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.

General Comments:

This manuscript uses measurements from a boreal forest to compare the relative importance of alkyl nitrate formation via NO_3, O_3, and OH oxidation pathways during both day and night. They find, somewhat surprisingly, that NO_3 oxidation of BVOCs accounts for up to half the daytime production of alkyl nitrates, and that there are approximately equal rates of alkyl nitrate production during day and during night. Additionally, the authors calculate a relatively short steady-state alkyl nitrate lifetime of 2 hours, implying that heterogeneous hydrolysis is likely an important loss process in this environment. These are interesting results on the fractional contribution of different oxidation pathways to alkyl nitrate production and on the lifetime of alkyl nitrates in a boreal forest. The paper is well organized and does a nice job accounting for the uncertainties in various calculations. I recommend publication. Some questions and comments to improve the manuscript can be found below.

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

Major comments:

1. Some parts of the manuscript would benefit from being more quantitative. For example, on page 5, line 14 (and similarly on page 7, line 1), the authors state that "only the handful of biogenic VOCs listed contributed significantly." More quantification (i.e., biogenic VOCs contributed to >x% of the observed reactivity) would be helpful.

We now write:

(P5L14) 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.

(P7L1) The total OH-reactivity (k_{OTG}^{OH}) was calculated using the measured concentrations of monoterpenes and isoprene as other VOCs (e.g. aldehydes, acids, alkanes, alkenes) contributed less than 6% (Fig S2).

Additionally, (page 10, line 6), please be quantitative and specify the aerosol surface area measured, instead of discussing it in purely relative terms.

Done: (see also comment below about the uptake coefficient)

The aerosol surface area is NO_3 plotted in (additional) Fig. S3 of the supplementary information.

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2. It would be helpful if the authors were able to observationally constrain some of the numbers they estimate in the manuscript. For example, on page 5, line 26 the authors assign an alkyl nitrate yield of 0.7 to unattributed VOCs because they suspect the missing reactivity is from highly reactive BVOCs with high yields. Could this number be observationally constrained using the quantified missing reactivity and the ANs production rate?

The uncertainty associated with the calculation of the ANs production rate (see sections 3.1, 3.2 and 3.3) are large (65% for NO_3, 70% for OH and 60% from O_3) and can therefore not be usefully applied to constrain e.g. the yield of ANs from unattributed reactivity of NO_3.

Likewise, is it possible to get an observational constraint on the alkyl nitrate deposition velocity (page 9, line 29)?

We cannot constrain the deposition velocity as the loss of ANs is (likely) due to a combination of deposition and particle uptake / hydrolysis. However, considered individually we can place an upper limit: We now write:

Taking a value of $V_{dep} \sim$ 1-2 cm s^{-1} for ANs (Farmer and Cohen, 2008; Nguyen et al., 2015) and an average, noon-time boundary layer height of 570 m, we derive an average lifetime w.r.t. deposition of 8-16 hours, substantially longer than that observed. Conversely, a deposition velocity of $\sim$ 8 cm s^{-1} would result in a lifetime of ~2 hours, consistent with our observations.

Or at least compare the HNO3 production implied by the estimated hydrolysis rates to observed increases in aerosol inorganic nitrate?

The short lifetime of the ANs indicates that a large fraction is transferred to the particle phase, the rest being lost by deposition. As the referee correctly infers, this must result in an increase in particulate nitrate either as organic nitrate or, after hydrolysis, as HNO_3. Aerosol composition measurements (AMS) were available for the campaign, though the instrument was operational only for about 10 days altogether between the 5th and 22nd of Sept. We have correlated the AMS-nitrate measurement to the total production rate and added a Figure (new Fig. 7) and text to describe the results.

If, as suggested, the gas-phase organic nitrates formed via the three pathways above are indeed transferred to the aerosol-phase on short times-scales we would expect to find some correlation between the total production rate and aerosol nitrate content, either as organic nitrate or, following hydrolysis, HNO_3. AMS measurements of aerosol composition were available for a ~10-day period during the campaign, and we show a plot of AMS-nitrate versus the total ANs production rate in Figure 7. The AMS-nitrate mass loading (μg m^{-3}) was converted to a mixing ratio using a mass of 63 amu (i.e. assuming HNO_3).

The Figure illustrates that the highest nitrate aerosol content is correlated with high AN production rates, with the ~zero intercept indicating that the formation of particulate nitrate independent of ANs formation is

negligible. As the formation of ANs requires NO_X, this is not surprising as in the absence of NO_X, particulate nitrate formation would also tend to zero. However, a plot of AMS-nitrate versus NO_X over the same period (Fig S4 of the supporting information) is more scattered, supporting the contention that the combination of BVOC oxidation in the presence of NO_X (i.e. ANs formation) is a major source of aerosol nitrate in this environment.

