Summer variability of the atmospheric NO_2:NO ratio at Dome C, on the East Antarctic Plateau

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Revision Notes

Dear Dr. Thorsten Bartels-Rausch,

Thank you for giving us the opportunity to submit a revised draft of our manuscript "Summer variability of the atmospheric NO_2:NO ratio at Dome C, on the East Antarctic Plateau" to the journal *Atmospheric Chemistry and Physics*. We appreciate the time and effort that you and the reviewer have dedicated to providing us valuable feedbacks on our manuscript. We are grateful to both of you for your insightful comments on our paper. We have been able to incorporate changes to reflect most of the suggestions provided. These changes are denoted in red in the revised manuscript. Here is a point-by-point response (in bold) to the reviewers comments and concerns (in italics) followed by the answers to yours.

Albane Barbero on behalf of the other authors.

Manuscript information

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Title: "Summer variability of the atmospheric NO_2:NO ratio at Dome C, on the East Antarctic Plateau"

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Anonymous Referee #1 comments: *Note: Anonymous referee #1 will be referred here as RC1.*

1. *Line 11-12: remove parenthesis to respect consistency with the rest of the text*

We thank RC1 for the suggestion. It has been edited in the text.

2. *Line 19-21: this sentence reads weird, please rephrase*

We have revised the text to address the concerns of RC1 and hope that it is now clearer. Indeed, the phrase "The collection and interpretation of polar ice cores has led to the growing interest in the atmospheric chemistry of these regions, as well as their relatively unpolluted nature free of local anthropogenic emissions (Wolff, 1995)" has been replaced by the following "The relatively unpolluted nature of these regions, free of local anthropogenic emissions, has led to the growing interest in their atmospheric chemistry, allowing the collection and interpretation of numerous polar ice cores (Wolff, 1995)".

3. *Line 22: I suggest writing "most suitable" instead of "last continent scale"*

We thank RC1 for the suggestion. It has been edited in the text.

4. *Line 24: I suggest using "peroxy" over the entire text*

We thank RC1 for the suggestion, but we would prefer to keep "hydroxyl and peroxyl radicals" to keep the list of oxidants detailed.

5. *Line 27: please provide a citation since you make a quite strong statement*

We agree with RC1 and have updated the text by adding references from different campaigns.

6. *Line 37 – 38: Considering the low concentration of Br and I with respect to NO_x species (4 order of magnitude for iodine and 3 for Br) in the inner Antarctic plateau, only Cl might have a role in the NO_2 production.*

The comment of RC1 is correct. However, from the list of reactions given in Appendix G of the manuscript, one can see that the chemical sources of NO_2 and sinks from RO_x and XO have similar rates, therefore the total amount of X should be considered having a role in the NO_2 production. We hope that the Reviewer will be ok for leaving the notation X here.

7. *Line 43: Please do not claim anything stronger than what reported in the paper.*

We have revised the text to address the concerns of RC1 and remove the end of the sentence: "[…], and the main source of HONO comes from the snowpack emissions, as shown on Figure 1" from the manuscript.

8. *Line 43-61: are all these citations relevant?*

We appreciate RC1's question. Nevertheless, we believe that a detailed review of the previous measurement campaigns and their results prepares the reader for the discussions that follows.

9. *Line 47: remove either "South Pole" or "Antarctic continent"*

We thank RC1 for the suggestion. It has been edited in the text.

10. *Line 89: how much is the wind speed on average?*

Following RC1's question, we have modified the text. The new sentence reads as follows : "The annual wind speed, $W_{speed-mean}$ = 4.0 ± 2.1 m s^{-1}, […]"

11. *Line 114: please provide citation*

We thank RC1 for the suggestion. The following citations has been added to the text: "[…] the heterogenous reaction of NO_2 and H_2O (Finlayson-Pitts et al., 2003; Barbero et al., 2020)."

12. *Line 154: "The spectral radiometer was mounted on a mast at 2 m from the snow surface on a mast (Fig. 3)" please remove the repetition*

We thank RC1 for pointing this out. We have revised the manuscript.

