The Cryosphere Discussions

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Comment on tc-2021-32

Anonymous Referee #1

Referee comment on "Observation of strong NO_x release over Qiyi Glacier, China" by Weili Lin et al., The Cryosphere Discuss., https://doi.org/10.5194/tc-2021-32-RC1, 2021

This manuscript reports summer measurements of atmospheric nitrogen oxides (NO_2, NO_x) of several ppbv above Qiyi Glacier on the Tibetan Plateau (4600 m asl). Based on a close correlation of NO_x with observed UV-B radiation, negative vertical NO_x gradients and presence of nitrate in snow the authors conclude the local snow pack must be an important source of atmospheric NO_x, possibly a stronger source than polar snowpacks. While this is an interesting hypothesis related to understanding the atmospheric oxidising capacity above the Tibetan Plateau, I am afraid the study as presented has significant gaps both in the method description as well as data interpretation, and lacks scientific rigour overall. These factors together currently do not support any of the above conclusions.

Most importantly the authors chose to use the LMA-3D Luminox monitor (Unisearch Associates Inc., Ontario, 55 Canada) to measure atmospheric NO_2 (NO_x), which is to my knowledge currently not used in studies of the remote atmosphere. The company developed this instrument in the 1980s based on a wet-chemical luminescence producing reaction (Drummond et al., 1989), but stopped production to move on to optical methods, which had likely to do with the instrument performance (Joseph et al., 1986; Kelly et al., 1990). After Kelly et al. (1990) there are three main issues to take into account when applying this method:

1) the luminol method has a non-linear response at low (<2ppbv) ambient NO_2 concentrations (e.g. Fig. 1 in Kelly et al., 1990), and therefore raw data require correction. This study gives no indication on how, over what concentration range and how frequent the detector was calibrated. If unaccounted for, the error in the reported observations (0.5-2.5 NO_2 ppbv) could be an overestimate of 100% or more!

2) Luminol, the reagent solution, undergoes ageing over a period of a few days, resulting in significant changes of sensitivity of >15% (Fig.3 in Kelly et al., 1990), making frequent calibrations and solution exchange mandatory. In this study, no detail is given on how often the solution was changed and what its composition was. Furthermore, frequent baseline measurement is also needed to correct for instrument drift, partially due to changes in reagent solution; again no detail is given in this study.

3) And finally, interferences from other atmospheric trace gases, especially at low ambient NO_2 (<2ppbv) can introduce significant positive bias in the measured NO_2, but are not discussed in the mansucript. One interference is ozone (O_3) - assuming O_3 levels of 28-96 ppbv previously measured above the central Tibetan Plateau (Xu et al., 2018) and a cross-sensitivity of 0.0033 ppbv in NO_2 per ppbv O_3 (Kelley et al., 1990), one obtains a potential overestimate of 0.09-0.3 ppbv of NO_2, thus up to 50% of the reported NO_2 (Fig.3-4, this study) depending on the time of day. This can be overcome by using an O_3-scrubber, which however also removes some of the NO_2, again requiring careful calibration. It is not clear if such filter has been used in this study or not. The other interference is from peroxyacetyl nitrate (PAN) with a 25% cross-sensitivity of NO_2 (Kelley et al., 1990). Assuming a previously measured range of 0.36-0.44 ppbv ((Xu et al., 2018) one obtains a potential bias of 0.1 ppbv in NO_2. The only way for correction is either measuring PAN simultaneously or assuming a reasonable summer value.

In summary, given the lack of detail on the NO_x method regarding accuracy and precision, and required data corrections (zero offset, nonlinearity, and ozone and PAN interferences) there is little to no confidence in the reported NO (NOx) values and statistical significance of the vertical mixing ratio gradients. In fact, the NO_x values are very likely significantly overestimated. Thus further discussion on a potential snowpack source is not warranted at this stage. Another flaw is that the discussion about the relative importance of a NOx snowpack source based on gas phase concentrations does not include analysis of other relevant parameters (turbulence, boundary layer height) and processes (e.g. transport via down-ward mixing from the free troposphere). I therefore cannot recommend to go any further with this manuscript.

SPECIFIC COMMENTS

L10-11 concentrations or flux?

L14 “hardly” detected? Below limit of detection?

L16 "vertical experiments” - you mean gradients?

L42-3 Antarctic surface snow nitrate concentration can be even higher (e.g. Erbland et al., 2013)

L58 LOD of <10 pptv? this is either a typo or evidence such as a calibration curve needs to be presented (see comments above)

Section 3.2 - where and how were snow samples taken, i.e. just surface snow or pit profiles?

Section 3.4 -were vertical gradients of NOx measured through the same inlet? If not, was as an inlet comparison done? The variability (error bars) is large, and often the difference in concentrations does not seem significant.

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