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. Line numbers refer to those in the preprint.

The present work provides an evaluation of NO_3 radical fates in a semi-rural site thanks to direct NO_3 reactivity measurements during the TO2021 campaign in summer 2021. A Flow-Tube Cavity Ring Down Spectrometer (FT-CRDS) setup was used to measure the NO_3 total reactivity and to estimate the contribution of BVOCs to this total reactivity. During this campaign, a number of other relevant measurements (NOx, O_3, actinic flux, VOCs, …) were performed to allow for a comprehensive interpretation of the observations.
This study is fully relevant and the FT-CRDS is a very interesting technique to better understand the role of NO_3 in the night-time chemistry. The paper is well written and provides detailed information on the experimental setup as well as a very thorough interpretation of the observations, and it is very much appreciable. In general, the scientific quality of this work is very good and once the authors have addressed the following minor points, I would be happy to recommend its publication in ACP.
We thank the Referee for this positive evaluation of our manuscript.

Specific comments:

61: more detailed reactions should be provided to better explain the formation of $RONO_2$ from VOC+NO_3 reactions
R10 and R11 do not intend to do more than indicate that NO_3 initiated oxidation of unsaturated VOCs can lead to $RONO_2$ and SOA. Given the large number of different VOCs involved and the complexity of the chemistry, a detailed description of the reactions leading to $RONO_2$ and SOA is not waranted here. For this we provide several references. We have replaced VOC with R=R to indicate that unsaturated VOCs are involved:
$NO_3 + R{=}R\ (+\ O_2) \rightarrow\rightarrow RONO_2$

175: it is not clear why the PTR-MS (VOCUS) was not calibrated with the standard used for the other PTR-MS (Ionicon). Could the authors provide an explanation?
Fragmentation patterns in the VOCUS PTR-MS are not yet completely characterized. We now write:
Fragmentation patterns in the VOCUS PTR-MS are not yet completely characterized and first results (using the same gas standard as for the Ionicon PTR8000) suggest that different monoterpenes fragment differently on several masses in the VOCUS instrument, which impedes calibration of the monoterpene data based on the alpha-pinene standard.

170 and 290: the authors mention that sesquiterpenes were measured but no data/plot have been provided. If available, please provide these data in Figure 3 or in SI. Were sesquiterpenes monitored during previous campaign using GC techniques? Even though sesquiterpenes mixing ratios are expected to be very low, they are suspected to significantly contribute to NO_3 fate due their high reactivity. More information about the role of sesquiterpenes on NO_3 loss would be useful.
The sesquiterpene data is already provided in the SI in Fig. S4b. We now explicitly refer to it in L176:
In order to extend data availability, the VOCUS data for isoprene, monoterpenes and sesquiterpenes was scaled to that of the PTR8000 data set (which suffered from less

fragmentation, thus associated with less uncertainty) applying constant factors during the common time period (see Fig. S4b in the Supplement).

Unfortunately, no speciated measurements of sesquiterpenes on the KF are available, which is why we used the rate coefficient of beta-caryophyllene to account for their contribution to NO_3 losses:

To calculate NO_3 loss rates resulting from its reaction with sesquiterpenes, we used the IUPAC-recommended rate coefficient for NO_3 + β-caryophyllene since this was the compound used to calibrate the PTR8000. Speciated sesquiterpene measurements on the KF are not available.

The authors do not consider the role of RO_2 radicals in the NO_3 Do they consider that it is negligible? Previous field studies (e.g. Sommariva et al, 2007) suggest that reactivity with RO_2 radicals is not negligible even though RO_2 concentrations are very low. This point should be discussed and arguments should be provided for not considering these reactions.

A maximum RO_x mixing ratio of 20 pptv has been reported on the KF (Handisides, 2001), which would correspond to an NO_3 loss rate of 0.001 s^{-1}, which is insignificant compared to other losses. We now mention this in L317:

Losses due to reaction with RO_2 radicals on this site are expected to be insignificant. Taking the average maximum RO_x mixing ratio of 20 pptv as measured by (Handisides, 2001) and the corresponding rate coefficient (IUPAC, 2022) results in an NO_3 loss rate of 0.001 s^{-1}, which is insignificant compared to the other loss rates mentioned above.

324: the authors cannot conclude that NO_3 significantly contributes to the BVOC oxidation during the daytime just because the reactions with BVOCs have been shown to significantly contribute to the NO_3 total reactivity. To state that, the BVOCs lifetimes due to NO_3 oxidation should be compared to those estimated for OH chemistry (using typical OH concentrations).

We did, in fact, NOT state that NO_3 contributes significantly to BVOC oxidation during the day. We wrote *"This underlines that NO_3, often considered to be important only at night, also contributes to the oxidation of BVOC during the day and thus potentially to the formation of organic nitrates (in competition to OH- and O3-initiated oxidation) throughout the diel cycle…"* , which is certainly true. However, as the referee has raised this point, we now present a simple calculation to roughly indicate the contribution of NO_3 to the daytime loss of a specific BVOC:

Assuming noon mixing ratios of 0.1 pptv NO_3 (see Fig. 9 below), 42 ppbv O_3 (see Fig. 3) and 10^6 molecules cm^{-3} OH (Lelieveld et al., 2016) and taking evaluated rate coefficients (IUPAC, 2022) the loss-rate constant of limonene towards these three oxidants would be 2.71 x 10^{-5} s^{-1}, 2.08 x 10^{-4} s^{-1} and 1.65 x 10^{-4} s^{-1}. NO_3 would thus contribute ca. 7 % to the noon-time oxidation of limonene.

340-387: A very detailed discussion on the NOx budget is provided but does not seems to be fully relevant here, in my opinion. It's not clear for me what the authors want to demonstrate here. As a minimum, this should be provided with a clearer objective and in a dedicated section. It has nothing to do in the section "fractional contribution of VOCs to NO_3 losses".

NO mixing ratios of several tens of pptv represent a significant loss for NO_3 and thus deserve close scrutiny. The presence of both NO and O_3 implies a significant NO_2 source, which was not reflected in the measured NO_2 mixing ratios, implying additional NO_2 losses. We now start a separate section and add an introductory sentence to point this out:

3.5 Effect of nighttime NO on NO_x budget

Figure 8 reveals a large night-to-night variability in the NO mixing ratio with minimum values close to the detection limit and maxima > 80 pptv in the presence of several tens of ppbv of O_3.

The presence of NO and O_3 at the mixing ratios observed implies a significant source of NO_2. In the following, we derive the NO emission and NO_2 deposition rates required to explain the observed NO, NO_2 and O_3 mixing ratios.

References

Handisides, G. M.: The influence of peroxy radicals on ozone production, PhD thesis, Fachbereich Geowissenschaften, Johann Wolfgang Goethe Universität, Frankfurt am Main, 2001.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation, edited by: 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., available at: http://iupac.pole-ether.fr/index.html, last access: 24 April 2022.

Lelieveld, J., Gromov, S., Pozzer, A., and Taraborrelli, D.: Global tropospheric hydroxyl distribution, budget and reactivity, Atmos. Chem. Phys., 16, 12477-12493, 2016.