13. *Fig. 4: Maybe you could change the color of UV radiation to see the variations*

We apologize for the wrong color choice. We have replace the shaded orange color with a shaded red color and arranged the scaling for a better view of the UV radiations in Figure 4. Additionally, some changes have been made in the text following the RC1's comments on Appendix D (please see answer to comment N°32 and lines 162, 163, 165 and 167 in the revised manuscript).

14. *Line 198 and Appendix F: the estimate of the PBL by model calculation should be considered as an approximation. The estimate of the PBL at Dome C is complex since it is normally rather close to the surface. This type of model often uses meteorological parameters for estimate, e.g. wind direction. This could result in a not precise estimate of the PBL. At Dome C there are routinely meteorological balloon measurements (daily frequency) that could help to verify the PBL estimate from the model.*

As RC1 explained, the routinely radio sounding is following a daily frequency which is not sufficient for our analysis, as we need the PBL height estimation with an hourly frequency. Additionally, trying to compare the PBLH (Polar Boundary Layer Height) given by the model MAR V3.11 (Amory et al. 2021) with the data obtained from IPEV/PNRA "Routine Meteorological Observation" (http://www.climantartide.it) at the time of

observations (19:00 LT), we noticed that the starting measurement heights from the radiosonde are too low for comparison: 3,239 m for both periods of observations (December and January). However, the regional climate model MAR was used in its latest Antarctic configuration: version 3.11 500 (Kittel et al., 2021) forced by ERA5 reanalysis (https://www.ecmwf.int/en/forecasts) to generate the Boundary layer height extracted every hour to match the timestamp of our observations. In the supplements of their article, Kittel et al stated that "the representation of the near-surface wind speed is improved". Additionally "MAR overestimates low temperatures (especially on the plateau or in winter) while it slightly underestimates the high temperatures (close to 0°C). This likely results from a bias in the radiative scheme itself (from the ERA-40 reanalysis) and/or the low-sophisticated one-moment cloud scheme in MAR." Therefore, we are quite confident in the use of this new version of the MAR model to extract the PBLH as it has recently been improved.

15. *Figure 5 upper panels: I found the figure a bit complex. The greatest change in NO_x seems to squeeze all the other timeseries. It might worth split to increase the height of the y axis.*

We modified Figure 5 to address RC1 concerns, we hope that it is now clearer.

16. *Line 210: I would say that the NO_2:NO ratio is systematically higher not only in the morning.*

We thank RC1 for pointing that out, "in the morning" has been removed from the text.

17. *Figure 7a and 7b: As previously suggest the MAR model give an estimate of the PBL height. Considering the length of the measurements campaign I might suggest to the authors to investigate the PBL height using also the meteorological balloon sounding. This could result in a more robust interpretation of the manuscript.*

We thank RC1 for his/her comment. As answered in comment N°14, a lack of data prevent us to compare the PBLH extracted from the new version of the MAR model to the measurements given by the radiosonde.

18. *Line 245. This is not clearly visible from Figure 5. Please consider my previous comments in re-arranging the timeseries presented in the figure.*

It appears that there was a misunderstanding, the statement from (previous) line 245 is linked to Figure 7. Clarifications have been added in the text.

19. *Line 265: The explanation given is robust, but I might suggest to the authors to evaluate an additional atmospheric parameter such as the relative humidity (RH) and the water vapor concentration (if this last parameter is available). The increase in RH could promote, in a simple way, the formation of ultrafine water droplets|ice nuclei where the atmospheric reaction could be promoted and might partially explain the difference between December and January. A link between mercury exchange between snow and atmosphere and the RH at Dome C has been found in Cairns et al. 2021. I am aware that the mercury chemistry is different compared to that of nitrogen species but it could be worth to include this parameter in the data interpretation.*

We thank RC1 for this interesting suggestion. An additional atmospheric parameter, the relative humidity (RH), was therefore studied in the light of this comment. RH data (%) were obtained from IPEV/PNRA "Routine Meteorological Observation" (http://www.climantartide.it). Here are the results of the study. Following what has been done in the manuscript, we calculated a daily profile for each period reported in the Figure below.

