Reply to comments of Referee No.2

We thank Referee No.2 for insightful comments which helped to further improve the manuscript. Referee comments (in italics) are addressed below. Revised text, keyed to the ACPD online version, is shown in blue, and is included in the final manuscript we will submit to ACP.

This manuscript focuses on observations of NO and NO_2 *from 10 cm into the firn up to 100 m above the snow surface, and measurement of the flux of* NO_x *(primarily) out of the snow, made at Dome C during the OPALE campaign. There were abundant supporting measurements available, allowing the authors to put important constraints on the factors controlling variations in the mixing ratios of the nitrogen oxides and the snow to air flux of* NO_x *over a range of time scales. At Dome C it is clear that the interplay between the strength of the snow source of* NO_x *and vertical mixing exerts primary control over the mixing ratio of* NO_x*, both over the course of a day and a season. To first order, the strength of the snow source can also be explained as a combination of the abundance of* NO_3^- *in the snow available for photolysis and the actinic flux in the 300-340 nm range. However, it is evident that variations in the strength of the snow source of* NO_x *depend on additional factors that are not fully understood. Authors suggest that the fraction of* NO_3^- *readily photolyzed can change, both within a single season and between years, and suggest more field, lab and model studies are needed to understand what makes some* NO_3^- *- photo-labile while other* NO_3^- *is not. The latter fraction is tentatively labeled photo-stabile, I suggest that we do not need a new word and that photo-stable or just stable should be adequate terminology.*

Reply: We replaced photo-stabile with photo-stable in the text.

In general, the results are clearly presented, and the arguments supporting conclusions are well laid out. I will suggest a few places where I feel that clarity could be improved in the list of detailed minor comments below. However, I feel that more detail is needed in the description of methods. Most importantly, the authors need to explain how the concentration gradients were measured. Seems that the 2-channel CLD allowed NO and NO_x *(and something like* NO_2 *by difference) to be determined simultaneously, but only one inlet could be sampled at a time. So, what was the cycle between 0.1, 1.0 and 4.0 m sampling heights? How much of each 10 minute interval was spent at each height? Was each height measured several times in the 10 minutes, or was it 0-3.333 minutes on one inlet, 3.333-6.666 on next and then 6.666-10 on the third? One presumes that there had to be some down time for zeroing and calibration, perhaps quite frequently, so did these essential intervals of housekeeping result in gaps during all or most 10-minute gradient measurements, or were they grouped into a longer period of no data once or several times each day?*

Reply: The measurement method as well as the duty cycle of the CLD during the gradient measurements were described previously in Frey et al. (2013). However, we repeat some of the requested details in the methods section.

Revised text 31287, after Line 17: The three sample inlets were connected inside the lab shelter to a valve box, which automatically switched the CLD between sampling heights on a 90 s duty cycle. As described below, the 10-minute average concentration difference ΔNO_x between the 0.01 and 1.0 m inlets is used to estimate flux. Therefore, 10-minute mean ΔNO_x values are calculated on average from two sets of two subsequent 90 s intervals, separated by a 90 s interval during which the 4.0 m inlet was measured. 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. The baseline was measured for 60 s every 13.5 min alternating between all three inlets. The NO sensitivity of the CLDs was determined every 14 h by standard addition to the sample air matrix of a 1 ppm NO/NO_2 mixture (UK National Physics Laboratory traceable BOC certified), which is further diluted to 4 ppbv of NO. During standard runs also the conversion efficiency (CE) of the photolytic converter was determined by addition of a known mole fraction of NO_2. This was achieved by gas phase titration of the NO/NO_2 mixture to NO_2 by O_3 generated from a pen-ray lamp, and monitoring the un-titrated NO mole fraction. 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 a pure air generator (Eco-Physics PAG003). The artefact was measured every 14 h, offset by 7 h to the calibration runs.

I also feel that more detail needs to be provided regarding the measurements of snow nitrate in the field lab. It is stated that samples were collected every few days, but I am curious if they were analyzed right after collection (that day or the next), or allowed to pile up and then run in larger batches several times through the season, or maybe even all in one bunch near the end (this last option might be the best answer, but seems unlikely). In general, this would not seem something to worry about except for the fact that Berhanu et al. also have a manuscript on OPALE in review at ACPD right now, and indicate some uncertainty about nitrate measurements at Dome C during the 2011-12 season. Specifically, they measured what was supposed to be the same snow in 2 different artificial snow pits 12 different times through the season and found a range from 1200 1700 ppb (around a stated true value of 1450 ppb). This variability was not seen in samples run in a single batch, rather was expressed as large shifts between samples run on different days. Were the samples in present study and those reported by Berhanu et al. all run by same technician on the same instrument (commingled in batches)?

