future work).

8) The discussion of the Leighton steady-state ratio (beginning of section 4.3) should be significantly shortened. The very limited Leighton mechanism does not apply to the Dome C system, so why bother starting with the Leighton-derived steady-state equation (8) and discussing this scenario in some depth? It would be better to jump right into the equation (9) material, discuss inferred [Ox], and show the Leighton ([Ox] = 0) case simply as a line on Fig. 10 with a sentence of discussion about this limited case.

Reply: The simple ‘Leighton’ case is in fact not discussed. What is discussed, is the assumption of steady state and reaction (8) material, discuss inferred [Ox], and show the Leighton ([Ox] = 0) case simply as a line on Fig. 10 with a sentence of discussion about this limited case.

Edited text: The observed ratios can be compared to predictions of steady-state ratios to estimate concentrations of oxidants other than O\(_3\) such as peroxy and halogen radicals. The steady-state assumption might not apply since significant snow emissions predominantly in the form of NO\(_2\) can shift the NO\(_2\):NO ratio, i.e. converting average NO\(_2\) flux to a volumetric production rate yields values of the same order of magnitude as NO\(_2\) formation via R3, especially when the air is stably stratified. However, a closer examination of the median ratios reveals that they are very similar at the 1.0 m and 4.0 m level throughout the day, whereas at 0.01 m and in firn air they differ, especially during daytime when the NO\(_x\) flux reaches its maximum (Fig. 11). The ratios
are therefore suggested to be perturbed by photolytic \( \text{NO}_2 \) release in firn air and at the snow surface, but likely reach a pseudo steady-state after transport of some distance away from the snow source, i.e. here to the 1.0 m level.

Atmospheric \( \text{NO}_2 : \text{NO} \) ratios were therefore calculated using an extended Leighton mechanism as derived in Ridley et al. (2000). For small carbon number peroxy radicals (\( \text{RO}_2 \)) \( k_{R4} \sim k_{R6} \) and for \( \text{XO} = \text{BrO}, \text{ClO} \) \( k_{R4} \sim 0.5k_{R7} \). The ratios can then be written as:

\[
\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_{R4}[\text{O}_3] + k_{R4}[\text{OX}]}{J_{\text{NO}_2}}
\]

(1)

where the total radical concentration \( \text{[OX]} = [\text{HO}_2] + [\text{RO}_2] + 2[\text{XO}] \). Ozone measurements were available from Concordia station and \( \text{NO}_2 \) photolysis rates \( J_{\text{NO}_2} \) were calculated with TUV-snow using observed \( \text{O}_3 \) columns and assuming a standard atmosphere under clear-sky conditions. Scaling of modeled actinic flux to broad band UV measurements allowed to account for cloudy skies. Observed ratios are found to deviate significantly from the simple Leighton steady-state (\( \text{[OX]} = 0 \)), and they do so more strongly than at Halley (Fig. 11).

2 Minor comments

1) The manuscript is generally written well, but there is some text that is either awkward or unclear:

a. Page 2, lines 12-15. Edited text: In particular, the average \( (\pm 1 \sigma) \) \( \text{NO}_x \) 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\(^{-1} \) and explains the 3-fold increase in mixing ratios in the early evening when the boundary layer becomes very shallow.

b. Page 14, lines 15-17. Edited text: Secondly, parameters describing turbulence in the atmospheric boundary layer were derived from direct measurements and included friction velocity \( u^* \), Monin-Obukhov length \( L \) and the turbulent diffusion coefficient \( K \).

c. Page 14, lines 28-29, specifically the phrase The above suggests. . . Edited text: Noon maxima of \( u^* \) and \( K \), 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.

d. Page 15, lines 18-21. Edited text: Thirdly, the mixing height \( Z_{\text{mix}} \) of the boundary layer was observed to show significant diurnal variability at Dome C (King et al., 2006). Chemical budget calculations require knowledge of \( Z_{\text{mix}} \) as it determines the air volume into which snow emissions are transported.

e. Page 18, line 25. Summit/Greenland should be Summit, Greenland. This occurs in at least one other location. Done.

f. Page 21, line 20 (beginning of the sentence). Edited text: Instead, observed \( \text{NO}_x \) flux is compared with model calculations of a potential \( \text{NO}_x \) production rate ...

g. Page 23, line 3. It would be clearer if the text from Ratios of. . .\( \text{NO}_2 \) and \( \text{NO} \) were replaced with something such as The atmospheric \( \text{NO}_2: \text{NO} \) ratio. . . Done.

