

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 statement:

This paper presents two summer field campaigns (2011 and 2015) of organic nitrate data at an urban influenced mountain site, focusing on measurements of alkyl nitrate formation and implications for production of ozone, and measurements of peroxy nitrates, both using a thermal dissociation – cavity ringdown instrument, which detects these species via thermal dissociation and then detection of NO₂. Reference is made to an earlier instrument paper for the measurement methodology and data corrections to account for some known interferences, the focus in this paper is in interpreting the field observations, including comparing across two years with different meteorological conditions.

This paper presents a novel combined dataset that will be of interest to the atmospheric chemistry community. I do see a few opportunities to extend the analysis and to compare to additional available measurements, which I mention below, and recommend publication after these revisions.

We thank the referee for this informed and thorough review and overall positive assessment of our manuscript. The manuscript has been improved in line with the comments listed below.

Major suggestions:

1) There are a few additional studies that I would suggest citing to inform your analysis, and to enable comparisons with your data:

- Kiendler -Scharr et al (2016) have just published a series of measurements of aerosol-phase RONO₂ around Europe using AMS, and they comment on the ubiquity of NO₃ sourced nitrates – this would be a good point of comparison. (“Organic nitrates from night-time chemistry are ubiquitous in the European submicron aerosol,” Geophys Res Lett, 10.1002/2016GL069239, 2016.)

This very recent paper is now also cited in the context of loss of ANs to the particle-phase: “It is well established in chamber studies that the NO₃ induced oxidation of biogenics leads to highly functionalized ANs that partition largely to the aerosol phase and that the NO₃ oxidation of biogenic VOCs can lead to appreciable organo-nitrate content in atmospheric particulate matter (Fry et al., 2011; Fry et al., 2014; Boyd et al., 2015). Ambient measurements of aerosol composition show that nighttime-generated organic nitrates formed in NO₃ + BVOC reactions are efficiently transferred to the condensed phase (Rollins et al., 2012; Fry et al., 2013; Xu et al., 2015; Kiendler-Scharr et al., 2016), which is confirmed by modelled vapour pressures of the OH- and NO₃- initiated organic nitrate products from BVOC oxidation, the latter being substantially lower (Fry et al., 2013).”

- Fry et al. (2013) measured ΣPNs and ΣANs at an urban-influenced Colorado site, also in summertime, including doing the same O₃/ ANs slope analysis to assess nitrate branching and relevance to O₃ formation. Compare yield and VOC mix? (“Observations of gas-and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011,” Atmos. Chem. Phys., 13, 8585-8605, 2013.)

We have added text describing the results and conclusions of this paper in different places. “Likewise, neglecting terms for entrainment and loss of ANs and O₃ will introduce a variable bias into calculations of $\alpha(OH)_{av}^{\Sigma ANs}$. The loss of multifunctional ANs from terpene oxidation will bias the analysis to low values of $\alpha(NO_3)$ (Fry et al., 2013). In the absence of information regarding the condensation rate or efficiency of deposition of a mixture of multi-functional nitrates or O₃ to the topographically complex terrain at the Taunus Observatory a more detailed analysis is not warranted. The analysis does however make comparison with similar analyses for ΣANs measurements possible, and our derived values of $\alpha(OH)_{av}^{\Sigma ANs}$ are consistent with those summarised by Perring et al (Perring et al., 2013) obtained both by observation of ΣANs ($7.1\% > \alpha(OH)_{av}^{\Sigma ANs} > 0.8\%$) and calculated from VOC measurements ($10.6\% > \alpha(OH)_{av}^{VOCi} > 0.1\%$) in various rural and urban locations. A similar analysis by Fry et al. (2013) of ΣAN and O₃ mixing ratios obtained during summer at a forest site with urban influence resulted in a value of $\alpha(OH)_{av}^{\Sigma ANs} = 2.9\%$, intermediate between the value presented here for the PARADE and NOTOMO campaigns.”