By taking up ANs, particles effectively integrate the ANs production term over time and the slopes of the solid lines in Fig. 7 represent integration times of 2.8 h (upper bound) and 0.5 h (lower bound) factored by the efficiency of uptake. The latter may be related to several factors that control the transfer of gas-phase ANs to the particle phase, including relative humidity, temperature, available aerosol surface area, release of HNO_3 back to the gas-phase and (competitively) dry-deposition. Colour-coding the data in Fig. 7 for various parameters (temperature, relative humidity, aerosol surface area or other particle properties (ammonium, sulphate, organic mass) revealed that that the larger slopes are associated with higher organic content (Fig. S4), which in turn is expected to be associated with more aged aerosol. No trend was found in parameters such as temperature and relative humidity, suggesting that their influence on the transfer of ANs to the particle phase is weak. We cannot explore the role of dry-deposition of ANs in detail, but suggest that this is unlikely to vary sufficiently to induce the observed variation in the slopes observed in Fig. 7. If we assume 100 % transfer of ANs to the particle phase, the integration time (upper bound to the data in Fig. 7) represents a maximum lifetime (with respect to deposition) of 2.8 hrs for the aerosol.

And lastly (page 10), can you use the aerosol surface area that was measured to estimate an aerosol uptake efficiency for alkyl nitrates, rather than simply saying the "efficiency could be >0.1"?

We have made this calculation and added an extra figure (aerosol surface area) to the supplementary information. We now write.

Where γ is the uptake coefficient, A the aerosol surface area density (in $cm^2\ cm^{-3}$), $\bar{c}$ the average thermal velocity (in $cm\ s^{-1}$). The mean aerosol surface area observed during IBAIRN was $2 \times 10^{-7}\ cm^2\ cm^{-3}$ (range $0.4 - 6 \times 10^{-7}\ cm^2\ cm^{-3}$, see Fig. S3 of the supplementary information). For a C10 alkyl nitrate derived from monoterpene oxidation such as $C_{10}H_{14}NO_7$, (Yan et al., 2016; Lee et al., 2018) $\bar{c}$ ~15000 $cm\ s^{-1}$ at 290 K. The average uptake coefficient required to reproduce a loss rate constant for ANs of $5.6 \times 10^{-4}\ s^{-1}$ would then be 0.8, which is orders of magnitude larger than values of 10^{-3}-10^{-4} reported for water soluble organics (Wu et al., 2015; Crowley et al., 2018). However, the high molecular weight, biogenically derived ANs in the boreal forest have low vapour pressures and transfer via condensation to existing particles is likely to be important. In this case transfer to the particle phase may be controlled by diffusion and accommodation and the effective uptake efficiency could be much larger.

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3. I am curious how much the seasonal changes over the course of the IBAIRN study affected the various production and loss processes for alkyl nitrates. Do averages from the first half of the study (summer) and the second half of the study (autumn) give significantly different results, or are there minimal differences?

Within the measurement uncertainty, there is no observable trend in the ANs production (or concentration) when comparing the first and seconds halves of the campaign. Short term variations in temperatures, insolation etc. are too large (conversely, the campaign was too short). We write:

We found no significant change in the production rate of ANs in transition from summer to autumn, though the short duration of the campaign and variability in temperature and insolation would mask such effects.

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4. Is it possible to connect the individual alkyl nitrates observed by CIMS to the production rates of alkyl nitrates calculated from individual VOCs? Could this give any indication as to which VOCs contribute to the missing reactivity?

This is a good idea, but unfortunately, in this case, not feasible. As we state in the text, the I-CIMS data are only used in a qualitative sense owing to the different inlet positions and heights (and diel profiles) when compared to e.g. the ΣANs or NO_3-reactivity measurements, and are not suitable for investigation of the individual contributions of single BVOC to AN formation.

Minor comments:

1. Page 2, line 12: Why is reaction with O_3 only relevant in the boreal forest?

We did not seek to imply this and have made the text more general:

The reaction with O_3 represents an additional sink for biogenic VOCs (BVOCs) (Peräkylä et al., 2014; Yan et al., 2016) which, in the presence of NO, can also lead to the formation of alkyl nitrates.

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2. Page 2, line 30: Clarify to say "… the branching ratio to AN formation via NO3 oxidation is generally…"

Correction made. We now write:

"The branching ratio to AN formation via NO_3 oxidation is generally much larger than that for organic peroxy radicals reacting with NO…."

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3. Equation 4: Typo–should include k5 rather than k3.

Correction made

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4. Page 6: Should RO2 loss via reaction with NO2 to form PANs also be accounted for? Or is it insignificant?

