Reply to Anonymous Referee #2

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.

The authors report on studies of NO3 reactivity during 'nighttime' experiments in the SAPHIR chamber, with a primary focus on isoprene chemistry. An FT-CRDS system is used to determine the NO3 reactivity with respect to stable products in the chamber, while a box model analysis is used to assess additional NO3 losses (reaction with peroxy radicals, chamber wall losses) not determined by the FT-CRDS system. Among the key findings are the following: the FT-CRDS accurately measures the NO3 reactivity towards isoprene, and functions well under the conditions studied; stable products of the NO3/isoprene chemistry do not contribute significantly to NO3 reactivity; the generic (and highly uncertain) RO2 + NO3 rate coefficient may be a factor of two or more higher than current estimates. Overall, this is a very solid paper that certainly is publishable in ACP. The paper is well written, and assumptions and uncertainties in the measurements are generally presented in detail. A few questions and suggestions are presented below for the authors to consider.

We thank the referee for the positive evaluation of our manuscript and the useful comments.

1. Referee's comments

There are assumptions and caveats associated with equation (1), line 220 – Could there be significant reaction products that the PTR-MS is unable to detect? Could some products not make it into the flow tube for detection by the k(NO3) instrument? NO3 losses due to chamber walls and radicals are not measured by the k(NO3) instrument. Most (or maybe all) of these are dealt with at different points in the manuscript, but a clear statement or two delineating these at this point might be helpful to the reader.

This is indeed necessary for validity of Eq. (1). We now write (L219):

The VOC contribution to the NO_3 reactivity is the summed, first-order loss rate coefficient attributed to all non-radical VOCs present in the chamber that can be transported to the FT-CRDS according to Eq. (1):

Can the authors be more quantitative regarding the b-caryophyllene expt (Fig 3a)? -e.g., What is its expected lifetime? The k(NO_3) instrument is clearly not seeing the full impact of the stated addition of 2 ppbv b-caryophyllene.

Assuming 120 ppbv of O_3 and a rate constant of 1.2×10^{-14} $cm^3molecule^{-1}s^{-1}$ (298 K, IUAPC) for the reaction between β-caryophyllene and O_3 leads to a loss rate of 0.035 s^{-1}. Neglecting secondary oxidation, only 11 pptv of β-caryophyllene (resulting in k^{NO_3} of 0.005 s^{-1}, which is the setup's LOD) are left after 150 s. The instrument was zeroing until a couple of minutes after the injection of β-caryophyllene and thus detected only the last residues of this sticky monoterpene. We add this point to the manuscript and now write (L258):

The instrument was zeroing until shortly after the injection of this terpene. ~~The presence of β-caryophyllene explains the small increase in the NO₃ reactivity after 08:30 UTC.~~ As the lifetime of β-caryophyllene is extremely short in the chamber under the given conditions (~ 150 s), only the small fraction of unreacted β-caryophyllene contribute to the k^{NO_3} signal observed after 08:40 UTC.

Line 265 / Fig 3b: Isoprene loss here is due to reaction with O3, I assume (maybe also OH formed in the ozonolysis)? Does the agreement noted between the k(NO3) instrument and the k[isoprene] calculation imply that major isoprene ozonolysis products are also comparatively unreactive towards NO3? (Also, a minor detail, but the isoprene decay seems more rapid than would be implied by the O3 concentration given?)

Correct, the isoprene loss is mainly caused by ozonolysis but also by dilution during the first three hours between 06:50 and 09:50 UTC. Using stated initial concentrations and rate coefficients at 298 K (IUPAC, 2019) calculated losses are as follows:

$$k_{loss}(isoprene) = k_{ozonolysis} + k_{dilution} = [O_3] * k_{O_3 + isoprene} + k_{dilution}$$
$$= (3.11 * 10^{-5} + 1.5 * 10^{-5})s^{-1} = 4.61 * 10^{-5}s^{-1}$$

$$[isoprene](3\ h) \approx [Isoprene]_0 * \exp(-k_{loss}(isoprene) * 10800\ s)$$
$$\approx 4\ ppbv * \exp(-4.61 * 10^{-5}s^{-1} * 10800\ s) \approx 2.4\ ppbv$$

After 3 hours 2.4 ppbv of isoprene causing an NO_3 reactivity of 0.038 s^{-1} which is in good agreement with the measurement. The sudden decrease in isoprene (and k^{NO_3}) after 09:50 UTC is caused by an increase of the dilution flow by a factor of 10 in scope of a humidification process.

We agree, the good agreement between the FT-CRDS measurement and k[isoprene] suggests a neglectable contribution of products from the ozonolysis. Given the low reactivity of stable ozonolysis products (e.g. MACR, MVK, formaldehyde) and the non-detection of radicals/Criegée intermediates this seems to be a valid conclusion. We include these aspects to the manuscript (L267):

Isoprene depletion is dominated by ozonolysis at this phase, whereas the sudden drop in k^{NO_3} is caused by an increased dilution flow during humidification of the chamber around 10:00 UTC. The absence of NO_2 results in a more accurate, less scattered measurement of k^{NO_3} and underscores the reliability of the measurement under favourable conditions. All of the observed reactivity can be assigned to isoprene that was injected at 06:52 UTC. This implies that stable secondary oxidation of products from isoprene ozonolysis (such as formaldehyde, MACR, MVK) are insignificant for k^{NO_3} which is consistent with the low rate coefficients (e.g. $k_{MACR+NO_3} = 3.4\ x\ 10^{-15} cm^3 molecule^{-1}\ s^{-1}$ as highest of the three; IUPAC, 2019).

Line 312 or so - It should be noted here that NC4CHO is only one of many products that can be formed.

Correction made, we now write (L319):

One of several ~~The~~ major, stable oxidation products according to MCM is an organic nitrate with aldehyde functionality ($O_2NOC_4H_6CHO$, NC4CHO).

In Figure 9, it is not clear to me that the increased RO_2 + NO_3 rate coefficient improves the model/measured NO_3 comparison?

This statement referred to the very first phase after the isoprene injection, but we agree that in the last phase of the experiment (old) model 2 shows a worse agreement with the NO_3 measurement than (old) model 1. We now write (L419):

The higher rate coefficient for reaction of NO_3 with RO_2 would be sufficient to ~~not only~~ explain the observed discrepancy between the overall reactivity $k_{nss}^{NO_3}$ and k^{NO_3} within the uncertainties associated with the analysis. ~~but also results in a better reproduction of the NO₂ measurement during the isoprene-dominated period.~~

2. Additional changes

L423: Optimum agreement irrespective of uncertainties would be achieved with a value of 9.2 x 10^{-12} cm³molecule^{-1}s^{-1} for $k_{\mathrm{RO_2+NO_3}}$ (i.e. a factor of 4 higher than in MCM) which is demonstrated in a comparable experiment under dry conditions on the 10th August (see Fig. S4 in the supplement).

L443,483: "within uncertainties" added

Caption Fig. S4: The results of the numerical simulation using MCM v.3.3.1 (with NO$_3$ and N$_2$O$_5$ wall loss rate of 0.016 s^{-1} and 3.3 x 10^{-4} s^{-1} respectively) for each of the reactants is shown by a red line, whereas the blue line shows the result of the same model with ~~a doubled reaction constant for NO$_3$ + RO$_2$ reactions ($k_{NO_3+RO_2}$~~ = 9.2 x 10^{-12} cm³molecule^{-1}s^{-1}~~).~~

3. References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.) http://iupac.pole-ether.fr/index.html., 2019.