h. Page 23, line 21: emission. Edited text: . . . especially during daytime when the \( \text{NO}_x \) flux reaches its maximum...

i. Page 24, lines 6-7; . . . which are attributed . . . \( \text{NO}_2: \text{NO} \) ratios. Edited text: With the extended Leighton ratio we calculate a season mean for \( \text{[OX]} \) of \( 7.4 \times 10^8 \) molecule m\(^{-3} \) (38 pptv), a value about 9 times the \( [\text{HO}_2] + [\text{RO}_2] \) observed at South Pole (Eisele et al., 2008) and 3 times of \( [\text{HO}_2] + [\text{RO}_2] \) seen at Summit (Sjostedt et al., 2007).

j. Page 25, lines 13-14: . . . accumulation of \( \text{NO}_x \) mixing ratios . . . Edited text: . . . lead to significant accumulation of \( \text{NO}_x \) above the snow surface...

k. Page 25, line 26: The diurnal radiative forcing at Dome C . . . Are you referring to the magnitude of the diurnal variation in radiative forcing or the absolute forcings? Edited text: The magnitude of the diurnal variation in radiative forcing at Dome C...

l. Page 26, lines 11-14. Edited text: Currently known factors leading to enhanced \( \text{NO}_x \) concentrations above the East Antarctic Plateau region in summer are...

2) Reaction R11 has the incorrect products. Instead of 2 \( \text{OH} \), it should be \( \text{OH} \) (hydroxyl radical) + \( \text{OH}^- \) (hydroxide ion).

Reply: Thanks for spotting this. Corrected.

3) Page 13, lines 3 6: Corrections from PHI decreased (increased) flux during stable (unstable) conditions. . . Using parentheses to indicate the opposite case of the main sentence is confusing. It is better to have a
4) Page 19, line 24. What times are meant by night time? Is this referring to the small peak around 23 02 hours?
Edited text: The median diurnal cycle of NO\textsubscript{x} flux reveals a small secondary maximum during the night (2300-0300 LT), which reflects the release of NO\textsubscript{x} produced in the upper snowpack to the atmosphere by wind shear generated turbulence.

5) Equation (7): (a) The rate constant should be \(k(\text{NO}_2+\text{OH})\), as it is in text below (where parentheses here indicate subscripted text). (b) More importantly, the addition sign between [NO\textsubscript{2}] and [OH] should be a multiplication sign.
Reply: Corrected.

6) Page 21, line 15: 9.4 should be 9.4E12.
Reply: Corrected.

7) Table 1, precision, % row. It is not clear what is meant by precision or how it was determined. Is this the average relative standard error from the 1-minute averages? If not this, what?
Clarified in text and footnote.
Edited text: Average precision calculated as the mean relative 1-σ standard error from the 1-minute averages.

8) Table 2. (a) Is the first entry for the NO\textsubscript{x} flux the value over the entire study period? A footnote in the table is needed to clarify this. (b) Make it clear in the table (not in a footnote) that the NO\textsubscript{x} fluxes are measured and NO\textsubscript{2} fluxes are modeled.
Reply: a) All concentration and flux values apply to the period 22-December 2009 – 28 January 2010 as stated in the table header; exceptions are concentrations at 1m as explained in the footnotes. b) done.

3 Overall Assessment

This is a nice set of data and analysis that makes a significant contribution to our understanding of nitrogen chemistry in the East Antarctic. The major changes needed are improving the modeling by including a nitrite contribution (and by providing more details of the inputs and outputs) and an explicit treatment of the uncertainties in the model-measurement comparison.
Reply: Agreed and addressed in replies to comments 4-7.

References


Figure 1: The median diurnal variation of NO\textsubscript{x} flux (F-NO\textsubscript{x}) at Dome C during 22 December 2009 – 28 January 2010 compared to model calculations: F-NO\textsubscript{x} observed between 0.01 and 1 m (blue line) and its uncertainty (error bars indicating the 1-\sigma standard error of the median calculated as 1.253 \( \sigma / \sqrt{N} \), where \( \sigma \) is the systematic error of 10-minute flux values and \( N \) is the number of samples per 1-hr bin (e.g. Maindonald and Braun, 2003)). Modeled F-NO\textsubscript{x} from NO\textsubscript{2} photolysis only (Reaction R10, grey line) and including also contributions from NO\textsubscript{3} photolysis (Reaction 12) assuming a maximum NO\textsubscript{3} concentration in snow of 0.5 ppbw (black line). The shaded area and dashed lines show the range of F-NO\textsubscript{x} based on all measured NO\textsubscript{3} snow profiles.