Reply to RC2

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 paper by Dewald et al. describes a summer-season field study of NO_3 reactivities measured in a temperate forest in France. Measurements were made in a small clearing close to ground and on a 40 m tower. The results are discussed in terms of diurnal variations of contributions from VOCs, NO and photolysis to the overall NO_3 reactivity, with VOC reactivities found to be significant during night and day. Based on measured and estimated concentrations of OH, O_3 and NO_3, the relative importance of these reactants for the oxidation of selected BVOCs is estimated, revealing a significant contribution of oxidation through NO_3, again during night and day, at least close to ground.

We thank the referee for taking the time to assess our manuscript and for the provision of helpful comments.

The paper is relevant, well written and structured and therefore suitable for publication in ACP. However, the work would gain relevance if information on the BVOC composition were available and if there is any missing NO_3 reactivity. In other words: how well is the k^{VOC} understood in this environment?

The main objectives of this work are to identify factors that control the temporal and vertical variability in NO_3 reactivity and to assign the contribution of VOCs, NO and photolysis to NO_3 removal. A rigorous assignment of k^{VOC} to specific compounds is not (yet) possible due to lack of speciated monoterpene measurements at ground level. Several of the authors of this publication plan to address this question in a further publication (including NO_3 measurements at 5.5 and 40 m), as soon as speciated VOC measurements at ground level are available. In the reply to reviewer 1, we outline why combining these papers is neither necessary nor conducive to readability.

Below are some comments that may be considered in a revised version of the paper.

Specific comments

Line 22: Given the strong variability and peak values of the k^{VOC} at night, an arithmetic mean and a standard deviation are not useful to summarize the results. Consider using a range instead or percentiles.

We agree and now provide the 25th and 75th percentiles of k^{VOC}_{night} and modified L22, L250 and L282 accordingly:

L22: At nighttime, mean values (and 25th-75th percentile ranges) of $k^{VOC}_{night}(5.5\ m) = (0.24^{+0.32}_{-0.06})$ s^{-1} and $k^{VOC}_{night}(40\ m) = (0.016^{+0.018}_{-0.007})$ s^{-1} indicate a significant vertical gradient […].

L250: The higher mean nighttime value ($k^{VOC}_{night}(5.5\ m) = (0.24^{+0.32}_{-0.06})$ s^{-1} compared to $k^{VOC}_{day}(5.5\ m) = (0.12 \pm 0.04)$ s^{-1}) is a result of accumulation of BVOCs in a shallow, sub canopy layer with reduced rates of canopy-venting owing to temperature inversions.

L282: . In contrast, the average value (± 25th and 75th percentile, respectively) of $k^{VOC}_{night}(40\ m) = (0.016^{+0.018}_{-0.007})$ s^{-1} is approximately one order of magnitude lower than $k^{VOC}_{night}(5.5\ m)$.

Line 28: The "total loss rate" L^{NO_3} is later defined (Eq. 1) as the total NO_3 reactivity, i.e. a (pseudo first-order) loss rate coefficient. Loss and production rates are usually named *L* and *P* but defined as products of concentrations and rate constants resulting in units of $cm^{-3}s^{-1}$ (or ppb h^{-1}, dependent on context). k^{TOT} would be a better choice (see technical comments).

We agree and changed L^{NO_3} to k^{tot} throughout the whole manuscript.

Line 30: Perhaps clarify that the conclusions regarding the contribution of NO_3 to α-pinene degradation and the chemical lifetimes of BVOCs are based on measured OH and O_3 concentrations and estimated steady-state NO_3 concentrations.

We now write in L30:

Based on **measured** OH, O_3 and **calculated** NO_3 concentrations […].

Line 60: Both photolysis reactions recycle NO_x but only (R7b) recycles NO_2. Consequently, (R7b) also regenerates O_x (NO_2 + O_3) but (R7a) is a net daytime loss of O_x, another perhaps underestimated daytime effect of NO_3 chemistry.

Thank you for pointing this out, we rephrased the sentence in L60 accordingly:

While both the reaction with NO (R5) and photolysis (R7) recycle either NO or NO_2, […].

Given the slow rate coefficient of ca. 3 x 10^{-17} cm^3 $molecule^{-1}$ s^{-1} at 298 K (IUPAC, 2024) for the reaction between NO_2 and O_3, the impact of (R7b) on the recycling of NO_3 is expected to be very minor.

Line 120: Was the transmittance of BVOCs through the combination of sampling lines, filter, and glass flask tested? BVOCs with low volatility and high reactivity may get lost on the way to the flow tube.

