Reply to Anonymous Referee #1

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.

Dewald et al. present measurement of NO_3 reactivity (k^{NO_3}) resulting from the reaction of NO_3 with isoprene and stable trace gases in an atmospheric simulation chamber with different initial conditions. The agreement between $\sum k_i[VOC]_i$ and k^{NO_3} indicates that NO_3 reactivity is dominated by the reaction between NO_3 and isoprene. Box model simulation results indicate that the discrepancy between measured k^{NO_3} and non-steady-state reactivity $k^{NO_3}_{nss}$) is caused by the uncertainty in $k_{RO_2+NO_3}$.
Instrument analysis is adequate. However the authors should expand the description of instrument calibration for PTR-TOF-MS (see minor comments below).
Overall, this study reports high quality data obtained from well designed experiments. The data should be of interest to the atmospheric science community. This manuscript is well within the scope of ACP. I recommend that the manuscript be published in ACP after minor revision.
We thank the referee for the positive evaluation of our manuscript and the useful comments.

1. Minor comments

2.3 VOC measurements: PTR-ToF-MS: Please describe how often were the instruments calibrated during the campaign.
Calibration of PTR1000 was done once per day (around 5 p.m.) following the procedure as described in Holzinger et al. (2019) and took around 10 min. VOCUS PTR performed calibrations on an hourly basis for 5 minutes. This information has been integrated into the manuscript:
L151: Data processing was done using PTRwid (Holzinger, 2015) and the quantification/calibration was done once per day following the procedure as described recently (Holzinger et al., 2019).
L154: Calibration was performed on an hourly basis for 5 minutes.

Please show the variability of the instrumental sensitivities during the entire campaign period.
The sensitivity mostly varies with the primary ion signal as long as other conditions are kept constant (not the case for the whole campaign). The authors therefore do not see the benefit of providing this information in scope of this analysis.

Please be more specific about the uncertainty used in instrument comparison. It would be useful to add a figure showing the VOCs mixing ratios measured by the two PTR-TOF-MS from the same air sample.
The uncertainty associated with the isoprene measurement is 14 %. A new figure (S1) showing the isoprene mixing ratios measured by the two PTR-ToF-MS during two exemplary experiments has been added to the supplement and is mentioned in the manuscript (L155):
The isoprene measurements of the two instruments agreed mostly within the uncertainties (14 %). An exemplary comparison between the two instruments of an isoprene measurement can be found in the supplement (Fig. S1).

2.5 Box model: "FACSIMILE/CHEKMAT" is a dated tool. A quick search of it didn't return much useful information. It would be great if the simulations in this study were run in an open source, modern box model, such as BOXMOX (Knote et al., 2015), F0AM (Wolfe et al., 2016), and CAABA (Sander et al., 2019). Doing so enables the reader to run the simulation on their own computer and play around with the configurations, such as the reaction rate constant $k_{RO_2+NO_3}$, the wall loss rates of NO_3 etc.

We present the full chemical scheme used in the simulations. Anyone who wants to reproduce or check our simulations has all the necessary information and can make their own choice of numerical integration tool.

Page 8, Line 227: “no propene data was available”: is this due to the unavailability of propene in the standard gas? If so, the expected sensitivity of propene can be calculated using the method described in Holzinger et al. (2019). The uncertainty of propene mixing ratios introduced from using expected sensitivity should be smaller than using model estimation. Please justify why the propene mixing ratios were assessed with the model instead of calculated using its sensitivity.

The reviewer is right that, in principle, propene VMR could be assessed from basic reaction kinetics according to Holzinger et al. (2019). However, the $C_3H_6H^+$ ion is also a prominent fragment originating from several compounds (e.g. isoprene) and therefore we used modelled concentrations. In addition, propene was not detectable by the VOCUS PTR as a low mass filter was used.

Page 8, Line 242: Please provide output from the unweighted linear regression (e.g., correlation coefficient, p-value), and incorporate the output into your discussion on the agreement between $\sum k_i[VOC]_i$ and k^{NO_3} measurements.

Done. We provided the correlation coefficient r of 0.95 (also denoted in Figure 2(b)) and now write (L245): A correlation coefficient of 0.95 underlines linearity of the whole data set despite increased scatter caused by the unfavourable conditions during type 2 experiments.

Page 13, Line 388–395: Please merge the model output (with $k_{wall} = 0\ s^{-1}$) in Figure S3 to Figure 9, this could help the reader better visualize the effect of introducing the NO_3 and N_2O_5 wall loss.

Done. Figure 9 has been changed accordingly. In order to preserve legibility of the NO_3 and N_2O_5 measurements after implementation of the model output in (old) Fig. S3 to Fig. 9 the order and sizes of the panels were changed. Old Fig. S3 has been removed. The caption of Fig. 9 now reads:

Figure 9: O_3, NO_2, NO_3, N_2O_5 and isoprene mixing ratios and NO_3 reactivity on 2nd August (black). The grey shaded area symbolizes the overall uncertainty associated with each measurement. Orange circles denote the reactivity obtained using Eq.(3). The results of the numerical simulation using MCM v.3.3.1 with NO_3 and N_2O_5 wall loss rates set to 0 s^{-1} (model 1) are shown by black lines. The model output with introduction of NO_3 and N_2O_5 wall loss rates of 0.016 s^{-1} and 3.3×10^{-4} s^{-1} respectively for each of the reactants is shown by a red line (model 2), whereas the blue line (model 3) shows the result of model 2 with the rate coefficient for reaction between NO_3 and RO_2 set to 4.6×10^{-12} $cm^3 molecule^{-1} s^{-1}$, which is twice the value estimated by the MCM.

