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.

General Comments:

This concise and clear paper reports on measurements of alkyl nitrates in the boreal forest, with coincident measurements of organic trace gases enabling an assessment of the relative source strength of OH, NO3, and O3 oxidation in producing these alkyl nitrates. In this NO_X-limited environment, NO3 oxidation is found to be the dominant source of alkyl nitrates both night and day. The paper is clearly written and the figures are helpful. I suggest addition of a bit more auxiliary data to enable readers to better interpret the conclusions.

We thank the referee for this positive assessment of our manuscript.

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1) As I read this paper and sought to understand the key observations, I found myself wondering about the [NO] and relative concentrations of different organic trace gases. These data are perhaps in other papers cited, but for convenience of the reader I urge the authors to include this data here. I suggest to include an NO trace in the top panel of Figure 2, and add a panel to that figure showing BVOC timeseries, perhaps split out by isoprene and summed terpenes since they likely have different diel patterns, and since their relative reactivities is different and can help the reader interpret the day/night observations.

We have followed these suggestions and added mixing ratios of NO and the terpenoids to the plot.

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2) For similar reasons, it would be helpful to add another panel to the diel average figure 4, showing NO2 and BVOC traces. In particular, I was curious why the NO3-initiated production of ANs would peak at 19:00 local time and then decrease? Given your statement that monoterpene concentrations build up overnight, I might have expected this to continue increasing. Is it that the NO2 is fully consumed by then?

We have added the requested plots (Fig 4b). The reason for the reduction in the ANs production rate after 20:00 is lower NO_2 and O_3 mixing ratios. We have added text to explain this:

The peak in the night-time production rate of ANs at 19:00 coincides with large O_3 and NO_2 mixing ratios (Fig 4b), the reduction of both between ~ 20:00 and mid-night (UTC) resulting in the decrease in $\sum P_{ANs}^{NO_3}$ during the night, though changes in relative concenrations of the terpenes may also play a role.

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3) I agree with Jacqui, Figure 5 is not necessary.

Figure 5 summarises (perhaps better than words can) one of the major findings of this study, that NO_3 reactivity in this region/season is so high that it contributes to ANs production not only at night-time, but also during the day. The plot does not take up much space we would prefer to keep it as Figure and graphical abstract.

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4) Abstract line 22: “strongly controlled by biogenic emissions” – ? seems inconsistent with your discussion in the manuscript body. There, you describe this as due to rapid deposition to particles?

We have re-worded this part of the abstract.

The lifetimes of the gas-phase ANs formed in this environment were of the order of 2 hours due to efficient uptake to aerosol (and dry-deposition), resulting in the transfer of reactive nitrogen from anthropogenic sources to the forest ecosystem.

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5) Around p. 3 line 23-24: Could you list the dominant terpenes here? (and / or, on p. 5 around line 13 where you state that only a handful contributed significantly to reactivity – include a brief ranked list?) Also, what anthropogenic emissions are observed from the cities & sawmill – just NOx, or NOx and SO2?

In response to a suggestion of Referee #1, we have added the following text:

A large selection of VOCs was measured (a listing is given in the caption to Figure S2 of the supplementary information) but the 5 biogenic VOCs listed (α-pinene, β-pinene, carene, limonene, isoprene) accounted for > 98 % of the attributed NO_3 reactivity.

From the sawmill we saw an increase in BVOCs. From the cities an increase in NO_X (not SO_2). This is now mentioned:

Anthropogenic emissions from two larger cities (Tampere and Jyväskylä) and a local sawmill occasionally impacted the site, the former resulting in an increase in NO_X levels, the latter in BVOCs.

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6) On p. 8 around line 18: say something about why the NO3 initiated formation of ANs peaks at 19:00

See comment 2. We have added a Fig. 4b and the following text:

The peak in the night-time production rate of ANs at 19:00 coincides with large O_3 and NO_2 mixing ratios (Fig 4b), the reduction of both O_3 and NO_2 between ~ 20:00 and mid-night (UTC) resulting in the decrease in $\sum \mathrm{P}_{\mathrm{ANs}}^{\mathrm{NO_3}}$ during the night, though changes in relative concenrations of the terpenes may also play a role.

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7) On Figure 6, the error bars on the bottom panel look very large compared to the reported slope uncertainty of +/- 0.5 hr. Please explain how this error bar is determined – it looks to me like the slope could even be negative within the uncertainties.

The uncertainty was calculated in a weighted linear fit considering errors in the y-axis data only. The quoted uncertainty was correct.