“Ambient measurements of aerosol composition show that nighttime-generated organic nitrates formed in NO₃ + BVOC reactions are efficiently transferred to the condensed phase (Rollins et al., 2012; Fry et al., 2013; Xu et al., 2015; Kiendler-Scharr et al., 2016), which is confirmed by modelled vapour pressures of the OH- and NO₃- initiated organic nitrate products from BVOC oxidation, the latter being substantially lower (Fry et al., 2013).”

“(Fry et al., 2013) have shown that, at an urban / forested site in Colorado, the peak in particle phase organic nitrates occurs at night-time.”

- The Ng et al. 2016 review paper that you cite discussed some observations and general trends about organonitrate losses, including hydrolysis that would be valuable to consider in the context of your claims that nighttime nitrates may be lost more rapidly under damp and foggy conditions during NOTOMO, in contrast to the first year. There are several primary papers cited in Ng that might be relevant here, for example Boyd et al 2015 (“Secondary organic aerosol formation from the β -pinene+NO₃ system: effect of humidity and peroxy radical fate,” Atmos. Chem. Phys., 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.) –but in general I think the conclusions here would be at odds with your observations: nighttime NO₃ +terpene produced organonitrates are expected to be mostly primary and secondary nitrates, which appear to have longer lifetimes, not shorter, than daytime produced OH-initiated nitrates (which would include more tertiary nitrates).

To improve the discussion of the day-time versus night-time concentrations and losses of ANs we have adjusted the emphasis from hydrolysis (and its influence on deposition) to partitioning between the gas and aerosol phase. The section has been re-written: “Although we calculate similar production rates of ΣANs during the night when NO₃ is present, the daytime maximum in the ΣANs mixing ratio is significantly larger, which has a number of likely causes. The first is related to missing OH reactivity, which, depending on the hydrocarbons involved, could potentially increase the OH-initiated rate of formation of ΣANs yield by large factors. For example, if the hydrocarbons we measured would account for only 50 % of the OH reactivity and the missing ones were biogenic in nature (i.e. terpenoids with large AN-yields) we could expect more than a factor of two increase in calculated $P(\Sigma ANs)_{day}$. A further potential cause for larger daytime ΣANs mixing ratios is a reduced loss of daytime ΣANs with respect to chemical and depositional loss and condensation. This being a consequence of the different chemical composition and volatility of the ANs generated from

NO_3^- compared to OH-initiated oxidation. It is well established in chamber studies that the NO_3 induced oxidation of biogenics leads to highly functionalized ANs that partition largely to the aerosol phase and that the NO_3 oxidation of biogenic VOCs can lead to appreciable organo-nitrate content in atmospheric particulate matter (Fry et al., 2011; Fry et al., 2014; Boyd et al., 2015). Ambient measurements of aerosol composition show that nighttime-generated organic nitrates formed in $\text{NO}_3 + \text{BVOC}$ reactions are efficiently transferred to the condensed phase (Rollins et al., 2012; Fry et al., 2013; Xu et al., 2015; Kiendler-Scharr et al., 2016), which is confirmed by modelled vapour pressures of the OH- and NO_3^- initiated organic nitrate products from BVOC oxidation, the latter being substantially lower (Fry et al., 2013).

Table 3 shows that (of the BVOCs measured) limonene accounts for 40 % of the NO_3 loss rate, myrcene 30% and α -pinene 29 %. Studies of the reaction between α -pinene and NO_3 show that the yield of secondary organic aerosol (SOA) is less than 10 % (Hallquist et al., 1999; Perraud et al., 2010; Fry et al., 2014; Nah et al., 2016) with reports of the alkyl nitrates formed being exclusively in the gas-phase (Fry et al., 2014). This contrasts strongly with the situation for limonene, where SOA yields of up to ≈ 60 % have been reported, with more than 80 % of the alkyl nitrates formed being in the aerosol phase. There is no experimental data on SOA yields in the reaction between NO_3 and myrcene nor on the gas-aerosol partitioning of the alkyl-nitrates formed. Recent experiments on β -pinene (Boyd et al., 2015) have shown that the SOA yield is neither strongly dependent on the relative concentrations of HOx and NOx, which determines the nature of the end-products formed, nor on the relative humidity or seed-aerosol used. If we make the broad assumptions that 1) the SOA yield from myrcene is the same as limonene and 2) that the fraction of ANs in the condensed phase is comparable to those found for limonene, we calculate that > 60 % of the alkyl nitrates formed at night at this site will be present in the aerosol phase and thus not detected by our instrument. In other words we would expect equation (3) to yield production rates of ΣANs that exceed those derived from gas-phase ΣAN measurements by a factor between two and three.

