

Interactive comment on “The diurnal variability of atmospheric nitrogen oxides (NO and NO₂) above the Antarctic Plateau driven by atmospheric stability and snow emissions” by M. M. Frey et al.

Anonymous Referee #1

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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 NO_x 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 NO_x 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.

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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 they're 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? 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.

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.

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?

3. Page 13, lines 20-23. The authors state that “. . .NO_x variability on calm days lacks any correlation with UV irradiance. . .”. It is not clear what they mean by “variability”. If this means variability in NO_x mixing ratios, then I agree with the sentence. But if they mean the variability in NO_x fluxes then I disagree (as does the text on page 19, lines 13-16, where they describe the close relationship between NO_x flux and irradiance). This should be clarified.

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4. There are a number of assumptions that the authors make in their NO_x 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 peroxy 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 NO_x 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 NO_x source in the model. Overall, the median NO₂ flux from the model was 30% lower than the measured median NO_x flux. This difference seems well within the uncertainties inherent in the model assumptions. Similarly, the NO₂ 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?

5. Page 20, lines 17-19: More details are needed about the model-measurement comparison at night. The modeled NO_x production rate is “. . .of the order of magnitude needed to explain the evening rise of NO_x 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?

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

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$j(\text{NO}_3^-)$ values as a function of depth (see Page 21, line 27) and (b) modeled NO_x production rates over the course of a “median” day compared to the flux measurements.

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 NO₂⁻ detection limit corresponds to 11 nM of nitrite in the melted snow sample. Based on Chu and Anastasio (2007), $j(\text{NO}_2 \text{ to NO})/j(\text{NO}_3^- \text{ to NO}_2)$ is approximately 200 at South Pole on 12/21, midday; values at Dome C are likely to be higher. Therefore 11 nM of NO₂⁻ is the NO_x-producing equivalent of approximately 2 μM of nitrate. This nitrate-equivalent concentration is probably lower than the (unspecified) measured concentrations of nitrate at the surface (5 - 10 μM, typically?), but large enough that nitrite could be a significant component of the NO_x flux budget. Furthermore, NO₃⁻ concentrations at depth are probably at, or lower than, 2 μM, 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.

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.

Minor Comments.

1. The manuscript is generally written well, but there is some text that is either awkward

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or unclear: a. Page 2, lines 12-15. b. Page 14, lines 15-17. c. Page 14, lines 28-29, specifically the phrase “The above suggests. . .” d. Page 15, lines 18-21. e. Page 18, line 25. “Summit/Greenland” should be “Summit, Greenland”. This occurs in at least one other location. f. Page 21, line 20 (beginning of the sentence). g. Page 23, line 3. It would be clearer if the text from “Ratios of. . .NO₂ and NO” were replaced with something such as “The atmospheric NO₂:NO ratio. . .”. h. Page 23, line 21: “emisson” i. Page 24, lines 6-7; “. . .which are attributed. . .NO₂:NO ratios.” j. Page 25, lines 13-14: “. . .accumulation of NO_x mixing ratios. . .” 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? l. Page 26, lines 11-14.

2. Reaction R11 has the incorrect products. Instead of 2 OH, it should be OH (hydroxyl radical) + OH⁻ (hydroxide ion).

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 separate sentence, or at least a parenthetical phrase, to discuss the second case. This sentence structure also occurs on page 14, lines 19-22.

4. Page 19, line 24. What times are meant by “night time”? Is this referring to the small peak around 23 – 02 hours?

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 [NO₂] and [OH] should be a multiplication sign.

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

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?

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8. Table 2. (a) Is the first entry for the NO_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_x fluxes are measured and NO₂ fluxes are modeled.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 22309, 2012.

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