

Interactive comment on “Atmospheric nitrogen oxides (NO and NO₂) at Dome C, East Antarctica, during the OPALE campaign” by M. M. Frey et al.

Anonymous Referee #2

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This manuscript focuses on observations of NO and NO₂ 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 NO₃⁻ in the snow available for photolysis and the actinic flux in the ~300-340 nm range. However, it is evident that variations in the

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strength of the snow source of NO_x depend on additional factors that are not fully understood. Authors suggest that the fraction of NO₃⁻ 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 NO₃⁻ photo-labile while other NO₃⁻ 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.

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 NO₂ 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?

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

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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)? How much would modeled NO_x fluxes change if snow nitrate was adjusted up or down by nearly 20%? 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.)? 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.

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

11 interference by pernitric

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).

61 do not need “mixing ratios” and “levels” both in this sentence

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.

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)

116 CLD employed also converts nitrous

126-158 to me, it would flow more smoothly to switch the order of these 2 paragraphs,
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dealing with possible HNO₄ artifact on the NO₂ measurement right after HONO/NO. Then talk about how both possible problems and any vertical gradients might impact the NO_x gradients.

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.

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 NO₂ formed escapes the firn before any of it can photolyze, or convert to HNO₃, HONO, HNO₄.

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

268-269 to late December average (not Nov)

270 2.5 times that

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 10¹³. The smaller range in the text comes from Table 1 which compares season long medians for noon and midnight.

276 almost 5 times (or, “about 4.7 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?

316 the anticorrelation between NO₂ and O₃ 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.

351-354 seems the details of the MAX DOAS data reduction should have been in Methods

370-371 this statement begs for at least a back of the envelope attempt at quantification. You earlier estimated that HNO₄ might contribute 33-66 ppt artifact to NO₂, so what would happen if you reduced NO₂ by this much in the steady state calculation? Hard to believe this would account for much of the factor of 20 discrepancy.

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.

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. Can't 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.

451 "corresponds to days of " should this be "to # days"? 452 in quantum yield is

453 don't think "stabile" is a word and stable would probably work

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.

480 is an O₃ sink

491-493 as noted earlier, should estimate how big a part HNO₄ might explain

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 31281, 2014.