We conclude that the apparent lower lifetime of night-time generated ΣANs is thus likely to be the result of an increased fraction of low-volatility ANs formed from terpenes initially reacting with NO_3 compared to OH-initiated oxidation, leading to a larger relative rate of SOA formation and partitioning of ANs to the condensed phase. (Fry et al., 2013) have shown that, at an urban / forested site in Colorado, the peak in particle phase organic nitrates occurs at night-time. The condensed phase ANs can undergo hydrolysis to HNO_3 (over a period few hours (Lee et al., 2016b)), and thus irreversible loss from the gas-phase, the latter enhanced by the lower temperatures and higher relative humidities encountered at night-time (Hallquist et al., 2009; Lee et al., 2016a)."

2) In my view, the weakest point in the paper is the explanation of the difference in PAN/AN ratio and apparent O_3 AN branching ratio across the two years. It would be great to find more evidence to support and interpret this difference.

We have extended the discussion on this. In response to the comments below and those of reviewer 1, we have added a new section and now write:

4.5.1 Inter-annual / seasonal differences in $\alpha(\text{OH})$, PARADE versus NOTOMO

The difference in $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ between the July-2011 PARADE campaign ($7.2 \pm 0.5 \%$) and the Aug-Sept. 2015 NOTOMO campaign ($< 2 \%$) is significant and cannot be explained by the uncertainty in the measurements of $[\text{O}_3]$ or $[\Sigma\text{ANs}]$ (see section (3.1)).

There are a number of potential causes for the apparent difference in $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ between the two campaigns. We first consider the validity of the assumption (Eq. 6) that losses and/or entrainment of ANs and O_3 can be neglected. Xiong et al. (2015) have shown that losses of isoprene derived nitrates (IN) due to reaction with OH (Lee et al., 2014) and photolysis can be rapid and start to deplete IN before photochemical production maximises at the peak of the daytime OH-profile. They also indicate that early morning entrainment of IN from the residual layer (where pre-dawn AN mixing ratios may be a factor of 10 larger) can influence its diel profile. Along with photochemical degradation, dry deposition / hydrolysis can contribute to the alkyl nitrate sink, especially for those derived from biogenic VOCs (Jacobs et al., 2014; Rindelaub et al., 2015). Xiong et al. (2015), report efficient wet and dry deposition of nitrates derived from isoprene with significantly lower mixing ratios measured in conditions of reduced photochemical reactivity / rain. The restriction of the analysis period to close to the maximum of the OH profile should reduce a bias introduced by the assumptions inherent to Eq. 6, but clearly will not remove them totally. As the lifetime with respect to chemical loss/ deposition of alkyl nitrates derived from biogenic VOCs is expected to be shorter than that of O_3 , the sampling of progressively aged air masses will bias $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ to low values when calculated from $\text{O}_3 / \Sigma\text{AN}$ correlations. A low value of $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ during NOTOMO could conceivably be the result of sampling on average older air masses than during PARADE. The lower NO_x levels in NOTOMO would support this contention, though in the absence of NO_y measurements, is not conclusive.

