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Comment on acp-2022-163

Anonymous Referee #1

Referee comment on "Fate of the nitrate radical at the summit of a semi-rural mountain site in Germany assessed with direct reactivity measurements" by Patrick Dewald et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-163-RC1, 2022

The present work provides an evaluation of NO_3 radical fates in a semi-rural site thanks to direct NO_3 reactivity measurements during the TO2021 campaign in summer 2021. A Flow-Tube Cavity Ring Down Spectrometer (FT-CRDS) setup was used to measure the NO_3 total reactivity and to estimate the contribution of BVOCs to this total reactivity. During this campaign, a number of other relevant measurements (NOx, O_3, actinic flux, VOCs, …) were performed to allow for a comprehensive interpretation of the observations.

This study is fully relevant and the FT-CRDS is a very interesting technique to better understand the role of NO_3 in the night-time chemistry. The paper is well written and provides detailed information on the experimental setup as well as a very thorough interpretation of the observations, and it is very much appreciable. In general, the scientific quality of this work is very good and once the authors have addressed the following minor points, I would be happy to recommend its publication in ACP.

Specific comments:

- 61: more detailed reactions should be provided to better explain the formation of $RONO_2$ from VOC+NO_3 reactions
- 175: it is not clear why the PTR-MS (VOCUS) was not calibrated with the standard used for the other PTR-MS (Ionicon). Could the authors provide an explanation?
- 170 and 290: the authors mention that sesquiterpenes were measured but no data/plot have been provided. If available, please provide these data in Figure 3 or in SI. Were sesquiterpenes monitored during previous campaign using GC techniques? Even though sesquiterpenes mixing ratios are expected to be very low, they are suspected to significantly contribute to NO_3 fate due their high reactivity. More information about the role of sesquiterpenes on NO_3 loss would be useful.
- The authors do not consider the role of RO_2 radicals in the NO_3 Do they consider that it is negligible? Previous field studies (e.g. Sommariva et al, 2007) suggest that reactivity with RO_2 radicals is not negligible even though RO_2 concentrations are very low. This

point should be discussed and arguments should be provided for not considering these reactions.

- 324: the authors cannot conclude that NO_3 significantly contributes to the BVOC oxidation during the daytime just because the reactions with BVOCs have been shown to significantly contribute to the NO_3 total reactivity. To state that, the BVOCs lifetimes due to NO_3 oxidation should be compared to those estimated for OH chemistry (using typical OH concentrations).
- 340-387: A very detailed discussion on the NOx budget is provided but does not seems to be fully relevant here, in my opinion. It's not clear for me what the authors want to demonstrate here. As a minimum, this should be provided with a clearer objective and in a dedicated section. It has nothing to do in the section "fractional contribution of VOCs to NO_3 losses".