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 statement:

Sobanski et al. present analysis of the measurements of organic nitrates from two field deployments at the Taunus Observatory in Germany. This analysis is a useful contribution to our understanding of the role of organic nitrates in the NOx budget on a global scale, and raises interesting questions about the relative fate of organic nitrates during the day and night. I would suggest publication after the following comments are addressed.
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.

General comments:

1. When calculating average production rates of alkyl nitrates during day and night, the authors use campaign average values for each term. Given the variety of conditions sampled during the campaign, it seems possible that using campaign averages will bias the results (if, for example, the mixture of VOCs and therefore the alkyl nitrate yield is different on nights with higher concentrations of NO2 and O3). The use of campaign average values in calculations should either be avoided or the consequences of them discussed.
The referee refers to use of equations (1) and (2). We appreciate that using campaign averages in these calculations will result in inclusion of data that cover a large spread in conditions and thus production rates. As far as equation (2) is concerned (night-time production), this variability can be expressed by considering the standard deviation in the NO_2 and O_3 concentrations and the mixing ratios of the BVOCs. The overall uncertainty in the production rate depends on the uncertainty in the branching ratio to ANs and the rate coefficient for the reaction between NO_2 and O_3. We have added a Table (3) with details about the concentrations and added more information about the calculation to derive the effective campaign averaged, branching ratio and the uncertainty in the ANs branching ratio. We have modified the text as follows: "To estimate the night time-production of ANs, we consider the reaction between NO_2 and O_3 to be the only NO_3 precursor. Of the measured VOCs, isoprene, α-pinene, myrcene and limonene account for > 95% of the NO_3 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 NO_3-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 NO_3 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 NO_3 + myrcene is simply estimated as 50 ± 30 %, in line with other terpenes (IUPAC, 2016). The final, averaged yield of alkyl-nitrate is $\alpha(NO_3) = (0.41 \pm 0.31)$. The uncertainty we quote is progagated from uncertainty in the rate coefficient and the individual alkyl nitrate yields as reported by IUPAC and also the standard deviation of the mean concentration of the BVOC during the campaign. Clearly, given the large variability in night-time BVOC at this site, uncertainty associated with alkyl nitrate yields and the assumption that all BVOCs with sinificant reactiviy for NO_3 were measured, this campaign average value of $\alpha(NO_3)$ should be

considered only as a rough indicator. Assuming that each NO_3 generated reacts rapidly with a BVOC, the night-time production rate of ANs is then given by:

$$P(\Sigma\mathrm{ANs})_{\mathrm{night}} = \alpha(\mathrm{NO_3})k_{(\mathrm{NO_2+O_3})}[\mathrm{NO_2}][\mathrm{O_3}] \qquad (2)$$

Taking the mean night-time mixing ratios of $[NO_2]$ (2.7 ± 2.1) ppbv and $[O_3]$ (45 ± 11 ppbv) over the same time period, using the temperature dependent rate coefficient for the reaction between NO_2 and O_3 (1.4×10^{-13} exp(-2470/T) cm^3 $molecule^{-1}$ s^{-1}) we calculate the production rate of ANs (Eqn. 2) to be: $P(\Sigma\mathrm{ANs})_{\mathrm{night}} \approx 90$ pptv hr^{-1}. This analysis implicitly assumes that indirect loss of NO_3 via the heterogeneous loss of N_2O_5 was insignificant compared to direct loss via reaction with BVOCs. This is expected for a forested region in summer and has been shown to be the case for the Taunus Observatorium (Crowley et al., 2010; Sobanski et al., 2016b) where, except for few occasions when the residual layer is sampled, the NO_3 lifetime with respect to gas-phase reactions with BVOCs is too short for indirect, heterogeneous loss to compete unless the mountain-site is in fog.

Given the large uncertainty associated with $\alpha(NO_3)$ and also the variability in NO_2 and O_3 this average value can be considered consistent with the increase in ANs observed in the two hours following sunset during either the PARADE or NOTOMO campaigns."