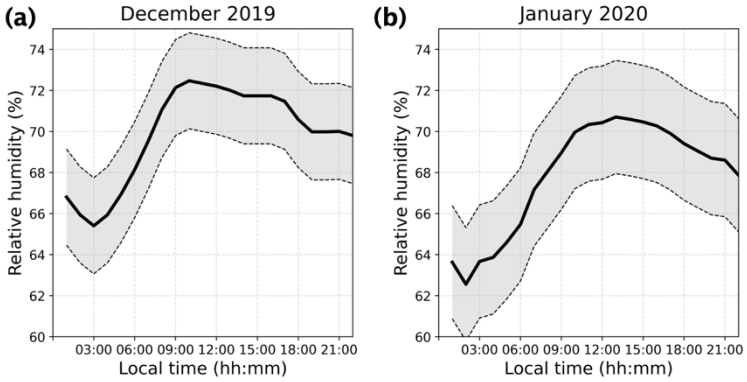

Figure 1: Relative humidity (RH in %) daily profile for both period of atmospheric observations: December (a) and January (b).

As shown in Fig.1, both profiles have very a similar shape, different from the one observed on the NO_x species and the NO_2:NO ratio, represented in Fig.7a and Fig.7b of the manuscript. The ratio $R_{RH} = \frac{RH_{December}}{RH_{January}}$ was also calculated from both profile. This ratio stay stable throughout the day: $R_{RH-min} = 1.013$, $R_{RH-max} = 1.046$, $R_{RH-mean} = 1.027 \pm 0.011$. Additionally, RH (with respect to water) is less than 100 % but RH with respect to ice is likely superior than 100 % at night, which could form ice crystals if ice nucleating particles (INPs) are present or direct onto surfaces (crystals), and can contribute to scavenging and wet deposition of HNO_3; but NO_x is not sticky, therefore, it should not be affected by this phenomena.

Dr. Amaelle Landais, from the LSCE (Laboratoire des Sciences du Climat et de l'Environnement) was kind enough to share with us unpublished data of Water vapor (w_v) from PICARRO measurements at Dome C. Those data allowed us to study the humidity mixing ratio (unit ppmv) at Dome C. Figure 2 below shows daily profile for each period following what has been done in the manuscript.

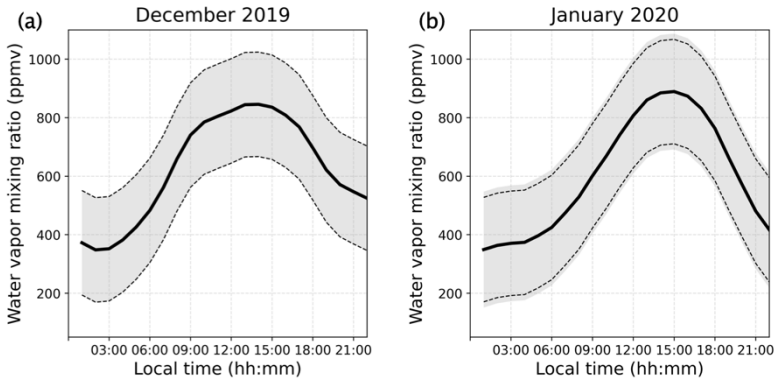

Figure 2: Water vapor mixing ratio (Wv in ppmv) daily profile for both period of atmospheric observations: December (a) and January (b).

As shown in Fig.2 the profiles have a different shape, especially in the morning that could play a part in the difference in the explanation of the NO_2:NO ratio deviation from equilibrium during de December period. However, the ratio $R_{Wv} = \frac{Wv_{December}}{Wv_{January}}$ was also calculated from both profile. The ratio stay stable throughout the day: $R_{Wv-min} = 0.913, R_{Wv-max} = 1.259, R_{Wv-mean} = 1.051 \pm 0.115$, which seems insufficient to explain our observations.

