

## Comment on acp-2022-163

Anonymous Referee #2

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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-RC2>, 2022

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The authors report measurements of NO<sub>3</sub> reactivity in a summer campaign at Kleiner Feldberg in Germany. They analyse the measurements in terms of different contributions of reactants to the total NO<sub>3</sub> loss and draw conclusions about emissions and losses of nitrogen oxides at that place. Results are compared with results from previous campaigns. The manuscript is overall well written and within the scope of the journal. There are some open questions and simplifications that need to be further explained and discussed before the manuscript can be published.

L29: NO<sub>2</sub> is only a net ozone production, if emitted as NO<sub>2</sub>. The majority of net O<sub>3</sub> is produced from peroxy radical reactions with NO.

L140: What could have been the reason for the higher loss rate in the large tube?

L143: It would be good, if numbers for the NO<sub>3</sub> concentrations that is used in the reactivity instrument were given and compared to ambient concentrations that are expected.

L161: Did you test if the calibration gas standard used to calibrate the CLD gave the correct concentration in the CRDS instrument?

L175: Why was the VOCUS PTR-MS not calibrated with the same gas standard as the other PTR instrument? Was the scaling factor that needed to be applied to the VOCUS instrument constant for a specific mass for the period, when both instruments measured together?

L195: How was the zero-value determined of the CLD? How often was this done and how stable was the zero?

Fig. 1: Why is there only a limited period of monoterpene measurements shown, if the VOCUS PTR was used to complete the measurements as shown in Fig. S4?

L253: Was the height of the vegetation below the tip of the inlet?

Fig. 4: It would be useful to indicate the inlet height and the height of the vegetation.

L 297: It does not make sense to give 3 counting digits for the fractional distribution, if the accuracy of measurements does not provide this accuracy.

L289: Can you justify, why you expect the same contributions of monoterpenes like in the other campaign? Seasonality, meteorological conditions, changes in the vegetation may highly impact the mix of emissions. This should be further discussed and not neglected as indicated in the in the text.

L290: Why is beta-caryophyllene a suitable proxy for the measurement of the sum of sesquiterpenes?

Fig. 5b: It is not clear, what the grey boxes are.

Fig. 5c: Was there no other (unaccounted) NO<sub>3</sub> reactivity on average?

L 294 and Fig. 5a: The figure gives the impression that monoterpene species can explain the NO<sub>3</sub> reactivity. However, it would be easier to judge this if the x-scale was wider and/or the time period was split into 2 panels.

L 303ff and Fig. 6: It looks as if there are more data points than shown in the figure. The large symbol size and using also black colour for the error bars makes it is hard to see details. What is the correlation coefficient? The distribution is very wide and shows that there are also a high number of points where numbers are not the same. A plot of the time series of the difference between calculated and measured NO<sub>3</sub> reactivity could give more insights if this is due to statistically or systematic differences during specific periods of the campaign.

L314ff and Fig. 7: It should be emphasized / defined that NO<sub>3</sub> reactions with VOCs are meant, if you say "fractional contribution F".

L319: What are the reasons for the increase of the contribution of NO<sub>3</sub> + VOC reactions?

L324: Can you give an estimate how the reaction rate of VOCs with OH and O<sub>3</sub> were during daytime to support your statement about the importance of NO<sub>3</sub> reactions for the oxidation of BVOCs during the day?

L327: Do you want to say that local anthropogenic emissions existed only during daytime? Why would this be the case?

L339ff: As discusses a bit later, you may expect a strong gradient of NO concentrations with height also within the surface layer due to the rapid reaction with O<sub>3</sub> unless the mixing is fast, which may not be expected specifically in the night. Does your estimate of the NO concentration consider such a gradient, if the inlet of the NO instrument is at a certain height? I assume that the NO source from soil would need to be significantly higher, if this is taken into account.

L366ff: Does the model also include O<sub>3</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> deposition? If so, this should be mentioned, if not it needs to be justified, why no deposition is assumed. These loss processes would all contribute to the loss of odd oxygen, and it may not be easy to distinguish between the loss for the different species. How can you justify that a 0-D box model is applicable for modelling measurements made close to the ground in night-time conditions, when mixing is poor?

L456ff and Table 1: It would be good to see the comparison of NO measurements and have this discussed in more detail in the text. If the explanation for the high NO in this campaign is soil emissions, what for example could be reason, why this was not observed in the other campaigns?

Technical comments:

General technical comment: It makes it easier to read and follow the manuscript if less

abbreviations are used in the text.

L36: "OH reactions being most important" instead of "OH reactions most important"

L61: subscript RONO<sub>2</sub>

Fig. 2: You may need to increase the font size if these figures become 1-column figures.

L312: comma missing after (j\_NO3).

L401: Units of production rates are pptv s-1 and not s-1.