We have also modified the text related to equation (3): "Bonn et al. (2014) report a maximum uncertainty of a factor two for [OH] derived in this manner. For an approximate estimate of day-time ANs prodution, we take the campaign mean mixing ratios of each VOC between 11:00 and 13:00 UTC as listed in Table 1. Based on the individual rate coefficients, alkyl nitrate yields and mean, noon-time concentrations of the VOCs measured (also listed in Table 1) and using equation (3);

$$P(\Sigma\mathrm{ANs})_{\mathrm{day}} = \Sigma_i\big(\alpha_i(OH)k_{OH+RH_i}[OH][RH_i]\big) \qquad (3)$$

we obtain a noon-time ANs production rate of $P(\Sigma\mathrm{ANs})_{\mathrm{day}} \approx 70^{+70}_{-35}$ pptv hr^{-1} where the reported uncertainty is due only to the uncertainty in OH concentrations. As illustrated in Table 1, ~80% of the total, noon-time, ΣANs production rate is accounted for by the four biogenic VOCs measured: limonene, myrcene, α-pinene, and isoprene. Given that the concentrations of these short lived biogenics are expected to be variable due to the spatial inhomogeneity of emission sources and their dependence on temperature and light levels, the use of campaign averages can provide only a rough indicator of AN production rates. In addition, there is considerable uncertainty associated with the AN yields of the biogenics, which in the absence of measurements, partially stem from structure-reactivity relationships (Perring et al., 2013). The largest uncertainty is however related to the assumption that the reactions of OH are accounted for by the VOCs measured. In forested regions "missing" OH reactivity has been frequently reported (Nölscher et al., 2012; Nolscher et al., 2013), indicating unknown sinks for OH with organic trace gases, which can account for up to 80 % of the observed reactivity. In the case of missing reactivity, the ΣANs yields calculated via Eq. (3) are lower limits. Moreover, this expression also neglects the formation of peroxy radicals from the Cl-atom initiated oxidation of VOCs, which may also react with NO to form ANs. As $ClNO_2$ was observed at elevated concentrations on some days during PARADE (Phillips et al., 2012) its main influence on oxidation processes is in the early morning, when OH levels are comparably low. Despite these uncertainties, the calculations above indicate that the value of $P(\Sigma\mathrm{ANs})_{\mathrm{day}}$ thus obtained is comparable with the estimated night-time production, which is consistent with the conclusions of (Fry et al., 2013) also made at a forested site with urban influence."

2. The discussion of the differences in alkyl nitrate yield between PARADE and NOTOMO should be expanded further. While the proposed explanation, that BVOC emissions were lower during NOTOMO, is plausible, I would appreciate further discussion of alternative explanations for the observations. In particular, the authors should consider the possibility that the NOTOMO observations of O3 and ANs represent a highly aged airmass where the assumptions required for Eq. 6 do not apply.

We have extended the discussion in a new section (4.5.1) with the following text

4.5.1 Inter-annual / seasonal differences in α(OH), PARADE versus NOTOMO

The difference in $\alpha(\mathrm{OH})_{av}^{\Sigma\mathrm{ANs}}$ between the July-2011 PARADE campaign (7.2 ± 0.5 %) and the Aug-Sept. 2015 NOTOMO campaign (< 2 %) is significant and cannot be explained by the uncertainty in the measurements of $[O_3]$ or $[\Sigma\mathrm{ANs}]$ (see section (3.1).

There are a number of potential causes for the apparent difference in $\alpha(\mathrm{OH})_{av}^{\Sigma\mathrm{ANs}}$ 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. This may be particularly relevant for our mountain site, where influence from the free troposphere can be significant. 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 any bias introduced by the assumptions inherent to Eq. 6, but will not remove it 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 $\alpha(\mathrm{OH})_{av}^{\Sigma\mathrm{ANs}}$ to low values when calculated from O_3 / ΣAN correlations. A low value of $\alpha(\mathrm{OH})_{av}^{\Sigma\mathrm{ANs}}$ 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 $\alpha(\mathrm{OH})_{av}^{\Sigma\mathrm{ANs}}$ during NOTOMO is that the average lifetime of ΣANs was shorter than during PARADE, due e.g. to chemically distinct ANs being generated, a result of there being 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. This may also have been relevant for the relative impact of entrainment from aloft, i.e. influence from the lower free troposphere.

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 from the mixed vegetation 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 $\alpha(\mathrm{OH})_{av}^{\Sigma\mathrm{ANs}}$ (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)."

Specific Comments:

Page 1, Line 26-27: Since HNO_3 does not appreciably return NOx to the atmosphere, it is incorrect to describe NOx as being temporarily sequestered as HNO_3.
We have corrected the text, which now reads: "In the troposphere, a significant amount of NO*x* can be temporarily sequestered as organic nitrates."

