We thank the reviewers for their comments. Our specific response can be found below. The reviewers' comments are in italics and changes made to the manuscript are in quotation marks. All changes made are minor and do not affect the conclusions in the manuscript.

<u>Response to Reviewer 2</u>

1. The manuscript by Ng et al. provides an overview of NO3-BVOC chemistry in the atmosphere, and how and how this impacts atmospheric aerosols. The review has stemmed from a workshop on NO3-BVOC chemistry, and provides a review of recent laboratory studies of kinetics and reaction mechanisms, field measurements/techniques, leading to a series of recommendations for future work.

<u>Response</u>: We thank the reviewer for these comments.

2. However, the manuscript provides little by way of critical review, and, perhaps owing to the comprehensive nature of the review, in several places lacks the detail required for a tutorial-style review.

<u>Response</u>: Please see responses below for addition of details that aid in the tutorial-style review. In addition to answering several of the more detailed comments, we have added a new figure to the introduction to illustrate features of nighttime chemistry and anthropogenic-biogenic interactions that are central themes of the review.

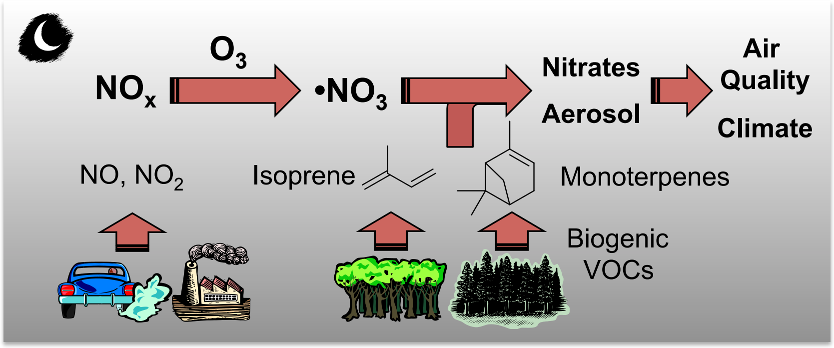

Figure 1. Schematic of nighttime NO_3-BVOC chemistry

We have also added two new figures in the section on organic nitrates to summarize observations of these species in aerosols in the U.S. and Europe.

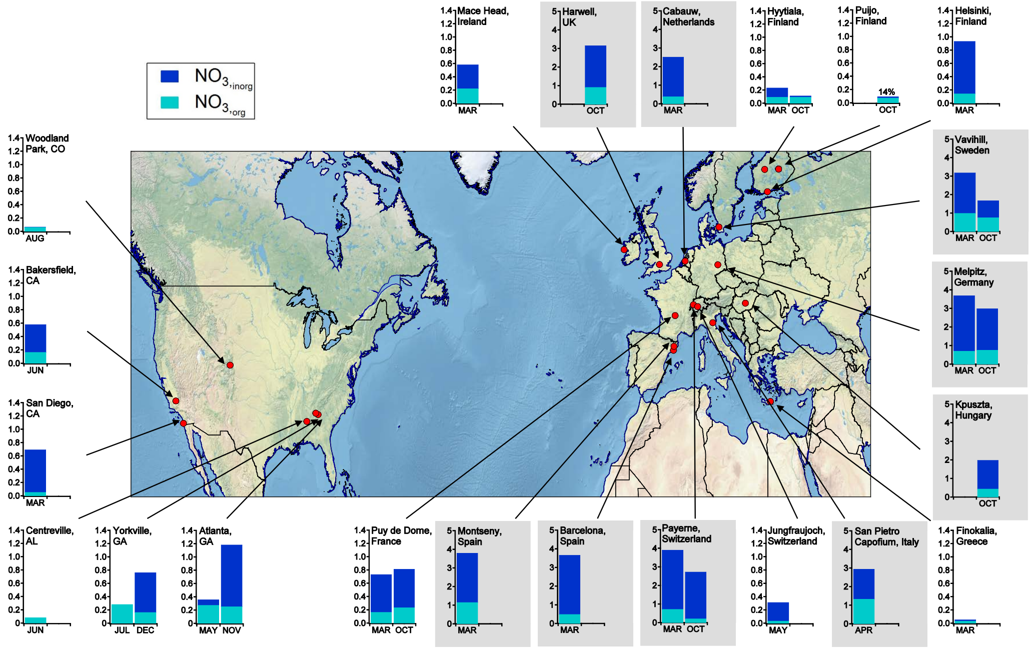

Figure 2.5.2a Average mass concentrations (in mg m-3, ambient temperature and pressure) of submicrometer particulate organic nitrates (NO3, org) and particulate inorganic nitrates (NO3, inorg) in different months at multiple sites. The concentrations correspond to mass concentrations of –ONO2 functionality. Note that the y-axis is different for site with total nitrate greater than 1 mg m-3 (shaded). Detailed information and measurements for each site are provided in Table SI-5 in the Supplement.