A further, related explanation for low values of $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ during NOTOMO is that the average lifetime of ΣANs was shorter than during PARADE, due e.g. to chemically distinct ANs being generated, this resulting from a different hydrocarbon mix present during the campaigns. As no BVOC measurements were taken during NOTOMO we can only speculate on potential reasons for this. We first note that the campaigns were in different seasons and propose that the mountainside vegetation was in different (seasonal) growth phases as NOTOMO (2015) took place during July, and was characterised by recurrent damp and foggy conditions whereas the PARADE campaign (2011) took place later in the year (mid-August to mid-September) during the transition from summer to autumn. The plant-physiology controlled BVOC emissions depend not only on the temperature and insolation during the two campaigns, which were comparable, but also on the weather (temperature, rainfall etc.) during the preceding months, which displays a large inter-annual variability at this mountain site. For example, a switch from α -pinene dominant to β -pinene or limonene dominant emissions could influence not only the ΣANs production rate (there is considerable uncertainty associated with the AN yields, see above) but also the degree to which the ANs are transferred to the particle-phase as evidenced by the different yields of secondary organic aerosol formed in these systems (Mutzel et al., 2016). Measurements of OH reactivity at this site in 2011 indicate seasonal differences in the production and emission of BVOCs and suggest that unmeasured primary biogenic emissions contribute significantly to the observed OH reactivity, especially in late summer (PARADE) (Nolscher et al., 2013).

Given the mixed forest / urban location, the hydrocarbon mixture can also be influenced by different, average contributions from anthropogenic emissions. An increase in the relative abundance of anthropogenic to biogenic VOCs during NOTOMO would decrease the value of $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ (see above) and thus reduce the production rate of ΣANs . If a substantial

anthropogenic contribution to the VOC mixture was indeed present during NOTOMO, a further reduction in the apparent NOTOMO yield of ANs compared to PARADE could result from increased rates of deposition of the ANs of anthropogenic origin, which are smaller and have more oxidised functional groups per carbon and should thus be more hydroscopic (Fry et al., 2013).

- even though you don't have VOC measurements in year 2 (bummer!), could you look at e.g. temperature / sunshine differences correlated with VOCs measured within the PARADE period where you DO have the GCs running, and then extrapolate to the conditions during the second year of measurements?

Yes, the lack of biogenic VOCs or alkenes during NOTOMO is unfortunate. There are no permanent GC or PTRMS measurements at the site and the research group which normally does these measurements was participating in a parallel MPI-campaign. Some measurements of alkanes were taken, but these do not contribute significantly to AN generation at this site. While BVOC emissions are known to be temperature / sunlight dependent, they also depend on the seasonal growth stage and local weather in the preceding months. We have expanded the discussion of the differences in the two campaigns as described above.

- Or even use any other GC data taken at that site, whenever, to be able to say something about the potential range of year-over-year variability?

The long-term measurements at the site are meteorological in nature (operated by the German weather service) and some trace gases and particle-measurements by the HNLUG. There are no long term records of VOCs at this site. The PARADE campaign was the first, large intensive campaign at the site in which VOCs were measured using multiple instruments. We have expanded the discussion of the differences in the two campaigns as described above.

- Can you find literature to point to on how oxidized VOCs like nitrates deposition depends on met conditions (your claim at the top of p. 13)?

We now suggest that different air mass ages, hydrocarbon mix (and associated ANs formation rates and different rates of gas-to-particle conversion of the ANs) that all may contribute to the difference between the two years. We have expanded the discussion of the differences in the two campaigns as described above.

- Does the NO: NO₂ ratio during the two years support the apparent differences in PAN vs. ANs formation rate?

The noon-time NO₂-to-NO ratios in PARADE and NOTOMO were 4.0 and 3.8, respectively and cannot explain the different PNs to ANs ratios. This information is now added: "A number of factors influence the relative concentrations of PNs and ANs. In general, higher temperatures are the result of higher levels of insolation and are thus usually related to higher O₃ concentrations and rates of photochemical processing of VOCs. This should lead to higher concentrations of both PNs and ANs. Higher levels of insolation will lead to higher NO to NO₂ ratios (noon-time NO₂-to-NO ratios were 4.0 (PARADE) and 3.8 (NOTOMO) and, given sufficient NO, elevated temperatures will reduce the lifetimes of PNs. Altogether, higher temperatures and more insolation favour AN production over PN production. During the two campaigns. This is essentially the opposite to what we observe and we conclude that other factors, including the mechanism of organic nitrate production from oxidation of different VOC types and rates of loss of the organic nitrates play a major role in controlling the relative abundance of ANs and PNs at this site (see below)."

