

Reply to RC1

In the following, the referee's comments are reproduced (black) along with our replies (blue) and changes made to the text (red) in the revised manuscript. Line numbers refer to those in the initial submission.

General Comments:

The work by Patrick Dewald et al. is relevant to the atmospheric science community, well organized and well written. The quantitative details regarding NO₃ reactivity and fractional contribution to biogenic volatile organic compound (BVOC) oxidation appear robustly determined, clear and generally consistent with literature. Their results suggest an important conclusion that NO₃ can play a significant role during daytime oxidation which is counter to textbook atmospheric chemistry but not necessarily unheard of. However, there are a couple of points of concern.

We thank the reviewer for the positive assessment of our manuscript and for the provision of helpful comments.

First, the authors are reserving a more in-depth analysis of NO₃ oxidation from the same measurements and campaign for a future publication. These details seem highly relevant to information presented here and I question why they are better suited for an independent publication. Doing so removes context which would define the significance of the results.

The main objectives of this work are to identify factors that control the temporal and vertical variability in k^{VOC} and to assign the contribution of VOCs, NO and photolysis to NO₃ removal. We refrain from including explicit analysis of VOC and NO₃ measurements for the following reasons:

- 1) The scope of this paper is already well-defined and extensive. We believe that inclusion of the analysis of NO₃ and VOC measurements not only conceals the key message but also reduces the readability of the resulting (longer) paper.
- 2) A rigorous assignment of k^{VOC} to specific compounds is not (yet) possible due to lack of speciated monoterpene measurements at ground level.
- 3) Ideally, all directly related information from the campaign would be incorporated in one paper. However, as the reviewer will be aware, students, post-docs etc. need first author publications. Expanding this manuscript to cover detailed aspects of NO₃-reactivity as related to VOCs would not only make it unreadable but would also preclude first-author papers for the owners (French groups) of the VOC-data and the NO₃-measurements. As we already note in the paper, a comparison between calculated (steady-state) and measured NO₃ (or N₂O₅) mixing ratios above and below canopy level are going to be presented in the future publication along with an assignment of k^{VOC} to measured VOCs.

4) The concerns raised by the reviewer can be addressed with the data provided in the manuscript. We extend the discussion as detailed in the answers below.

Second, it is unclear if the cause for significant daytime oxidative contribution from NO_3 is due to reduced photolysis or increased VOC concentration. The answer to this point may be answered in the author's future publication but, again, it appears highly relevant here.

We agree that this point is highly relevant. In order to assess the impact of actinic flux reduction below the canopy, $F^{\text{VOC}}(5.5 \text{ m})$ was calculated using above-canopy values of J_{NO_3} and NO. This would result in an average daytime value for F^{VOC} of 33 %. This value is lower than the actual value of ca. 50 % and the reduction by a factor of 0.66 can be assigned to the attenuation of sunlight by trees and by the tower. However, even 33 % would be significantly higher than 20 % observed in a boreal forest in Hyytiälä, (Liebmann et al., 2018). This difference can be reconciled with higher daytime values k^{VOC} measured in Rambouillet. The increased daytime average of F^{VOC} thus stems from both reduced photolysis below the canopy and presumably from the higher abundance of highly reactive BVOCs. We accordingly extend the discussion in our manuscript in L264:

In order to assess the impact of this effect, we calculated F^{VOC} with above-canopy values of J_{NO_3} and NO. In this scenario, daytime F^{VOC} increases to 33 %, i.e. the reduction of photolysis frequencies increases F^{VOC} by a factor of 1.5. Liebmann et al. (2018) reported a daytime average for F^{VOC} of only 20 % in a boreal forest. Despite the fact that both sites are similarly affected by low NO and high monoterpene levels, this value is still significantly lower than 33 %, which can be reconciled with lower daytime values of k^{VOC} in the boreal forest. The comparatively high daytime contribution of VOCs to NO_3 consumption below the canopy thus stems from both reduction in J_{NO_3} and higher values of k^{VOC} , latter most likely due to higher concentrations of monoterpenes than in the boreal forest.