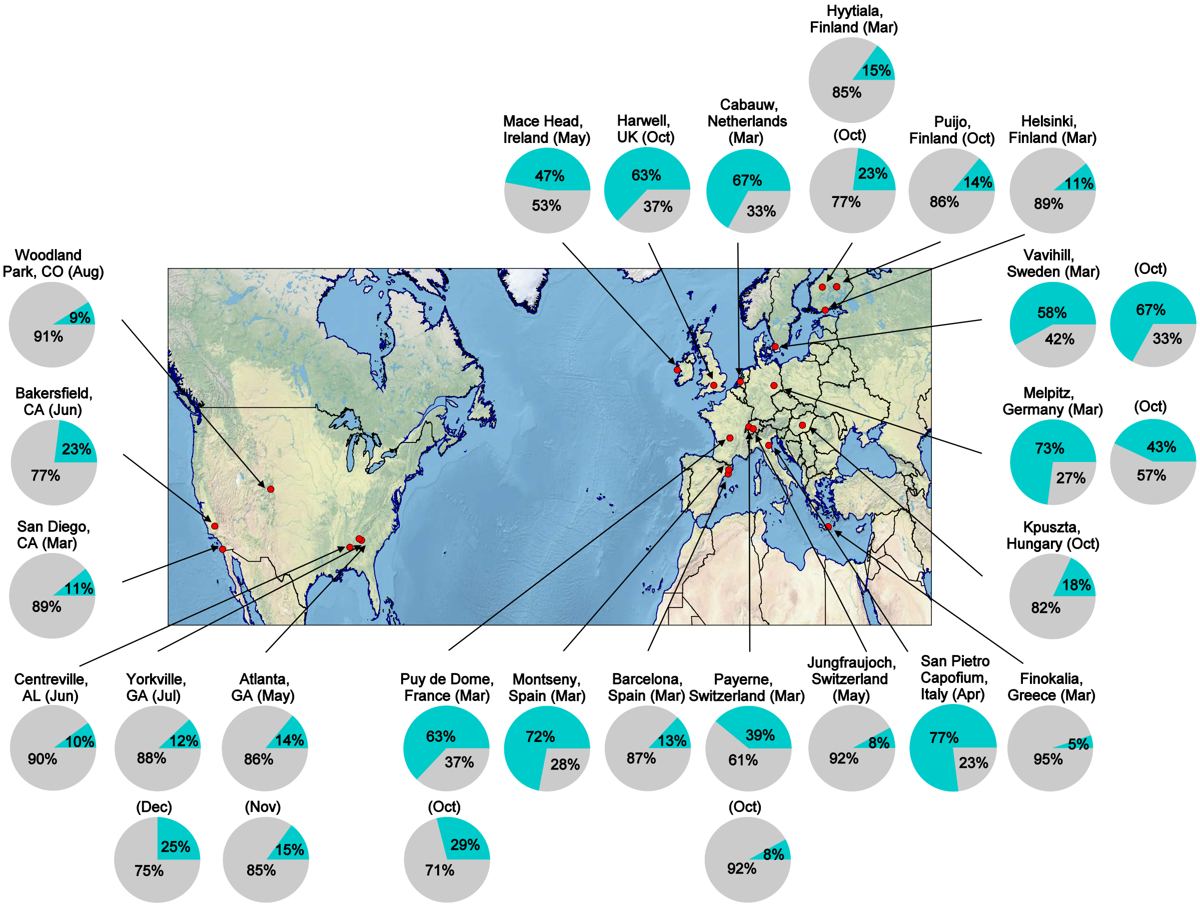

Figure 2.5.2b Percentage (by mass, cyan) of submicrometer particulate organic nitrate aerosols in ambient organic aerosols in different months at multiple sites. Detailed information and measurements for each site are provided in Table SI-5 in the Supplement.

3. For example, the rate coefficients for NO3+BVOC reactions determined in previous experimental work are listed in Table 1, and in many cases, the rate coefficients have already been reviewed by IUPAC, with no new recommendations/review of the data. It is not entirely clear what is gained by the inclusion of these data in this review.

Response: The reviewer is correct that some rate constant data are available through IUPAC, and where such data have been reviewed by IUPAC they are specified in table 1. However, the current compilation is more comprehensive and includes a larger array than is available through the IUPAC database. For example, IUPAC reviews rate constant data for 15 NO_3-BVOC reaction, whereas the current table 1 reviews 44 reactions, almost 3 times as many. Furthermore, this review collects all relevant rate constants in one place so that the interested investigator has a single reference to understand what is, and what is not, available from previous investigations of NO_3-BVOC rate constants.