Reply: During OPALE the skin layer of surface snow, i.e. the top few mm, was sampled every 3 days. Samples were stored together with the additional snow samples discussed in Berhanu et al. (2014) and then analysed for nitrate in batches by the same operator. There has been a systematic shift in the nitrate standard response in between individual batch runs due to a calibration issue, which may affect the time series of nitrate in surface snow (Berhanu et al., 2014). However we believe the trend during Period II and III (Fig.7c) is real for two reasons: a) all samples were analysed in random order, across several batches, but the temporal trend observed in surface snow concentrations is very similar in both the skin layer (top few mm) and in the top layer of adjacent snow pits (top 2cm) (Fig.4 in Berhanu et al., 2014). And b) nitrate maxima in Antarctic surface snow during summer are a robust feature observed at Dome C over the existing 2009-present period of year-round sampling (Fig. 7b shows 2011-12 and 2009-10), as well as in coastal Antarctica (e.g. Mulvaney et al., 1998). Thus the snow nitrate changes over a week with a typical amplitude of 800-1000 ppbw are repeatable and well above the spatial variability of 20-25% found at Dome C (France et al., 2011; Frey et al., 2013). See revised text further below.

How much would modeled NO$_x$ fluxes change if snow nitrate was adjusted up or down by nearly 20%?

Reply: The NO$_x$ emission flux scales with nitrate concentrations in snow as illustrated by equation 3, and therefore an uncertainty of 20-25% in nitrate concentration, which is in fact typical for the spatial variability seen at Dome C , will translate to a similar variability in F$_{NO_x}$ (see Fig.7c and discussion in Frey et al., 2013).

Are the higher values of skin nitrate in periods II and III in 2011-12 real, or related to standard drift (sensu Berhanu et al.)?

Reply: As discussed above the higher values during Period II and III represent in our opinion a real temporal trend.

Are the surface snow data in Fig. 7 of this manuscript the same as those in Fig 4 of Berhanu (seem similar, but maybe not identical)? At a minimum, authors need to make a good faith estimate of the precision and accuracy of their own snow nitrate concentrations given the apparent problems in the field during OPALE.

Reply: The nitrate concentrations in the skin layer of surface snow during 2011-12 used in this work (Fig.7b) are the same as presented in Fig.4 of Berhanu et al. (2014). The updated precision is 5% based on replicate standard measurements (see also reply to reviewer No.1 in the online discussion of Berhanu et al. (2014)). The overall accuracy including systematic errors in calibration and collection of just the top few mm of snow is of the order of 20%, comparable to the spatial variability of nitrate in surface snow at Dome C.

Revised text 31292, after Line 3: Samples were stored together with the additional snow samples discussed in Berhanu et al. (2014) and then analysed for nitrate in batches by the same operator. The precision is 5% based on replicate standard measurements. Due to a systematic shift in the nitrate standard response in between individual batch runs due to a calibration issue (Berhanu et al., 2014) the accuracy is larger than usual. The overall accuracy including systematic errors in calibration and collection of just the top few mm of snow is of the order of 20%, and is therefore comparable to the spatial variability of nitrate in surface snow at Dome C (France et al., 2011). Note that the temporal trend of nitrate concentrations observed in surface snow discussed below is significantly larger, i.e. $>50\%$.

Specific, mostly minor, comments keyed to line numbers in 9 Nov 14 Latex file.

11 interference by pernitric **Reply:** Done.

21-22 last sentence of abstract seems to clash with the one just before, and kind of comes out of the blue. Paper does develop this idea, but maybe it should just be in conclusions (or it needs to be brought into abstract less abruptly.

Revised text 31283, Lines 23-24: A remaining source of uncertainty and subject of future research is the quantum yield of nitrate photolysis in natural snow, which may change over time as the snow ages.

61 do not need mixing ratios and levels both in this sentence **Reply:** Corrected.

72-74 agreed that the quantum yield uncertainty is important, but probably not the dominant problem models are facing. Seems premature to highlight this again here. **Reply:** We removed this sentence.

104-105 only air from the bottom and sides could enter through small holes in the tube (might help to specify that the holes were x cm or mm above the bottom of the probe)

Revised text 31287, Line 6: ... from the bottom and sides could enter, using small horizontal holes at 0-10 cm above the bottom of the tube.

116 CLD employed also converts nitrous **Reply:** Done.

126-158 to me, it would flow more smoothly to switch the order of these 2 paragraphs, dealing with possible HNO_4 artifact on the NO_2 measurement right after HONO/NO. Then talk about how both possible problems and any vertical gradients might impact the NO_x gradients.