Specific Comments in order of line number:

1) Lines 100–108: Here, the authors describe the inlets however I did not see any discussion of inlet loss rates or the potential effects on reactivity measurements. I am concerned that the 40 m tall measurements (with a 20 m length and ~ 5 s residence time) may have wall loss of VOCs. Such an effect would result in reduced NO_3 reactivity as seen in Figure 1. Some mention of this point would strengthen the validity of these measurements.

During the week when switching between tower and ground measurement, the instrument not only sampled through the tubing (ca. 5 s residence time) but also through the glass flask (ca. 40 s residence time) throughout the diel cycle. The residence time in the PFA tubing is thus only of minor importance compared to the time spent in the flask. From the time before 18 July, no change in k^{VOC} levels was observed when switching between flask and bypass at 03:30 and 19:30 UTC, suggesting that no compounds significantly contributing to k^{VOC} are lost in the glass flask. Given the higher reactivity of uncoated borosilicate glass surfaces compared to PFA and the shorter residence time in the tubing, a significant transmission loss in the latter

appears unlikely. We now clarify this in the manuscript by adding in L118-120:

As the presence of NO_3 and N_2O_5 in ambient air would bias the measurement, **at nighttime** the air was sampled through a 2 L glass flask (**heated to 35°C**, ~ 40 s residence time) to ensure that ambient N_2O_5 is converted to NO_3 . All radicals including NO_3 , OH, RO_2 and HO_2 are lost on the glass walls and thus prevented from reaching the flowtube. **From July 18, air was sampled through the glass flask throughout the diel cycle. Note however that no difference in k^{VOC} levels was observed directly after switching between “daytime mode” (no flask) and “nighttime mode” (sampling through flask) during the period before. This implies that no compounds significantly contributing to k^{VOC} are lost in the glass flask.**

2) Section 3.1: the overall discussion here is clear, but I am left with a question of how the temperature inversion effects the production of NO_3 , which will contextualize the importance of the resulting k^{VOC} . As stated by the authors, the temperature inversions are associated with decreased O_3 (and presumed decrease in NO_3 production) but increased k^{VOC} . The effect of these two counteracting variables is absent from the discussion. I believe such a discussion is needed.

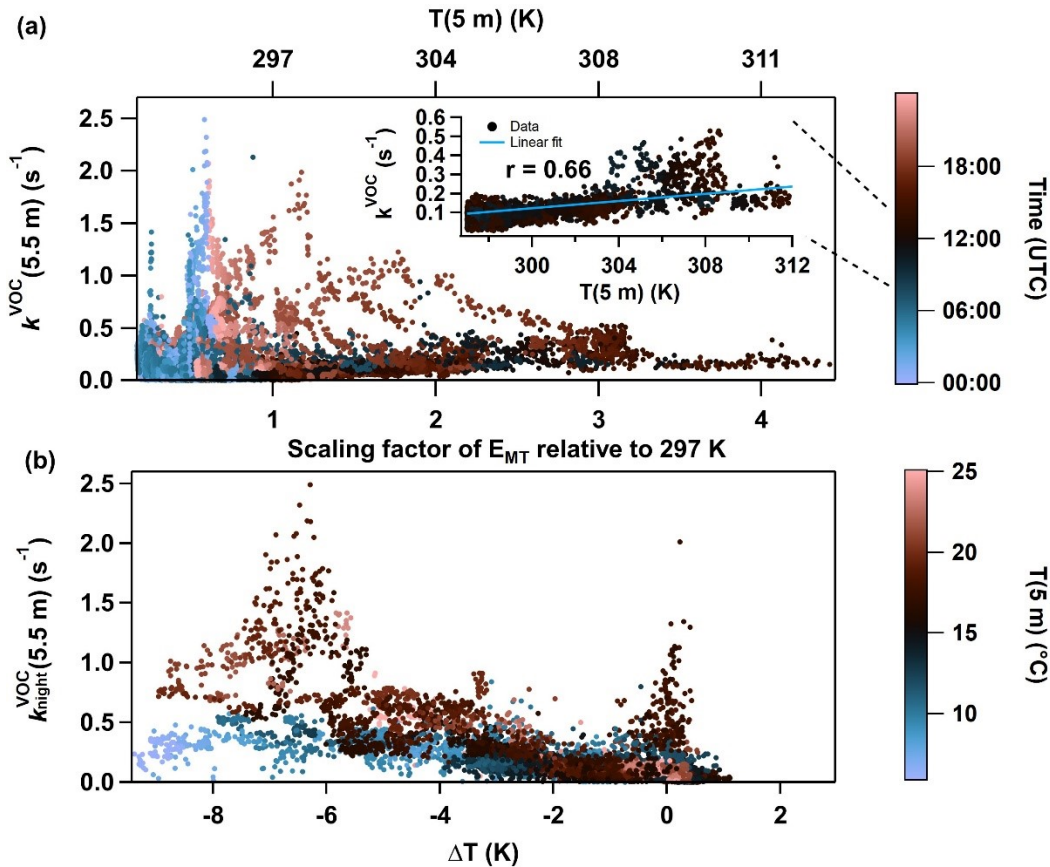
Such a discussion is misplaced in section 3.1 since the variability in k^{VOC} (main point of this section) is independent of the NO_3 production rate. The interplay only becomes relevant in the discussion of NO_3 mixing ratios. Note that “these counteracting variables” both lead to a reduction in NO_3 . As indicated in the answer to the general comments, an in-depth analysis of NO_3 production rates and mixing ratio will be addressed in a future publication. Instead, we emphasize this point even more than before in L330:

This is not only related to the reduced availability of O_3 but also to the increase in k^{VOC} , both of which were usually accompanied by temperature inversions.

3) Lines 220–222: The authors state that their analysis (Figure 3) suggests temperature is an important factor that influences NO_3 reactivity by BVOC emission. However, I do not find the same conclusion because such a relationship is not apparent in Figure 3. It is clear that the BVOC emission is dependent on temperature (by design) but, as the authors state in the discussion, the relationship between emission and NO_3 reactivity is clouded by competing oxidants during the daytime. The conclusion from this discussion appears to be simply that inversion has a strong effect (Figure 3b). I suggest the authors offer a better justification for their conclusion, remove this point, or provide additional VOC data to elaborate.

As already indicated in the manuscript, daytime chemistry affects VOC concentrations. Nevertheless, measured BVOC mixing ratios can clearly correlate with air temperature as shown for example with isoprene in Kalogridis et al. (2014). In spite of the reduced chemical selectiveness of OH compared to NO_3 , this is even reflected in temperature-correlated OH reactivities in environments dominated by BVOC emissions (Pfannerstill et al., 2021). Consequently, a correlation between air temperature and NO_3 reactivity appears plausible. We admit that the daytime correlation between $T(5\text{ m})$ and k^{VOC} is hard to see in Figure 3a, which

is why we now added an inset plotting daytime k^{VOC} (10:00 to 14:00 UTC) against air temperature along with a linear regression. The daytime values of k^{VOC} (black points due to a new color map, see below) are clearly correlated with air temperature (Pearson correlation coefficient $r = 0.66$). We modified the figure and caption and the text in L220-224 accordingly:



L220: Relative monoterpene emission factors are temperature-dependent and described by $\exp(\beta(T-297 \text{ K}))$ with $\beta = 0.1 \text{ K}^{-1}$ in forested environments (Guenther et al., 1993), resulting in a strong seasonal variation (Hakola et al., 2006; Vermeuel et al., 2023). As a consequence, correlations between air temperature and VOC mixing ratios and OH reactivity have been reported (Kalogridis et al., 2014; Pfannerstill et al., 2021). Figure 3a shows that, during the day (black data points), with temperatures varying from 297 to 311 K, an increase in $k^{\text{VOC}}(5.5 \text{ m})$ is observed. The inset contains daytime values measured between 10:00 and 14:00 UTC against air temperature and a linear regression suggests a fair correlation between the two (Pearson correlation coefficient $r = 0.66$). The expected factor of 4 increase in the emission rate over this range as reported in Guenther et al. (1993) is much larger than the observed change in $k^{\text{VOC}}(5.5 \text{ m})$.

