

## ***Interactive comment on “Direct measurements of NO<sub>3</sub>-reactivity in and above the boundary layer of a mountain-top site: Identification of reactive trace gases and comparison with OH-reactivity” by Jonathan M. Liebmann et al.***

**Anonymous Referee #2**

Received and published: 11 June 2018

The manuscript Liebmann et al. presents NO<sub>3</sub> and OH reactivity measurements at a forested mountaintop site in Germany. The data is compared to reactivity calculations based on individual VOC reactions and heterogeneous uptake. The data is also discussed with respect to meteorological conditions and their impact on the VOC sources.

Overall, the study presents interesting and high-quality data, but it seems that the take-home message of the manuscript is not entirely clear. The most innovative part is that of the error calculation of the speciated reactivity calculations and the question of the missing NO<sub>3</sub> sink. As I will outline below this section needs to be expanded to more

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clearly support its main conclusion. The comparison of NO<sub>3</sub> and OH reactivities is interesting, but I am not entirely clear what the significance of the comparison is (except for the question of the VOC mix, which could as easily be addressed through the VOC observations). Maybe it would be useful to add the speciated reactivity calculation for OH to determine which of the two radical chemistries is less certain. Aside from these possible improvements the manuscript is well written and with a few revisions, following my comments below, is suitable for publication in ACP.

Comments:

Section 2: Please add a subsection on the aerosol size measurements used later in the manuscript.

Page 5 line 15 - 16: Is this number in meters? Please add unit

Section 3.2: As mentioned before I applaud the authors for considering the uncertainty of the speciated reactivity calculation. However, this discussion is really confusing and I have a hard time following the statements made in this section. The fit in Figure S5 was performed using errors for  $k^{\text{NO}_3}_{\text{VOC}}$ , thus the uncertainty of the slope should be a statistical measure of the uncertainty of the missing reactivity. The manuscript does not currently explain where these errors come from. If they are the same errors as used for Fig 5, then the fit in Fig S5 seems to show a statistically significant missing reactivity. Fig 5 on the other hand seems to show that there is no statistically significant missing reactivity. This needs to be discussed in more detail. It seems to me that the fit in Fig S5 is a statistically more meaningful measure, and I would recommend moving this figure to the main manuscript. I also think it would benefit the scientific value of the manuscript if a statement on the main causes of the uncertainty and future steps to reduce them could be added.

Figure 4: Please add some measure for uncertainty to this figure and/or provide a more detailed discussion in the caption.

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Page 10, line 10: Why assume a 15% uncertainty and not use published uncertainties?

Section 3.3 vs Section 3.4: Unless I misunderstand the arguments in these two sections, they seem contradictory for the nighttime data. In section 3.3 and Figure 7 NO is needed at night to close the NO<sub>3</sub> budget. It appears that NO is responsible for around 50% of the NO<sub>3</sub> loss. However, in Section 3.4 NO seems to have been ignored at night, therefore leading to the 99% fractional contribution of NO<sub>3</sub> + organics. So which one is correct? Is there sufficient NO at night to destroy NO<sub>3</sub> or not?

Section 3.4: Should the title be "Contribution to NO<sub>3</sub> loss"? I don't see the NO<sub>x</sub> loss discussed anywhere.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-324>, 2018.