- Can you find any NO_x emissions data or traffic counts or similar to suggest that the NO_y mix arriving at the site might be different across the 2 years?

We now mention that NO was lower during NOTOMO, consistent with (but not proving) the air being more aged. In the absence of NO_y measurements, we cannot prove this. We write: “As the lifetime with respect to chemical loss/ deposition of alkyl nitrates derived from biogenic VOCs is expected to be shorter than that of O₃, the sampling of progressively aged air masses will bias $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ to low values when calculated from O₃ / ΣAN correlations. A low value of $\alpha(\text{OH})_{av}^{\Sigma\text{ANs}}$ during NOTOMO could conceivably be the result of sampling on average older air masses than during PARADE. The lower NO_x levels in NOTOMO would support this contention, though in the absence of NO_y measurements, is not conclusive.”

3) Figure suggestions

- It would be valuable to see some of the VOC variability in addition to reporting the mean noontime values in table 1. Could you add the reactively most important VOC or two to Fig. 1, to enable readers to see whether periods of high ANs/PNs correlate with higher VOC? Also, suggest to add the diurnally averaged version to Fig. 4 as well. Are all daytime-peaking or some nighttime? Could target trying to ID the dominant NO₃ +BVOC source of organonitrates at night vs. daytime RO₂+NO source, which will help you put the ideas about hydrolysis lifetime and it’s structure dependence in context.

Figure 1 has been expanded to show the time-series of isoprene (emission controlled by temperature and light, daytime peak) and α -pinene (emission rates controlled by temperature) as representatives of biogenic emissions. The diel profiles of isoprene and α -pinene are now also displayed in Figure 4.

- On Fig. 3, can you format the points so they don’t obscure one another? it looks like the black points are behind the red, so it’s hard to see their spread. Maybe use “+”s instead? Or bin /average data so there aren’t so many points on the plot?

The solid circles have been replaced by + symbols.

- Please “squish” Fig. 4 and 5 on the horizontal axis (or equivalently, make them taller) so they are the same width as Fig. 6, where the diurnal pattern is easier to see because of the larger height to width aspect ratio.

Figs 4 and 5 have been stretched vertically.

- Suggest to rethink color scheme on figures. Red/black don’t always means the same thing, leading to confusion. For example, could do dots vs solid for years, consistently, and always use color to refer to left/right axis?

Black and red are now used only to define different molecules / axes. The different campaign datasets in Fig 4 are now distinguished by line-type (solid or dashed).

- Suggest to add NO to figure 4

The diel average profile for NO has been added

- In caption to Fig. 5, briefly described how you separate out the rush-hour influenced Days. This was done by close inspection of individual days and is mentioned in the text where this figure is discussed.

- Fig. 7: how did you choose 11-13 UTC for the O₃ vs ANs slopes? Did you check consistency using different time periods?

The period between 11-13 UTC was chosen as this corresponds to the maximum value of $J(O(^1D))$ and thus OH concentration at the site (see Fig. 4). In the text describing this figure we now write: For both the PARADE and NOTOMO campaigns, we analysed the mixing ratios of ANs and O_3 between 11:00 and 13:00 UTC (around the peak in $J(O(^1D))$ and thus OH levels) to calculate $\alpha(OH)_{av}^{\Sigma ANs}$.