Reply: Agreed, and we changed the order.

187 given how important mixing height is for much of the discussion, I would like to see some indication that MAR has been validated. Ideally at DOME C (from tower, tether sonde, maybe aircraft profiles) but at least from somewhere on the Antarctic plateau.

Revised text 31290, Line 10: The MAR model has been validated previously over the Antarctic Plateau, focusing on Dome C, during winter (Gallée and Gorodetskaya, 2010) and now also during summer (Gallée et al., 2014).

Equation 3, might mention that this model probably estimates an upper limit for NO2 flux (if the quantum yield and actinic flux are correct) since it assumes all NO_2 formed escapes the firn before any of it can photolyze, or convert to HNO_3, HONO, HNO_4.

Revised text 31292, after Line 24: For the discussion below it should be borne in mind that the calculated F_{NO_2} is a potential emission flux assuming that NO_2 is vented immediately after release from the snow grain to the air above the snow pack without undergoing any secondary reactions.

265 intra-seasonal trend odd terminology, since it seems you are talking about the week long period

with enhanced mixing ratios, not really a trend through the 2 months
Reply: We replaced Intra-seasonal trend by "intra-seasonal variability" throughout the text.

268-269 to late December average (not Nov)
Reply: We clarify this.
Revised text 31293, Lines 15-16: After that NOx mixing ratios gradually dropped over 10 days (Period III-IV) to median concentrations of ~120 pptv, slightly lower than observed in late November (Table 2).

270 2.5 times that **Reply:** *Done.*

273 median (range) of 1.6 (0.4-2.9) this is a little misleading. The range shown in Fig 1 D is -1 to 10 x 10^{13}. The smaller range in the text comes from Table 1 which compares season long medians for noon and midnight.
Reply: *We believe to assess the range of flux values it is a more conservative measure to state median values at noon and midnight, which are less sensitive to extreme values and the occasional outlier present in relatively noisy flux estimates. We clarify this.*
Revised text 31293, Lines 21:*... with a median of 1.6 x10^{13} molecule m^{-2} s^{-1}. Median values of F_{NO_x} at midnight and at noon were 0.4 and 2.9 x10^{13} molecule m^{-2} s^{-1}, respectively (Table 1).*

276 almost 5 times (or, about 4.7 times) **Revised text 31293, Lines 24:** *almost 5 times*

305-309 Any speculation about why the nitrate profile in the pit under the disk so much different than away from all the activity?
Reply: *We have no definite answer to this question. The firn air probe was installed onto untouched snow, and only removed after the end of the atmospheric sampling period. Thus contamination is unlikely, but a local anomaly remains a possibility as pits 5m next to the lab shelter showed a similar increase of concentration with depth.*
Revised text 31295, Line 5: *The firn air probe was installed onto untouched snow, and only removed after the end of the atmospheric sampling period. Thus contamination due to local activity appears unlikely, but a local anomaly remains a possibility as snow pits 5 m next to the lab shelter showed a similar increase of concentration with depth (data not shown).*

316 the anticorrelation between NO_2 and O_3 is interesting, but the suggestion that it reflects enhanced nitrate in the snow is not supported. Profile in P3 does not get so deep and neither of the other pits shows a peak near 45 cm.
Revised text 31295, Line 11-13: *In particular, the drop of O_3 mixing ratios by >10ppbv at 45 cm depth was not an outlier since collocated NO_2 mixing ratios were also significantly elevated compared to adjacent snow layers. However, no snow nitrate measurements were available to further investigate the origin of the NO_2 peak.*

351-354 seems the details of the MAX DOAS data reduction should have been in Methods
Reply: *We moved this part to the method section.*

370-371 this statement begs for at least a back of the envelope attempt at quantification. You earlier estimated that HNO_4 might contribute 33-66 ppt artifact to NO_2, so what would happen if you reduced NO_2 by this much in the steady state calculation? Hard to believe this would account for much of the factor of 20 discrepancy.
Reply: *This is a very useful comment. In reassessing the potential HNO_4 interference we discovered a computational error, which reduces the estimated magnitude of the HNO_4 interference by a factor two. NO_2 mixing ratios are corrected, assuming that additional NO_2 is measured in the CLD from HNO_4 thermal decomposition, equivalent to 25% of ambient HNO_4 on the order of 130 pptv. We find that average steady-state estimates of oxidant concentrations are still a factor 10 larger than those*

observed (RO$_2$ and BrO). In the revised text we take this into account and put the role of HNO$_4$ as an interferent into perspective.