Page 3, Line 3: NOy should be defined in this manuscript.
We now write: "Early attempts to compare total reactive nitrogen NO*y* (where NO*y* = NO*x* + RO_2NO_2 + $RONO_2$ + HNO_3 + HONO + +) with the sum of individually measured species (Fahey et al., 1986; Buhr et al., 1990; Ridley et al., 1990) revealed that a substantial fraction of NO*y* was missing."

Page 3, Line 10: The abbreviation TD-CRDS should be defined here, the first time it is used, rather than on page 4.
We now define TD-CRDS on page 3: "We present here an analysis of organic nitrates and NO_2 measured using Thermal Dissociation Cavity Ring-Down Spectroscopy (TD-CRDS) during two field campaigns that took place at a forested, semi-rural mountain site in South-Western Germany."

Page 4, Section 3.1: Is the TD-CRDS measurement of ANs gas-phase only? Given the potential importance of particle-phase chemistry to understanding the nighttime concentration of ANs, the response of the TD-CRDS instrument to particulate organic nitrates should be discussed in this section.
The sampled air is drawn through Teflon membrane filters which prevent detection of particulate nitrate (as NO_2) following passage through the TD-regions. Text has been added (section 3) to illustrate this: "NO_2 and total gas-phase organic nitrates were measured during

both campaigns by TD-CRDS. Membrane filters were used to prevent aerosol from entering the CRD inlets, which would lead to severe reductions in the detection limit, degradation of the cavity mirrors and also to the detection of particulate nitrate (both organic and inorganic) in the TD channels."

Page 5, Line 25: Was J(NO2) measured directly, or was it modeled?
$J(NO_2)$ was measured. The sentence now reads: "……where $J(NO_2)$ is the photolysis frequency of NO_2 (measured using a METCON spectral radiometer) and $k_{(NO+O3)}$ is the rate constant for reaction of NO with O_3."

Page 9, Line 22: Given that direct measurements of NO_3 are available for this campaign, why are those measurements not used to calculate the nighttime alkyl nitrate production rate?
The AN production term is high even when NO_3 concentrations are "zero" or below the detection limit of the instrument (e.g. because BVOC levels are high). As long as reaction with VOCS is the dominant loss process for NO_3, it is appropriate to use the NO_2 and O_3 concentrations. It is mathematically equivalent to using NO_3 concentrations if NO_3 is not lost via reaction with e.g. NO or if N_2O_5 loss rates are competitive. Note that use of NO_3 concentrations to calculate AN production rates would necessarily involve the assumption that all BVOC were measured and that the reaction rate constants and AN yields are accurately known.

Page 9, Line 24 and Line 29: Which days were included when calculating mean night-time mixing ratios? All days, only days including in Fig. 6, or some other combination?
This has been calculated for both scenarios and there is no significant difference in the average mixing ratios of the BVOCs is the humid nights are considered or not. However, to be rigorous, we have modified the text to clarify this and added a table with the rate coefficients and AN-yields for reaction of each individual BVOC measured with NO_3: The text has been modified as outlined above in the reply to general comment (1).

Page 9, Line 25: A citation for these alkyl nitrate yields should be given.
We had in fact already cited Atkinson and Arey (2003) and Perring et al (2013) (page 9, lines 19 and 20). However, we now use the IUPAC recommendations instead and quote associated uncertainties and spread in yields as assessed by IUPAC.

Page 9, Line 27-28: Some justification for assuming that heterogeneous N2O5 loss is minimal should be included.
We add the following justification: "This analysis implicitly assumes that indirect loss of NO_3 via the heterogeneous loss of N_2O_5 are insignificant compared to direct loss via reaction with BVOCs. This is expected for a forested region in summer and has been shown to be the case for the Taunus Observatorium (Crowley et al., 2010; Sobanski et al., 2016b) where, except for few occasions when the residual layer is sampled, the NO_3 lifetime with respect to gas-phase reactions with BVOCs is too short for indirect, heterogeneous loss to compete."