4. Similarly, there is little information regarding the mechanisms of NO3-BVOC chemistry – some figures displaying mechanisms for some reactions/models at least may be helpful to aid comparison.

Response: We agree. Section 2.1.2 on mechanisms has now been re-written and expanded to include a discussion of the mechanistic features of NO_3 + isoprene and NO_3 + monoterpenes. A new figure 2.1 now replaces the older figure 1. The new text and figures are as follows:

"In general, NO_3 reacts with unsaturated VOCs by addition to a double bond (Wayne et al., 1991), though hydrogen abstraction may occur, most favorably for aldehydic species (Zhang and Morris, 2015). The location and likelihood of the NO_3 addition to a double bond depends on the substitution on each end of the double bond, with the favored NO_3 addition position being the one resulting in the most substituted carbon radical. In both cases, molecular oxygen adds to the resulting radical to form a peroxy radical (RO_2). For example, the major RO_2 isomers produced from isoprene and β-pinene oxidation via NO_3 are shown in Figure 2.1. The RO_2 distribution for isoprene oxidation by OH has been shown to be dependent on the RO_2 lifetime (Peeters et al., 2009; 2014), but no similar theoretical studies have been conducted on the NO_3 system. Schwantes et al., (2015) determined the RO_2 isomer distribution at an RO_2 lifetime of ~30 s for isoprene oxidation via NO_3. More theoretical and experimental studies are needed to understand the influence of RO_2 lifetime, which is long at night (~50-200 s for isoprene, Schwantes et al., 2015), on the RO_2 isomer distribution, as this distribution influences the formation of all subsequent products (Figure 2.1).

The fate of RO_2 determines the subsequent chemistry. During the nighttime in the ambient atmosphere, RO_2 will isomerize or react with another RO_2, NO_3, or HO_2. In order to monitor RO_2 isomerization reaction products, RO_2 lifetimes must be long in laboratory studies similar to the ambient atmosphere (e.g., Peeters et al., 2009, Crounse et al., 2011). The NO_3+BVOC reaction can be a source of nighttime HO_2 and OH radicals (Platt et al., 1990). Reaction with NO is a minor peroxy radical fate at night (Pye et al., 2015;Xiong et al., 2015). Few laboratory studies have contrasted the fates of RO_2 and their impacts on gas-phase oxidation and aerosol formation (Ng et al., 2008;Boyd et al., 2015;Schwantes et al., 2015). Boyd et al. (2015) examined how RO_2 fate influences SOA formation and yields and studied the competition between the RO_2-NO_3 and RO_2-HO_2 channels for β-pinene. Boyd et al. (2015) determined that the SOA yields for both channels are comparable, indicating that the volatility distribution of products may not be very different for the different RO_2 fates. In contrast, the results from NO_3 oxidation of smaller BVOC, such as isoprene, show large differences in SOA yields depending on the RO_2 fate (Ng et al., 2008), with larger SOA yields for second generation NO_3 oxidation (Rollins et al., 2009).

The well-established gas-phase first-generation products from the major β- and δ-RO_2 isomers formed from isoprene oxidation are shown in Figure 2.1 (adapted from Schwantes et al., 2015). Some of the products are common between all the pathways, such as methyl vinyl ketone for the dominant β-RO_2 isomer. However, some products are unique to only one channel (e.g., hydroxy nitrates form from RO_2-RO_2 reactions and nitrooxy hydroperoxides form from RO_2-HO_2 reactions). In this case, the overall nitrate yield and the specific nitrates formed from isoprene depend on the initial RO_2 isomer distribution and the fate of the RO_2. Furthermore, the distribution of gas-phase products will then influence the formation of SOA. For isoprene, the SOA yields from RO_2-RO_2 reactions are ~2 times greater than the yield from RO_2-NO_3 reactions (Ng et al., 2008).The less well-established first-generation products from β-pinene oxidation are also shown in Figure 2.1 (adapted from Boyd et al., 2015). There are still lingering uncertainties (shown in red) in the first-generation products formed from β-pinene oxidation. The product yields from the RO_2 + HO_2 channel are not well constrained largely due to the unavailability of authentic standards. In Figure 2.1, a carbonyl product is assumed to form directly from the RO_2 + HO_2

reaction instead of proceeding through an alkoxy intermediate consistent with theoretical calculations from different compounds (Hou et al., 2005a; 2005b, Praske et al., 2015). This is also uncertain, as few theoretical studies have been conducted on large molecules like β-pinene. The identification of the carbonyl compound(s) produced from RO_2 reaction with NO_3, RO_2, or HO_2 is unknown. Hallquist et al., 1999 detected a low molar yield (0-2%, Table 2.2) of nopinone, the most reasonable product, from β-pinene oxidation."