Revised text 31288, Line 29: *HNO$_4$ present at these values could potentially produce 16-32 pptv of NO$_2$ in the photolytic converter, equivalent to 8-16% of the average NO$_2$ mixing ratio measured at 1 m.*
Revised text 31297, Line 9-16: *The same steady-sate calculation as described in Frey et al. (2013) was repeated for austral summer 2011-12 and yields an average of 2.5 x10^9 molecule cm^{-3} or 129 pptv of total radical concentrations [OX] = [HO$_2$] + [RO$_2$] + 2[XO]. Observations based on median [RO$_2$] of 9.9 10^7 molecule cm^{-3} or 5 pptv (Kukui et al., 2014) and 3 pptv of BrO yield [OX] of about 11 pptv. Hence, the estimated total radical concentration exceeds observations by a factor 12. To estimate the impact of a potential interference by HNO$_4$ we corrected the NO$_2$ mixing ratios, assuming that additional NO$_2$ is measured in the CLD from HNO$_4$ thermal decomposition, equivalent to 25% (100%) of ambient HNO$_4$ on the order of 130 pptv. We then find that the average steady-state estimate of oxidant concentrations is still a factor 10 (3) larger than those observed. Thus, a least a part of the inconsistency may be explained by the interference with HNO$_4$ (not measured).*

375-385 this section is a little loose. Starts by saying that period II looks much like 2009-10 with peak 18-20:00 but the figure shows that in 2009-10 the peak lasted later into the evening. Indeed, in all of the intervals except II the evening peak lasts quite a bit past 20:00. Why would that be, since the mixing height is not getting much lower, and the snow source should be weakening.
Reply: *Thanks for pointing this out. Indeed, NO$_x$ mixing ratios typically show maxima lasting into the night time hours in 2009-10 and in 2011-12 (except Period II.), whereas NO mixing ratios peak during 1800-2000 LT in 2009-10 (Fig.5 in Frey et al., 2013) and in 2011-12 (data not shown). Assuming no significant changes in BL height after the initial collapse of the convective BL night-time peaks of NO$_x$ are plausible if the weakening of snow emissions was offset by a corresponding decrease of the chemical sink of NO$_x$, i.e. the NO2+OH reaction. This is consistent to a first order taking into account that observed OH concentrations and F-NO$_x$ vary in a similar way, by up to a factor 5 between local noon and midnight. We revise the text accordingly.*
Revised text 31297, Lines 18-28: *On diurnal time scales NO$_x$ mixing ratios at Dome C are controlled by the interplay between snowpack source strength and atmospheric physical properties, i.e. turbulent diffusion of heat K_h and mixing height h_z of the boundary layer. The median diurnal cycles of NO$_x$ mixing ratios in 2011-12 show with the exception of Period II (1-8 December) previously described behaviour (Frey et al., 2013), with a strong increase around 1800 LT to maximum values, which last into the night time hours (Fig.6a). Night-time peaks of NO$_x$ are plausible if the weakening of snow emissions was offset by a corresponding decrease of the chemical sink of NO$_x$, i.e. the NO$_2$+OH reaction, assuming no significant change in h_z. This is consistent to a first order taking into account that observed OH concentrations (Kukui et al., 2014) and F-NO$_x$ vary in a similar way, by up to a factor 5 between local noon and midnight.*

427-436 Another place text could/should be more precise. Assuming the snow nitrate concentrations are valid, the really high levels are only present at the end of II and beginning of III, not through both periods. Cant say much about NO$_x$ flux in II, but it clearly stays high through nearly all of III, despite an apparent steep drop in nitrate.

Reply: *We agree and therefore refined the description of the observations in the text accordingly.*
Revised text 31299, Lines 21-24: *Instead changes in F_{NO_x} can be linked to the temporal variability present in the snow skin layer. During the end of Period II. and beginning of Period III. skin layer NO$_3^-$ concentrations were up to two times larger than before and after (Fig.7b). F_{NO_x} is high during the end of Period II. and beginning of Period III., however drops off a week after the decrease of nitrate concentrations in surface snow.*

451 corresponds to days of should this be to No of days?

Revised text 31288, Line 29: *quantum yield ... decreased from 0.44 to 0.003 within what corresponds to a few days of UV exposure in Antarctica ...*

452 in quantum yield is **Reply:** *Corrected.*

453 dont think stabile is a word and stable would probably work **Reply:** *Corrected.*

455 Neff and Davis also advocating for different flavors of nitrate in snow, shown on their poster at AICI CASSI, with references to earlier work.
Reply: *Correct, thus we added a reference to the earlier work by Davis et al. (2008).*

480 is an O3 sink Corrected.

491-493 as noted earlier, should estimate how big a part HNO_4 *might explain* **Reply:** *See reply above.*

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