Also, could the iterative correction procedure that makes the ANs data look binned on fig. 7 be the reason for lower ANs concentration measurements, too? What is the relative error on these measurements in each campaign, based on the correction procedure? Could you put error bars on these plots? (Again, might be best to bin first to avoid having a too-busy plot). The correction procedures and the related uncertainty are described in detail in the Thieser et al and Sobanski et al. The average correction factor was between 1.1 (NOTOMO) and 1.2 (PARADE) but with excursions at high NO_x levels to a factor of 2. The uncertainty on the correction factor has been estimated to be $< 30\%$ (Thieser et al., 2016). We have added text in section 2.1 to mention this and now state that the difference between the years is significant. “The average correction factor for the ANs was 1.2, with maximum values of 2. The uncertainty associated with the correction procedure is estimated as $\sim 30\%$ (Thieser et al., 2016).” And later in the manuscript: “The difference in $\alpha(OH)_{av}^{\Sigma ANs}$ between PARADE ($7.2 \pm 0.5\%$) and NOTOMO ($< 2\%$) calculated from the O_3 and ΣANs datasets this manner is significant and cannot be explained by the uncertainty in the measurements of O_3 or ΣANs (see section (3.1). There are a number of potential causes for this difference between the two campaigns.....”

Minor or technical edits:

1) p. 2 line 1: “during the night (R6) (see below) to produce peroxy radicals which subsequently produce stable organonitrates by any radical terminal reaction. Organic peroxy radicals are also formed in...” **correction made**

2) p. 2 line 12 “ultimate to O_3 formation.” **correction made**

3) p. 2 line 31-32: suggest to include chemical formulae for each PAN, PPN, MPAN, analogous to how you show $RC(O)O_2NO_2$ on line 5 of this page. **Addition made**

4) p 3 line 4: “first measurements of total ΣPN s and ...” **correction made**

5) p 3 line 32: clarify that the long observed NO_3 lifetime here is presumed due to low VOC mixing ratio – correct? If so, could you note the mixing ratio compared to another time where you’re not sampling the residual layer?

We have added the lifetime information for “normal conditions”. “On some nights during PARADE, the instruments sampled air from a low lying residual layer which resulted in very high NO_3 steady-state lifetimes ($\approx 1h$). Otherwise the NO_3 lifetimes were generally less than 10 mins (Sobanski et al., 2016b).”

6) p 5 line 32 what does “HLUG” mean?

We have defined this in changed text: “Temperature, ozone, wind speed and wind direction data during NOTOMO were measured by the permanent instrumentation of the Hessian Agency for Nature Conservation, Environment and Geology (HLNUG) at this site.”

7) p. 6 line 10-11. This is unclear. Add symbols to help reader correlate to table 1, e.g. “alkyl nitrate yields (α (ANs) and production rate of alkyl nitrates (P (ANs)) and ozone (P (O₃)). The phrase “for ANs and PN_s, respectively” I don’t understand – P (O₃) is just based on ANs – what do you mean by the PN_s part?.

We have changed to text to clarify that the tabulated production rates are calculated from the OH concentrations and the VOC mixture: The VOCs measured during PARADE are listed in Table 1 along with their rate constants for reaction with OH (k_{OH}) and also the associated alkyl nitrate yields, α (AN). We also list calculated production rates of ANs (P (ANs)), and O₃ (P (O₃)) derived from midday OH levels during PARADE.

8) p. 6 line 16. HLUG again - ?? and typo in “summarizes” **correction made**

9) suggest to find/replace “see later” and change to “see below”, or vice versa, to make all consistent. **We now use “see below” consistently.**

10) p. 7 line 6: Maybe check if Lee et al’s SOAS paper also does the sumANS / individual ANs comparison that Beaver’s paper did? I think in the supplemental: <http://www.pnas.org/content/113/6/1516>

We now also cite Lee et al. when referring to CIMS measurements of speciated ANs.

11) p. 7 line 16-18: is this a chemical clock? Can you correlate with wind speed?

Given the complex terrain and heterogeneity of NO_x sources at the site, wind speed (or direction) will not correlate with chemical aging.

12) p. 7 line 22: “this site. Furthermore, the temperature dependence suggest that ..” (because it’s the T-dependent that suggests this, right? Not the f (NO_x) values). Also, the last sentence of this paragraph offers an alternative explanation, so maybe start with “However, note that low temperatures also increase ...” and then put some more evidence for one of the other potential explanations, from Major Suggestions #1 above, below in this section.