Therefore, we would prefer not to insert the relative humidity (RH) study nor the Water vapor (Wv) study in the manuscript.

20. Line 320: please explain how the coefficient was calculated

From appendix G, one can see that the reaction rates of the reactions involved are very similar, therefore we used an average of the three reactions rates to calculate the daily average rate coefficient for the reaction NO + XO → NO_2 + X. A clarification was added in the manuscript to avoid any confusion.

21. Line 322: I suggest moving this equation and the related text to section 2.3

We thank RC1 for its suggestion but we would rather keep this equation and the related text into this section as it allowed the reader to understand why the presence of halogenated radical is not sufficient to explain the observations and is, somewhat, introducing the study of the snow source developed after.

22. Line 326. Since direct atmospheric measurements of IO, BrO or ClO at Dome C are rare or almost absent an approximation could be done using the surface snow concentration. Iodine range is around 0.001 to 0.01 ppb while Br is between 0.1-0.2 ppb. Nitrate is between 20 to 40 ppb (average of first 20 cm, not the skin layer). The snow concentration tends to reflect the atmospheric concentration and could be used as initial approximation. Considering the 3 to 4 order magnitude less concentration of Br and I in surface snow (and presuming the ratio is preserved in the atmosphere), could this species be important in

the NOx cycle? Chlorine instead, opposite to I and Br, has a concentration similar to Nitrate and might be more relevant in the overall nitrogen cycle.

We agree with RC1. Unfortunately, no report on chlorine measurements are available for Dome C or the East Antarctic Plateau. The first approximation using the snow surface concentration could indeed lead to the 17 pptv of ClO needed (up to 64 pptv). Even though ClO measurements are crucially needed, the possible presence of such levels of ClO would induce fast destruction of O_3. Additionally, if such levels were present, NO levels would have been lower in December than in January, which was not observed during this summer campaign (Fig. 7 of the manuscript).

23. *Line 334 (section 4.4): I agree that snowpack emissions can contribute to the nitrogen species atmospheric concentration. At Dome C, during sunlight periods and almost every morning, it is possible to note a very thin brine layer formed during the "night" periods that normally disappears by noon. Could this brine layer play a role in the atmospheric nitrogen concentration? The increase in NO_2:NO ratio around 9:00 (figure 7a) may partially explain by the sublimation of the brine layer and so an enhancement of the nitrogen species release? You should consider that the brine has a higher specific surface area that might favor photochemical reactions. The formation and the thickness of the brine layer is likely connected to the RH. Please consider this comment as a suggestion rather than a question.*

We would like to thank RC1 to have bring this to our attention. We believe the Reviewer refers to riming, i.e., supercooled water droplets freezing onto surfaces. Brine is a concentrated salt solution, thus wrong term in this context. What actually is happening is resublimation and formation of ice crystals on surfaces at RH_{ice} > 100 %, however as detailed in the answer to comment N°19, there are no significant difference between both period of observation. This riming layer observed may play a role in the atmospheric nitrogen concentration but is likely not important.

24. Line 345: please express I_{act}

We are sorry for the omission and we would like to thank RC1 for pointing this out. The actinic flux I_{act} represents the spherically integrated radiation flux in the earth's atmosphere that originates from the sun, including the direct beam and any scattered components. In other words, the actinic flux is the number of photons crossing the unit horizontal area per unit of time from any direction at a given wavelength therefore in photons cm^{-2} s^{-1} nm^{-1}. Modification have been made in the manuscript.

25. Line 374: remove "higher":

We thank RC1 for the suggestion. The manuscript has been revised.

26. Line 377: express "FC":

We thank RC1 for the suggestion. The manuscript has been revised.

27. Fig. 12 and 13: check misspelling on axis label

We thank RC1 for pointing this out. The figures have been corrected.