However, we have now reconstructed Fig. 6 with x-axis errors and carried out a York fit to the data (errors in both x- and y-axes considered). The slope is now quoted as 2 ± 3 h. The new lifetime is listed in the Figure caption and in the text.

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8) Figure 7 makes me wonder whether it's possible that different sensitivities of I- CIMs to daytime vs. night-time BVOC mixes could explain the different amplitude of the diel cycle. Can you add anything additional information on this?

As we already write, neither the absolute nor the relative sensitivity (between different alkyl-nitrates) is known and we cannot examine this aspect in detail. However, we have added a sentence to indicate that this may contribute to the disparate profiles in Fig. 7:

In addition, we cannot rule out that this difference is due to different HR-L-ToF-CIMS sensitivity to day- and night-time ANs.

Technical corrections/suggestions:

p. 2 line 21: "OH radicals are largely absent"

We now write: At night-time, OH radical concentrations are very low

line 27: "Reaction 6a is a composite". Correction made.

p. 3 line 10: suggest to add reference to Ayres 2015 (https://www.atmos-chemphys.net/15/13377/2015/): this NO3 + BVOC dominance during the day was also observed at SOAS 2013. Reference added.

p. 3 line 30 "reached 100% during many nights" end. Correction made.

p. 3 / top of p. 4: Is 300 pptv the average NOx level for the whole campaign? Maybe also mention the [NOx] during the events where air masses arrive from the industrial sources.

We now write: The NO_x levels during the entire campaign were low (mean value of 320 pptv) with occasional increases (up to 1.4 ppbv) when the site experienced air masses with trajectories that passed over urban centres.

p. 4 line 4 "photolysis frequency, and the" Correction made.

line 21: remove extra ")" Correction made.

lines 25-26: "OH concentrations have an associated uncertainty of ~ 50%" Correction made.

line 33: add citation for I- CIMS high sensitivity to nitrates. Citation (Lee et al, 2016) added.

p. 5 Eq. 2: It's a little confusing that you use the average alpha in the equation but then talk about the individual ones first below the equation, and then define the average in Eq 3 below. Maybe combine Eq. 3 into 2 so you see the average and the summation simultaneously? Also, after the current Eq. 3, define the Ci term.

We have reorganized this and now write:

where $\overline{\alpha}^{NO_3}$ is an average AN-yield. Assuming that all the VOCs responsible for loss of NO_3 were identified and quantified the average yield can be derived (Eq. 3) from VOC- specific values of $\alpha_i^{NO_3}$ weighted by their relative contribution to $k_{OTG}^{NO_3}$.

$$\overline{\alpha}^{NO_3} = \frac{\sum \alpha_i^{NO_3} k_i^{NO_3} [C_i]}{k_{OTG}^{NO_3}} \qquad (3)$$

where $[C_i]$ is the concentration of the specific VOC.

Eqn 4: k3 should be k5? Correction made.

Line 24 “total measured reactivity”. Correction made.

p. 6 Eqn R12: meaning of the “delta” term is unclear. Δ has been replaced with the word isomerization.

line 27: “UTC). In order to account for this competition with HO2 reactions, equation (7) can be modified to:” Correction made.

p. 7 line 3: “the local sawmill, likely due to elevated reactivity with ….?” We now write: was associated with large BVOC mixing ratios in air masses originating from the local sawmill.

Line 4-5: This sentence sounds like you’re drawing a contrast to NO3, but I think this is true in that case as well. Perhaps make this sentence the first sentence of the next paragraph instead? Text re-organised

Line 11: “We show below that even if unattributed OH-reactivity reaches 50%, this would not significantly” Text changed as suggested.

Line 13: insert space “from [Ci]” Correction made.

Line 20: “Similarly as for OH-reactions,” We write: Similar to OH reactions.

p. 8 line 2: “was estimated to be ~ 60%” Correction made.

line 24: “ANs production rate occurs exclusively via NO3-initiated reactions.” Correction made.

p. 9 line 1 “which was 570 m” Correction made.

line 2: omit extra “)” Correction made.

line 7: “which is not the case (Eerdekens” Correction made.

line 20: “overall uncertainty represented by error bars, there” Correction made.

line 27: “well-mixed daytime boundary” Correction made.

line 28: include units on Vdep (here and in the line below “Vdep ~ 2”) Units included.

line 32: “can be assessed” Correction made.

p. 10 line 3: “For typical alkyl nitrate” Correction made line 18 & below: Shouldn’t the CIMS be designated the “I - CIMS” and not “I-CIMS”? We now name it the HR-L-ToF-CIMS as in section 2

p. 11 top 2 lines: C9 shows up in two categories ? Corrected, C9 now appears only once