

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-1018

Anonymous Referee #1

Referee comment on "Summer variability of the atmospheric NO₂ : □NO ratio at Dome C on the East Antarctic Plateau" by Albane Barbero et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1018-RC1>, 2022

Referee comments: Summer variability of the atmospheric NO₂:NO ratio at Dome C, on the East Antarctic Plateau"

The manuscript entitled "Summer variability of the atmospheric NO₂:NO ratio at Dome C, on the East Antarctic Plateau" presents for the first time direct atmospheric measurements of NO₂ Plateau at Dome C, Antarctica, during the early (December 2019) and late (January 2020) photolytic season.

The results show that NO₂:NO ratio can be explained by the extended Leighton's relationship, however a high NO₂:NO ratio was found in the morning during the early photolytic season, deviating from steady state equilibrium and not explained by the extended Leighton's relationship. The authors attribute the higher amount of NO₂ in the early photolytic season to enhanced NO₂ snow-source and to stronger UV irradiance caused by a smaller solar zenith angle near the solstice. Halogenated radicals might explain the observed O₃ levels but not deviations of the observed NO₂:NO ratio from the extended Leighton relationship, as in previous studies. Different meteorological conditions with respect to previous campaigns and different instrumental settings might also play a role in driving the NO_x signal.

I believe the content is appropriate for the journal Atmospheric Chemistry and Physics. The manuscript is well written and with a good level of English. The data used are of good quality and the measurements use a novel approach. The discussions are in general well-argued and supported by observations and references. I also appreciated that in the manuscript are reported the difficulties encountered during the field measurements. Before acceptance some improvements are necessary, and this is why I suggest major revision. However, I am confident that the authors can fully address my comments

Comments

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

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

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

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

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

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 NO₂ production.

Line 43: please do not claim anything stronger than what reported in the paper

Line 43-61: are all these citations relevant?

Line 47: remove either "South Pole" or "Antarctic continent"

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

Line 114: please provide citation

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

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

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.

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.

Line 210: I would say that the NO₂:NO ratio is systematically higher not only in the morning

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.

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

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.

Line 320: please explain how the coefficient was calculated

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

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

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 NO₂: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.

Line 345: please express I_{act}

Line 374: remove "higher"

Line 377: express "FC"

Fig. 12 and 13: check misspelling on axis label

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. Please explain

Line 420-421: "While the overall NO₂:NO ratio can be explained by the extended Leighton's relationship" I would add in certain periods\circumstances

Appendix A: I suggest explaining the choice of 5-d back trajectories and the starting heights. Please also add which meteorological data are used. 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 O₃ seems weak to me, I would rather explain it by the observed change in wind speed.

Appendix B, line 463: explain the "event"

Appendix D:

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

Table D1: can you explain why a is 0.0?

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 the bias would not be as large