The transmittance of BVOCs through this system was tested by switching between flask and bypass at 03:30 and 19:30 UTC and observing no change in k^{VOC} levels. This indicates that the compound that significantly contribute to k^{VOC} are not 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/filter, a significant transmission loss in the latter appears unlikely. We now clarify this in the manuscript by adding in L118-120:

From July 18, air was sampled through the glass flask throughout the diel cycle. No difference in k^{VOC} was observed directly after switching between "daytime mode" (no flask) and "nighttime mode" (sampling through flask), indicating that no compounds significantly contributing to k^{VOC} are lost in the glass flask.

In addition, the inlet filter was replaced every three days to ensure that aging of the filter does not lead to transmission loss. We thus further note in L106:

The filter was replaced every three days.

Line 132: Your correction subtracts the remaining NO reactivity from the measured reactivity to derive k^{VOC}. Under conditions with low k^{VOC} and [NO]>[O_3] the uncertainties are probably greater than the stated average 26%. Does your numerical simulation and correction procedure provide realistic, condition dependent uncertainty estimates?

Yes, as detailed in Liebmann et al. (2017), the calculation of the uncertainties takes ambient levels of k^{VOC}, NO_2 and NO at each data point into account. A few data points of k^{VOC} during the ACROSS campaign thus have an associated uncertainty > 50 %. The campaign-averaged value stated in the manuscript is supposed to serve as a ballpark value.

Line 154: "Photolysis rates" should be named photolysis rate coefficients or photolysis frequencies consistently throughout the text.

Done, we replaced "photolysis rates" with "photolysis frequencies" throughout the whole manuscript.

Line 157: The paper of Meusel et al., contains no information on NO_3 absorption cross sections. I assume you used IUPAC or NASA-JPL recommendations for quantum yields and cross section which should be cited here.

We used IUPAC- and NASA-recommended quantum yields and changed the reference in L157 accordingly:

Actinic fluxes were converted to photolysis frequencies of NO_3 and of other compounds using IUPAC- and NASA-evaluated absorption cross sections (Burkholder et al., 2016; IUPAC, 2024).

Line 246: A future publication on NO_3 measurements? In Sect. 3.6 it is stated that NO_3 mixing ratios were always below the LOD which is consistent with the steady-state estimates < 0.2 ppt in Fig. 8.

On some nights, NO_3 as well as N_2O_5 mixing ratios above LOD were detected on top of the tower and N_2O_5 was detected at ground level, which provides the basis for the above-mentioned future publication. We emphasized this point in L245:

The longer nocturnal lifetime of NO_3 at 40 m enabled it to be detected on some nights of the campaign, whereas NO_3 measurements were, unlike N_2O_5, always below LOD close to the ground. A detailed analysis of the NO_3 **(and N_2O_5)** measurements will be presented in a future publication.

Technical comments

Line 95: Specify where the wind measurements were made in the caption of the figure in the Supplement (5 m, 40 m?)

The wind measurements were carried out on top of the tower. We now mention this in the figure caption of Fig. S1.

Line 137: "L^{NO_3} which is the loss term" maybe better: "k^{TOT} which is the total reactivity"

Done, we replaced "L^{NO_3}" with "k^{tot}" throughout the whole manuscript.

Line 231, Eq. (1): k^{TOT} would fit better throughout the text with the upper index reserved for reactants, i.e. k^{TOT}, k^{VOC}, k^{NO} but τ_{NO3}, J_{NO3} with the lower index reserved for the target species if necessary. Define $k^{NO} = k_5[NO]$ and $J_{NO3} = k_{7a} + k_{7b}$

Correction made.

Line 297 ff: Better $k^{VOC} + k^{NO}$

Correction made.

Line 320 ff: Better "$k_{\alpha\text{-pinene}}$" than "$L^{\alpha\text{-pinene}}$"

Correction made.

Line 325: Better "…the ratio of production rates $k_2[NO_2][O_3]$ and overall loss rate coefficients k^{TOT}"

Correction made.

Figs. 4, 5, 6, 8: How was the nighttime period 03:30-19:30 determined? Local noontime is close to 12:00 UTC. The night ends before sunrise and starts before sunset (checked for July 10th).

The NO_3 photolysis rates as derived from actinic flux measurement on top of the tower served as measure for the estimation periods that were unaffected by sunlight (see e.g. Fig. S5).

References

Burkholder, J. B., Sander, S. P., Abbatt, J. , Barker, J. R, Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M.., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18," JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena: https://jpldataeval.jpl.nasa.gov, access: 23 July 2023, 2016.

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Liebmann, J. M., Schuster, G., Schuladen, J. B., Sobanski, N., Lelieveld, J., and Crowley, J. N.: Measurement of ambient NO_3 reactivity: Design, characterization and first deployment of a new instrument, Atmos. Meas. Tech., 10, 1241-1258, doi:10.5194/amt-2016-381, 2017.