Page 9, Equation 2: See general comment 1.
See reply to general comment (1)

Page 10, Line 5: What uncertainty in the calculated value of OH does this correlation introduce?
Bonn et al report an uncertainty of a factor of two in the OH concentration. We have added this information to the text and also use it to calculate error bounds for the AN production

rate. We now write: “Bonn et al. (2014) report a maximum uncertainty of a factor two for [OH] derived in this manner. For an approximate estimate of day-time ANs prodution, we take the campaign mean mixing ratios of each VOC between 11:00 and 13:00 UTC as listed in Table 1. Based on the individual rate coefficients, alkyl nitrate yields and mean, noon-time concentrations of the VOCs measured (also listed in Table 1) and using equation (3);

$$P_{\Sigma ANs} = \Sigma_i \alpha_i k_{OH+RH_i}[OH][RH_i] \qquad (3)$$

we obtain a noon-time ANs production rate of $P(\mathrm{ANS})_{\mathrm{day}} \approx 70^{+70}_{-35}$ pptv hr^{-1} where the reported uncertainty is due only to the uncertainty in OH concentrations. ”

Page 10, Line 6-7: Is the campaign mean calculated for all days or for only times included in Fig. 6?

This deals with the day versus nightime generation. The campaign means (e.g. of VOCs etc.) is for the entire campaign and not just for those with “dry” We now write: “For an approximate estimate of day-time ANs prodution, we take the campaign mean mixing ratios of each VOC between 11:00 and 13:00 UTC as listed in Table 1.”

Page 10, Line 10, Equation 3: See general comment 1.

See reply to general comment (1).

Page 10, Line 20: I typically think of deposition dropping to near zero at night, since turbulent mixing is low. The authors should discuss further the likelihood of enhanced nighttime deposition.

This is true. The emphasis should actually be on the different chemical composition of the NO_3 generated night-time ANs compared to the OH generated daytime ones, rather than on the influence of turbulent transport. The day versus nightime production has been re-written as follows: “Although we calculate similar production rates of ΣANs during the night when NO_3 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 $P(\Sigma\mathrm{ANs})_{\mathrm{day}}$. 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 night-time-generated organic nitrates formed in NO_3 + BVOC reactions are efficiently transferred to the condened 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 mycene 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 mycene 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 gormed 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)."

Page 10, Line 23-24: Can the SOA yields reported by Fry et al. 2011, 2014 be used to estimate the fraction of ANs produced that are likely to remain in the gas phase, and can that fraction be used to adjust Eq. 2 to describe only the gas-phase production of alkyl nitrates?

SOA yields of up to 60 % have been measured for limonene, which accounts for 40 % of the overall NO_3 reactivity (see new Table 3) but not for myrcene (30 % of the NO_3 reactivity). For β-pinene we know that the SOA yield is not strongly dependent on the relative humidity the seed aerosol or the relative HO*x* to NO*x* ratio (Boyd et al., 2015). We now add a rough estimate of the fraction of the alkyl nitrates that will be in the aerosol phase. The text now reads: "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 mycene or on the gas-aerosol partitioning of the alkyl-nitrtes 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 mycene 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 ANs that exceed those derived from gas-phase AN measurements by a factor between two and three.”

Page 11, Equation 5: The concentration of ozone and ANs should include the effect of chemical loss.

The equation has been modified to combine chemical and depositional losses:

$$\frac{\Delta O_3}{\Delta \Sigma ANs} = \frac{\int (P_{O3} - L_{O3} + E_{O3})dt}{\int (P_{\Sigma ANs} - L_{\Sigma ANs} + E_{\Sigma ANs})dt} \qquad \text{Eq. (5)}$$

In which *L* represents loss terms (chemical and deposition) and *E* represents entrainment, respectively.

Page 12, Line 3-7: Under the conditions of the NOTOMO campaign, what uncertainty in AN concentration does the correction procedure introduce?

The correction factor (0.8 to 1.5 with an average value of 1.1) and the total uncertainty in ANs for the NOTOMO campaign were discussed in Sobanski et al., 2016a. As the correction factor is NOx dependent and also NO / NO_2 ratio dependent it is not possible to quote a single uncertainty for the measurements. The following text has been added: “For NOTOMO, in which low mixing ratios of ANs were encountered, the vertical grouping of the data apparent in Fig. 7 (i.e. low resolution in concentration) is a result of the corrective procedure for extracting mixing ratios from raw data obtained in the hot and cold inlets, which involves iterative numerical simulation which converges when 1% agreement between observation and simulation is achieved. The average correction factor for ANs during NOTOMO was 1.1 (Sobanski et al., 2016a) and, based on a series of laboratory experiments, the (NOx dependent) uncertainty associated with this factor is expected to be less than 50 %.”