4) Lines 264–265: The point by the authors that Decker et al. (I am the first author of this cited paper) find NO_3 is a major oxidant during daytime for wildfire plumes due to their reduced photolysis rates is incorrect. Instead, the cited work concludes that NO_3 is a major daytime oxidant in wildfire plumes because smoke plumes are a huge source of reactive VOCs which

outcompetes photolysis. This point is (admittedly hard to find) most clearly argued for a smoke plume (Castle) with a $j\text{NO}_3$ of 0.14 s^{-1} sampled mid-day which is comparable to mid-day photolysis rates presented here (Figure 1). In that cited case, photolysis accounted for $\sim 0.6 \%$ of NO_3 loss but the large source of VOCs accounts for the remainder of NO_3 loss. The overall conclusion of the cited work is also that NO_3 oxidation can be significant during daytime (in the case of biomass burning plumes).

Thank you very much for clarifying this, we have corrected this point in L264/265:

This observation is consistent with even higher daytime VOC contributions to NO_3 loss of $>97 \%$ reported for sunlit wildfire plumes by Decker et al. (2021) who reconciled their result with VOC mixing ratios that were sufficiently high to outcompete photolysis and NO .

This brings up the question of whether the large daytime F^{VOC} here is the result of reduced photolysis or large BVOC concentrations (or both). As written, the authors appear to suggest that large daytime F^{VOC} is due to reduced sunlight although a definitive conclusion is not clear. The authors acknowledge that NO_3 production will also be affected by reduced sunlight, but the effect is not discussed.

A major conclusion of this work is that NO_3 is a significant daytime oxidant in this sub-urban forest yet a reason is not clear. Such a conclusion is counter-intuitive based on textbook atmospheric chemistry (as mentioned by the authors). As such, understanding the conditions that cause such a result is highly relevant and important to the atmospheric community. I feel strongly that an interpretation of the cause of a large daytime F^{VOC} would provide highly important context for the author's conclusion that NO_3 reactivity is significant during the daytime. I strongly suggest the authors provide further analysis (e.g. NO_3 production, information on BVOCs and concentrations) so that the importance of this result is better realized.

We have already addressed these points in the answer to the general comments above.

5) Section 3.6: I have a minor point that (to my understanding) equation 4 is a reactivity, not an oxidation rate, because it is first order and does not include the VOC concentration. Perhaps it could also be called the total loss rate as was done for NO_3 .

We agree and now call it, in analogy to NO_3 , loss rate coefficient throughout the whole manuscript.

Technical Details:

Line 283: “Recall however, that due its poor” typo here.

Correction made to “due to”.

Line 296: “Figure 2 (period p)” seems wrong.

Correction made to “Fig. 7”.

Figure 3(a): I suggest to change to x-axis label to something more interpretable by the reader such as “Calculated BVOC emission (unitless?)”.

Adjustment made, we changed the x-axis label to “ $E_{MT}(T) / E_{MT}(297\text{ K})$ ”.

Figure color scales: I encourage the authors to use color scales that are readable in grey-scale. This improves accessibility to color blind readers. For example, see Crameri et al. 2020 (<https://doi.org/10.1038/s41467-020-19160-7>).

Adjustment made, Fig. 2, 3 and S1 have been modified accordingly. We further note in the Acknowledgements:

The Scientific colour map “Berlin” (Crameri, 2023) is used in this study to prevent visual distortion of the data and exclusion of readers with colour-vision deficiencies (Crameri et al., 2020).

Figure markers: to the above point I encourage the authors to use opposing marker styles (such as filled and empty circles) so that the reader does not rely on color to differentiate these markers.

All figures have been modified accordingly.

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