

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 NO_3 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 NO_3 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.

First, the authors are reserving a more in-depth analysis of NO_3 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. 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.

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.
- 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.
- 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.
- 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 ~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).

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.

- 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 .

Technical Details:

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

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

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

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>).

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.