28. Line 413: Why the authors use "SZA in December and keep only the daily values (06:00 to 18:00 LT)"? in December the solar radiation occurs for 24h.

We are sorry for the confusion. We used the SZA in December for the normalization of the parameterization, and then, we decided to keep only the values between 06:00 and 18:00 LT because it is during this period that the solar angle is sufficient to induce de production of NO_x (see Fig. 7 of the manuscript). The manuscript has been modify to make it clearer to the reader.

29. Line 420-421: "While the overall NO_2:NO ratio can be explained by the extended Leighton's relationship" I would add in certain periods|circumstances.

We thank RC1 for the suggestion. The manuscript has been revised.

30. Appendix A: I suggest explaining the choice of 5-d back trajectories and the starting heights. Please also add which meteorological data are used.

We thank RC1 for the suggestion. The manuscript has been revised.

I believe a good amount of the trajectories end up in the ocean in less than 10 days, like the one on 23 Jan at 12 UTC. This explanation of the drop in O_3 seems weak to me, I would rather explain it by the observed change in wind speed.

It appears there had been a confusion and we are sorry for not explaining correctly. Using the HYSPLIT model, we are characterizing air masses arriving at Concordia, it appears that the 23rd of January, the air masses reaching Concordia were originating from the coast, explaining the drop of ozone as explained by Legrand et al. (2009). Indeed, Legrand et al (2009) showed that the origin of the air masses reaching Concordia is influencing the ozone level. The lowest values are observed when the air masses have spent at least one day over the ocean during the 5 days preceding their arrival at Concordia and the highest values when the air masses have always travelled over the highest part of the over the highest part of the Antarctic plateau. Modifications in the manuscript has been made to clarify the explanation.

31. Appendix B, line 463: explain the "event"

We are sorry for the lack of explanation in this section. The manuscript has been modify, from: "Looking at Figure B1c, this event occurred in late January, around the 23rd, strengthening our hypothesis of ocean air masses that might have reached Dome C at

the end of January" to "Looking at Figure B1c, a sudden change in the wind direction occurred in late January, around the 23rd, strengthening our hypothesis of ocean air masses that might have reached Dome C at the end of January, explaining the 10 ppbv O_3 drop" to make it clearer.

32. Appendix D:

- *Fig. D1: are the calculations inside the range of fitting?*

The range of UV radiations of the calculations periods for December [4.5 ; 54.2] W.m^{-2} and January [2.9 ; 50.0] W.m^{-2} are similar to the range used for fitting, [7.7 ; 54.6] W.m^{-2} and January [3.3 ; 50.3] W.m^{-2} for December and January, respectively.

- *Table D1: can you explain why a is 0.0?*

We thank RC1 for pointing this out. In the previous version of the manuscript, the *a* parameter was set to zero as the photolysis cannot take place when there are no UV radiations. Therefore, we fixed the intercept in Figure D1 to zero. In the revised version of the manuscript, we changed the equation's expression from $J = a + b \times UV + c \times UV^2$ to $J = a \times UV + b \times UV^2$to avoid any confusion. We hope that it is now clearer.

- *Fig. D3: what is the uncertainty of the fitting? Why are the residuals not symmetric around 0? You could consider using a higher degree polynomial. Table D2: the value of a doesn't seem to match the curve of Fig. D3*
- *Fig D4: can you improve the scale of this plot? Can you comment on this bias? Maybe with another fitting he bias would not be as large.*

We thank RC1 for his comment and we apologize for this error. Indeed, in the previous version of the manuscript, the minimization method used for the fitting was the Conjugate Gradient method (CG). The method was working well for the J_{NO_2} recovery. However, it was not for the J_{O^1D} as the initialization was not right and the fit was stuck in a local minimum. Therefore, thanks to RC1's comment, we were able to review the initialization using the Powell's method and avoid the minimization being trapped in a local minimum. Using this new method, the difference between the observations and their FIT (in December) has a mean of -1.16×10^{-5} and a of standard deviation 7.5×10^{-4} for J_{NO_2} and -1.77×10^{-7} (mean) and 4.23×10^{-6} (standard deviation) for J_{O^1D}, respectively. We adjusted Appendix D and its Figures as well as Section 2.2.3 regarding the new results.