Page 12, Line 20-22: This is likely an overestimate of the range of isoprene alkyl nitrate yield. Recent work on the isoprene branching ratio has generally found branching ratios on the higher end of this range (9-15%) (Teng et al., 2015, Xiong et al., 2015).

From their laboratory experiments, Xiong et al. report a value of 9^{+4}_{-3} %, in the centre of the range of 4-15 % reported in the literature. They also report 9-12 % from field data analysis. We have updated the text and now write: “Regarding the individual nitrate yields, some values used to calculate the average (see Table 1) are not precisely determined in the literature while others are estimated. For example, the most recent measurements of the yield of alkyl nitrates formed in the reaction of OH with isoprene in the presence of NOx (one of the best studied reaction systems) ranges from 6 to 13% (Xiong et al., 2015) and remains a significant source of uncertainty (Perring et al., 2013).”

Page 12, Line 33: Photolysis and chemical loss of alkyl nitrates is often a more important loss process than deposition (Xiong et al., 2015).

This can be true for isoprene (the subject of Xiong et al., 2015), especially under sunny, dry conditions. For nitrates derived from terpenes under conditions of low insolation and higher humidity (as found e.g. over long periods at the Kleiner Feldberg), the condensation /

deposition term is likely to gain in importance. We now write: “(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 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.”

Page 13, Line 6-9: Any explanation for the low concentrations of alkyl nitrates should also be able to explain the high concentration of ozone encountered during the NOTOMO campaign.
Different air mass ages would potentially explain this as would different hydrocarbon mixtures. We have extended the text and added a new section on the differences between the PARADE and NOTOMO campaigns as outlined above in the response to general comment (2).

Page 13 Line 7: Given that on average, NOTOMO was warmer and sunnier than PARADE (page 8), what magnitude of changes in VOC emissions is expected between the two campaigns? Is this change large enough to explain the low observed yield of alkyl nitrates?
It is not only the prevailing temperature and insolation that control emission strengths and nature of BVOCs but also the time of year, availability of water and the growing phase (for different vegetation types) and general growth conditions in the proceeding months. As the two campaigns took place at different seasons, it is not necessarily given that the BVOC emissions will be the identical. We have extended the text and added a new section on the differences between the PARADE and NOTOMO campaigns as outlined above in the response to general comment (2).

Page 13 Line 8: Based on the mixture of non-biogenic VOCs measured during PARADE, would decreased concentrations of BVOCs lead to a lower average value of alpha? Is this value low enough to explain the observed O3-AN slope during NOTOMO?
First, we note that the previously reported mixing ratios of pentene and butadiene are considered to be erroneous (too high) and have been removed from the Table and the calculation of alpha has been repeated. We have added the following text: “To emphasise the different efficiency of AN production from VOCs of biogenic origin (BVOC) and anthropogenic origin (AVOC), Table 1 is separated into biogenic and anthropogenic VOCs and from the separate summed P(ANs) and P(O_3) we calculated the effective value of $\alpha(\mathrm{OH})_{\mathrm{av}}^{\mathrm{VOCi}}$ that would have been obtained considering each class of VOC individually. The values thus obtained are $\alpha(\mathrm{OH})_{\mathrm{av}}^{\mathrm{BVOCi}} = 17.3$ % and $\alpha(\mathrm{OH})_{\mathrm{av}}^{\mathrm{AVOCi}} = 1.4$ %. Note that, for this particular hydrocarbon mixture, the O_3 production rates are much larger for the AVOCs (~ 1000 compared to ~400 for the BVOCS).”

Page 18, Line 20, Table 1: Several of the values in this table disagree with those listed in Perring et al, 2013, the listed source for the yield. This includes i-pentane(0.35/0.07), isoprene (0.044/0.07) and i-butane(0.255/0.096). The values in Table 1 should either be updated or new references given.
The values have been updated and the Table has been reorganised to separate the biogenic and anthropogenic VOCs.

Technical Corrections:

Page 1 Line 12: "Futher" should be "Further" Corrected
Page 6, Line 15: Extra period after Fig. 2. Corrected
Page 11, Line 14 Equation 4: There are some mis-matched parentheses in this equation. corrected
Page 18, Table 1: The mean noon time mixing ratio unit appears to be pptv, and not ppbv as written. Corrected.