Please discuss more about the effect of omitting the NO_3 and N_2O_5 wall loss and its cause of large discrepancies between the measurement and model simulation in NO_3, N_2O_5, and isoprene mixing ratios.

The changes in Figure 9 and this comment necessitated to following changes in the manuscript text (L396-410):

We examined the effect of introducing the NO_3 and N_2O_5 wall loss rate constants calculated as described above into the chemical scheme used in the box model (~~Model 1,~~ MCM v3.3.1). The results from three different model outputs for the experiment on the 2nd August are summarised in Fig. 9 which compares simulated and measured mixing ratios of NO_3, N_2O_5, NO_2, O_3 and isoprene (following its addition at 11:00) as well as the measured and non-steady-state NO_3 reactivities k^{NO_3} and $k^{\mathrm{NO3}}_{\mathrm{nss}}$. The omission of NO_3/N_2O_5 wall losses (Model 1) results in simulated NO_3 and N_2O_5 mixing ratios up to 1400 and 1600 pptv during the isoprene-free period, which exceed measurements by factors of 4-8. This is because the only loss process for these species in this phase is the dilution rate that is two orders of magnitude lower than the estimated wall loss rates. Such high amounts of NO_3/N_2O_5 in the ppbv range result in rapid depletion of nearly half of the total injected isoprene within the first minute which is why Model 1 cannot describe the measurements either before or after the injection. Model 2 (red lines) includes the estimated wall loss rates and reproduces the measurements more accurately: The NO_2 and O_3 mixing ratios are accurately simulated. Furthermore, NO_3 and N_2O_5 mixing ratios that are only 10 to 30% higher than those measured and therefore NO_3 reactivities lower than $k_{\mathrm{nss}}^{\mathrm{NO3}}$ (orange circles) are predicted. ~~We note that, in these isoprene-free phases, the omission of wall losses results in model predictions of NO_3 and N_2O_5 mixing ratios up to 1400 and 1600 pptv, which exceed measurements by factors of 4-8, as illustrated in (Fig. S3).~~

Please discuss how is the first-order wall loss rate for O_3 , H_2O_2, HO, HONO and HNO_3 derived in Table S1.

The wall loss rates were derived as previously described (Richter, 2007). Compared to losses by dilution and reactions, this is a very minor sink that does not have a significant impact on the fate of NO_3.

The appropriate reference was added to table S1.

Page 13, Line 391: "and isoprene (following its addition at 10:50)": from Figure 9 and Figure S2, NO_2 appeared to be injected at 10:50, isoprene appeared to be injected at 11:00, please clarify.

Correct. NO_2 was injected at 10:50 and isoprene at 11:00 UTC.

We corrected this in the manuscript.

Page 22, Figure 2(b): To better aid visual inspection of the dataset, please set the aspect ratio of x:y to 1:1, add grid to x-axis and y-axis, add border to the legend (not shown in the demo below). See Figure 2(b).

Done. Figure 2(b) has been changed accordingly.

2. Additional changes

L423: Optimum agreement irrespective of uncertainties would be achieved with a value of 9.2 x 10^{-12} $cm^3 molecule^{-1} s^{-1}$ 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_2O_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 (~~$\boldsymbol{k_{NO_3+RO_2}}$= 9.2 x 10^{-12} $cm^3 molecule^{-1} s^{-1}$~~).~~

3. References

Richter, C.A.: Ozone Production in the Atmosphere Simulation Chamber SAPHIR, Ph.D. thesis, Forschungszentrum Jülich GmbH, University of Köln, http://juser.fz-juelich.de/record/62596/files/Energie&Umwelt_02.pdf, 2007. (pp 37, 123)

Holzinger, R., Acton, W. J. F., Bloss, W. J., Breitenlechner, M., Crilley, L. R., Dusanter, S., Gonin, M., Gros, V., Keutsch, F. N., Kiendler-Scharr, A., Kramer, L. J., Krechmer, J. E., Languille, B., Locoge, N., Lopez-Hilfiker, F., Materić, D., Moreno, S., Nemitz, E., Quéléver, L. L. J., Sarda Esteve, R., Sauvage, S., Schallhart, S., Sommariva, R., Tillmann, R., Wedel, S., Worton, D. R., Xu, K., and Zaytsev, A.: Validity and limitations of simple reaction kinetics to calculate concentrations of organic compounds from ion counts in PTR-MS, Atmos. Meas. Tech., 12, 6193–6208, https://doi.org/10.5194/amt-12-6193-2019, 2019.