Editor's comments #1 :

The work adds to our knowledge on NO_y chemistry and the importance of snow cover. It presents new and novel data (time frame), applying a new method. Based on one referee comment and my own editor comment (see below), I'm happy to accept the manuscript for publication after minor revisions.

1. *Page 2, line 35. Consider stating the wavelength regions.*

Thank you for the suggestion. The manuscript has been revised.

2. *Page 3, line 40 Consider bullet list to increase readability.*

Thank you for the suggestion. We modified Figure 1 to associate the bullet list to the figure.

3. *Page 3, line 64: interference. Please explain in more detail and or give reference.*

Thank you for pointing this out and sorry for the missing explanation. The manuscript has been modified and references were added.

4. *Page 4, line 74 please define Leighton's relationship.*

Thank you for the suggestion. The manuscript has been revised.

5. *Page 4, line 80. At the end of the introduction, I'm a little puzzled about the novelty of the work, could you rephrase that paragraph to make it clearer.*

Thank you for the suggestion. The manuscript has been revised, we hope that it is now clearer.

6. *Page 10 line 205 and page 12 line 235 and in between:*
   This is a very interesting section. I find the time lag between NO_2 and NO interesting. Could you argue a little on this? Is this explainable by gas-phase kinetics (would surprise me). Another reason for time lag are of course different residence times in the porous snow after production there. Transport through snow can be slowed due to interaction with the snow interface like adsorption. Bartels-Rausch, T., S. N. Wren, S. Schreiber, F. Riche, M. Schneebeli and M. Ammann. "Diffusion of volatile organics through porous snow: Impact of surface adsorption and grain boundaries." Atmospheric Chemistry and Physics 13(14): 6727-6739.(2013). However, both NO_2 and NO are not adsorbed by snow (Bartels-Rausch, T., H. W. Gäggeler and M. Ammann. "The adsorption enthalpy of nitrogen oxides on crystalline ice." Atmospheric Chemistry and Physics 2(3): 235-247.(2002)). This links nicely to the discussion of RO_2 impact on the oxidation. RO_2 might be expected be adsorbed to snow more than NO_2 (similar to HNO_4: Ulrich, T., M. Ammann, S. Leutwyler and T. Bartels-Rausch. "The adsorption of peroxynitric acid on ice between 230 K and 253

K." Atmospheric Chemistry and Physics 12(4): 1833-1845.(2012)) and if produced in the snowpack be released later. Would this make sense? If so, please add to page 10, line 205.

Thank you very much for the opportunity of the discussion. Previous measurements campaigns at Dome C showed the interdependence between the $\frac{[OH]}{[RO_2]}$ diurnal profile and the J_{NO_2} profile (Kukui et al. 2014). Indeed, $\frac{[OH]}{[RO_2]}$ correlates with the daily profile of NO (see Fig. 2c of Kukui et al. 2014): "when the concentration of NO is small, the concentration of OH increases due to the enhanced recycling from RO_2 until the losses of RO_2 and OH in reactions with NO_2 become important compared to other loss processes." Therefore your point would make sense, and modification of the manuscript have been made.

7. *Page 14 „local chemical reactions play an important role in the diurnal O3 behavior."*

Thank you for pointing this out, the obvious statement was removed from the manuscript. We hope that it answers to your comment.

8. *Page 18 line 368: Could you summarize the conclusion of the paragraph here. Does this discussion allow first conclusion on the importance of snow?*

Thank you for the suggestion, a conclusion of the paragraph was added to the manuscript.

9. *Page 24: Taken that the chemistry in snow was so nicely detailed in the manuscript, I suggest to elaborate ton this a little more in the conclusion as well.*

Thank you for the suggestion, the conclusion has been revised to allow a bit more descriptions on the snow chemistry.