Correction made as suggested. We write: “The high values of f (NO_x) during periods of low NO_x is the result of efficient conversion of NO_x to longer lived organic nitrates in photochemically aged air masses at this site. Furthermore, the temperature dependence indicates that organic nitrate formation is not limited by NO_x. For a given level of NO_x, f (NO_x) is larger when temperatures are higher, reflecting stronger biogenic emissions, and more intense photochemical activity and thus conversion rates of NO_x to organic nitrates (Olszyna et al., 1994; Day et al., 2008). However, note that low temperatures also increase the rate of transfer of soluble organic nitrates to the aerosol phase, which acts on f (NO_x) in the same direction.”

13) p. 7 line 31: typo “emissions” **corrected**

14) p. 8 lin 1: unclear. do you mean the mean and daily maxima of each variable? reword.

We now write: “The campaign averaged, daily maxima in global radiation....”

15) p. 9 line 4: give number for the PARADE campaign too to compare.

Done. We now write: The most notable changes compared to Fig. 4 are the increase in [Σ ANs] during the night. For the NOTOMO campaign, the night-time [Σ ANs] represent ~60 % of the day-time value, for PARADE this is ~35%.

16) p. 9 line 15: typo “[NO₃] and” **corrected**

17) p. 9 line 25-26: are you accounting for differences in rate here too, or assuming there is abundant NO₃ to fully oxidize all VOCs? Elaborate.

This text section has been extended to describe the calculation more fully, and a Table has been added. We now write: “Of the measured VOCs, isoprene, α-pinene, myrcene and limonene account for > 95% of the NO₃ reactivity and have substantial yields of ANs. The mean night-time mixing ratios for these four compounds during PARADE (excluding data where RH > 92 %) are listed in Table 3 along with the corresponding NO₃-reaction rate coefficients (*k*) and the alkyl nitrate yields (*α*) as reported by the IUPAC panel (IUPAC, 2016). The effective alkyl nitrate yield for this VOC mixture can be calculated from the relative flux of NO₃ reacting with each BVOC (depending on the BVOC mixing ratio and rate coefficient) and the alkyl nitrate yield for each individual BVOC. Note that, in the absence of laboratory investigations, the alkyl nitrate yield from NO₃ + myrcene is simply estimated as 50 ± 30 %, in line with other terpenes (IUPAC, 2016). As can be seen from Table 3, reactions with the measured terpenes dominate and the final, averaged yield of alkyl-nitrate is $\alpha(\text{NO}_3) = (0.41 \pm 0.31)$.”

18) p. 10 line 15 typo “environment” corrected

19) p. 10 line 23: SOA yields could be even higher—see summary table in Ng 2016 paper.

This text section has been changed. We now write: “This contrasts strongly with the situation for limonene, where SOA yields of up to ≈ 60 % have been reported, with more than 80 % of the alkyl nitrates formed being in the aerosol phase. There is no experimental data on SOA yields in the reaction between NO₃ and myrcene nor on the gas-aerosol partitioning of the alkyl-nitrates formed. Recent experiments on β-pinene (Boyd et al., 2015) have shown that the SOA yield is neither strongly dependent on the relative concentrations of HO_x and NO_x, which determines the nature of the end-products formed, nor on the relative humidity or seed-aerosol used. If we make the broad assumptions that 1) the SOA yield from myrcene is the same as limonene and 2) that the fraction of ANs in the condensed phase is comparable to those found for limonene, we calculate that > 60 % of the alkyl nitrates formed at night at this site will be present in the aerosol phase and thus not detected by our instrument.”

20) p. 11 line 24: “than the loss terms, D and E, and Eq. 5 ...”

The equation has been modified (*D* is now *L*). We now write “In which *L* represents loss terms (chemical and deposition) and *E* represents entrainment, respectively. The ratio of O₃ to ΣANs after the OH oxidation of a VOC mixture has proceeded for a certain time, *dt*, is given by Eq. (5). At sufficiently high levels of OH, VOCs and NO, the photochemical production terms can be assumed to be larger than the loss or entrainment terms...”