Only a small fraction of the total RO_2 (i.e. α-carbonyls) are capable of forming a stable PAN, other RO_2 + NO_2 interactions are reversible on time scales of minutes and therefore not considered. We now write:

The RO$_2$ formed in (R1) and (R4a) do not form stable peroxy-nitrates in their reaction with NO$_2$, so this RO$_2$ loss process can be safely neglected.

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5. Page 8, line 8: Clarify to say that the ANs production from ozonolysis has a daytime minimum at noon (since the absolute minimum is really at night).

Corrected. We now write:

The rate of production of ANs from ozonolysis of BVOC has a daytime minimum at noon, with maximum values observed in the late afternoon.

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6. Figures 2 and 3: x-axis labels are confusing.

X-axes given as dd/mm

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7. Page 9, line 15: I think your estimate uses the "steady-state" approximation rather than the "stationary-state" approximation.

Correction made.

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8. Figure 6: Please define what your error bars are (standard deviation?). Additionally, the ends of some of the error bars are not visible in the plot. Is the fit you are doing to all points or only the average points that are plotted? What kind of fit are you using (OLS, RMA, York?)?

We have redrawn this Figure and added x-axis errors. We have used a York-type fit and now write:

Within the overall uncertainty represented by the error-bars, there is no significant difference between the day- and night-time data, with a linear fit through all the data indicating a lifetime of $\approx 2 \pm 3$ hours.

The caption mentions the fit-type:

The slope of the linear fit to the data (York-fit, errors in both axes considered, black line) indicates a lifetime of 2 ± 3 h.

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9. Page 9, line 25: Some alkyl nitrates (e.g., isoprene hydroxy nitrate) can be oxidized by OH with reasonable efficiency, and highly oxidized or carbonyl nitrates can be rapidly photolysed (see Muller et al., 2014 and Xiong et al., 2016). Are these not relevant during IBAIRN?

The studies mentioned deal with isoprene derived ANs, which were not important for IBAIRN. We clarify this by writing:

ANs are generally thought to react inefficiently with O$_3$, OH and NO$_3$ and low rates of photolysis mean that their lifetimes are likely to be controlled largely by dry deposition and / or heterogeneous hydrolysis on aerosol or hydrometeors (Browne et al., 2013). Known exceptions are some ANs formed from isoprene, which can react with OH and/or be photolysed with lifetimes on the order of an hour (Muller et al., 2014;

Xiong et al., 2016). During IBAIRN, isoprene derived ANs were however only a small fraction of the total and, in the absence of kinetic / photochemical data for terpenes, we disregard gas-phase, chemical loss processes.

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10. Page 9, line 32: Should be "assessed" instead of "accessed."

Correction made.

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11. Page 10, line 3: Was the calculation of average thermal velocity done at STP or at the average temperature and pressure during the campaign? Please specify.

We have amended the text and now write:

For a C10 alkyl nitrate derived from monoterpene oxidation such as $C_{10}H_{14}NO_7$, (Yan et al., 2016; Lee et al., 2018) $\bar{c}$ ~15000 cm s^{-1} at 290 K.

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12. Page 10, line 11: Consider citing Romer et al., 2016 and Zare et al., 2018 which also discuss ANs lifetimes and heterogeneous hydrolysis as a loss pathway for ANs.

Citations included.

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13. A separate conclusion section would be helpful to the reader (i.e. add a section header before the last two paragraphs).

We have added a section header "conclusions" and reorganized the text somewhat.

4 Conclusions

During the IBAIRN campaign in the boreal forest in southern Finland (5th-22nd Sept, 2016), alkyl nitrate formation was dominated by the reaction of NO_3 radicals with monoterpenes, both during the day- and night-time, with smaller contributions from both OH and O_3 initiated oxidation of BVOCs. This result highlights the important role of daytime NO_3 chemistry (with respect to organic nitrate formation) in this environment. The short, average lifetime of $\approx$ 2 h for the total alkyl-nitrates (ΣANs) indicates efficient uptake to existing particles and/or deposition.

These observations, of efficient daytime production of gas-phase ANs from NO_3 chemistry and short night-time lifetimes are entirely consistent with the results from recent studies at the IBAIRN site by Lee et al. (2018) who found that organic nitrates previously designated as resulting from night-time processing of BVOCS (Yan et al., 2016) were also present during daytime. In addition, they found relatively few organics with "night-time" character in the gas-phase compared to the aerosol-phase, indicating efficient transfer of gas-phase organic nitrates to the particle-phase at night-time, likely aided by low temperatures and high relative humidity. We found no significant change in the production rate of ANs in transition from summer

to autumn, though the short duration of the campaign and variability in temperature and insolation would mask such effects.