

Direct measurements of NO_3 -reactivity in and above the boundary layer of a mountain-top site: Identification of reactive trace gases and comparison with OH-reactivity

Journal: Atmospheric Chemistry and Physics

Manuscript ID: acp-2018-324

The manuscript by Jonathan M. Liebmann et al. describes direct measurements of NO_3 and OH reactivity at a mountain site in Germany during the late July to early August period, 2017. The reactivity measurements are supported by other instrumentation such as GC-MS/FID for VOC speciation and quantification and NO_2 , NO , and O_3 data. The diurnal profile of NO_3 reactivity towards organic trace gases, k_{OTG} , shows low nighttime and relatively higher daytime values as a result of the measurement site being decoupled by surface emissions for most nights. The measured k_{OTG} is in agreement with the calculated one using monoterpene and isoprene measurements, within the measurement uncertainty. As in previous work from the same group, the daytime NO_3 reactivity shows significant contribution from the reaction of NO_3 with biogenic VOCs (BVOCs) supporting the BVOC role to NO_x removal and the formation of organic nitrates at the measurement site. Finally, this work is the first to provide simultaneous NO_3 and OH reactivity measurements which enables the authors to explore the correlation between the two radical chemistries.

The manuscript is well written and the results and data interpretation is clearly presented. This work expands further the field observations on NO_3 reactivity and for the first time enables a direct comparison with OH reactivity measurements. Therefore, I recommend the article's publication in ACP. A few points for consideration are given below:

- * page 5, line 28-29 and page 6, line 5: I would suggest to add the magnitude/range of the corrections
- * page 6, line 24: adding supplemental information or a reference for the transmission experiments would be useful
- * Section 3.2, Figures 5: Did the authors compare measured and calculated NO_3 reactivity values for type 2 nights only, where BVOCs are the major contributors? I am wondering whether there is a systematic difference in reactivity due to "unknown" VOCs and not just random uncertainty in the measurements.
- * page 12-13, section 4: The authors should discuss, even briefly, the agreement between measured and calculated OH reactivity as shown in Figure S6. Is there any indication of missing OH reactivity? This comparison could provide more insight on "unknown" VOCs that might explain a possible systematic difference in both OH and NO_3 reactivity. For instance, would a plot of "missing" reactivities, dk_{OH} vs. dk_{NO_3} , be informative?

Other revisions / typos:

- * page 1, line 16: I believe it should be "high reactivity" instead of "reactivity high" and "but" should be replaced with "and"

- * page 4, line 1: replace “outer-diameter” with “O.D.”
- * page 4, line 2: is this flow at STP conditions?
- * page 4, line 13: should be “thermostated”
- * page 6, line 24: shouldn’t this be “NO addition” ?
- * page 7, line 20: sentence should read ”.. for 15 min (C₂-C₈) and 20 min (C₅-C₁₃), respectively ..”
- * page 7, line 28: spaces are needed in ”ms⁻¹”
- * page 15, line 19: should be “GCxGC-FID”
- * Figure 1: Fix NO₂ units