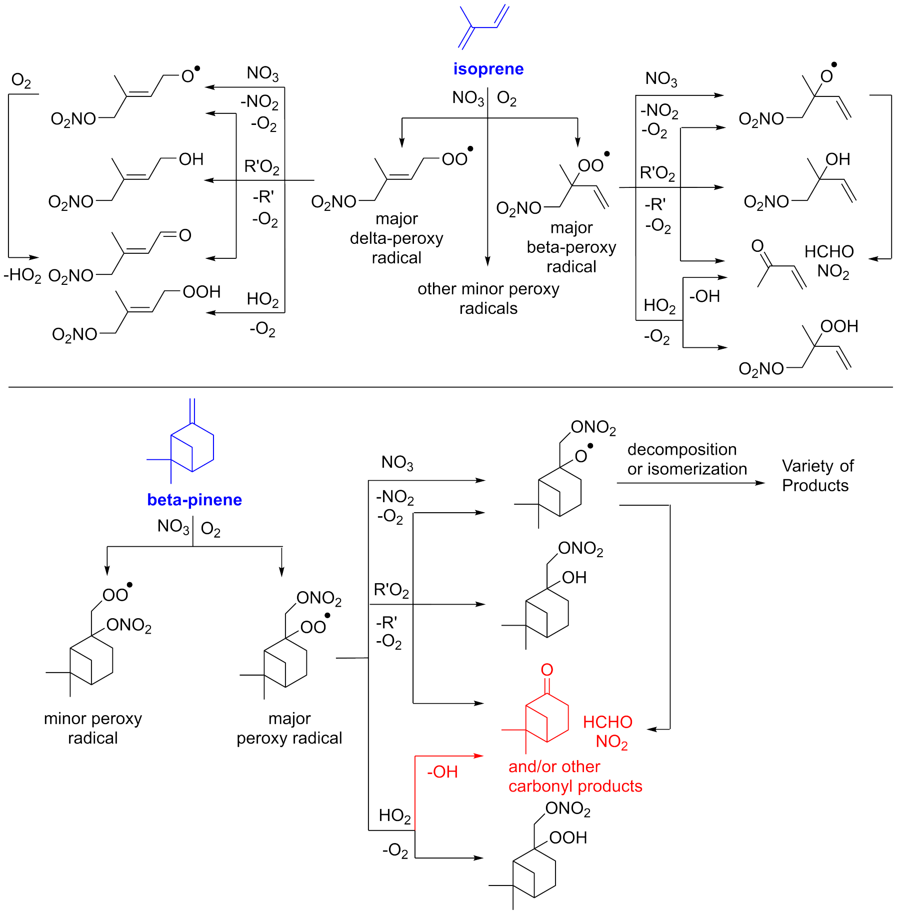

Figure 2.1. Condensed reaction mechanism for isoprene and β-pinene oxidation via NO_3. For brevity, only products generated from the dominant peroxy radicals (RO_2) are shown. R' represents an alkoxy radical, carbonyl compound, or hydroxy compound. Two of the largest uncertainties in β-pinene oxidation are shown in red: 1) quantification of product yields from the RO_2 + HO_2 channel and 2) identification of carbonyl products formed from RO_2 reaction with NO_3, RO_2, or HO_2 (see text for more details).

5. In addition, the overview of experimental techniques used to measure NO3 (and N2O5) in the atmosphere is covered in greater depth in the 2012 review by Brown & Stutz, with little/no new insights presented here.

Response: We agree that other reviews, including Brown & Stutz 2012, discuss experimental techniques for NO_3 and N_2O_5. However, this review also includes a discussion of experimental methods for other compounds relevant to NO_3-BVOC chemistry, such as gas and aerosol phase organic nitrates. It would be remiss of the authors within that context *not* to include a discussion of NO_3 and N_2O_5, even if such a discussion exists in a separate context elsewhere in the literature.

6. While the review does cover areas of interest to many atmospheric scientists, it does read somewhat as a summary of presentations at a meeting/workshop covering a broad range of topics, with the detail regarding each of the topics to be found elsewhere.

Response: We respectfully disagree. The topics and outline for this review were agreed upon through a series of breakout meetings and group discussions rather than through a compliation of individual presentations. The outline and flow of the manuscript is logical, beginning with the current state of the science and proceeding to discuss research needs within this topic.

7. In general, the tables are poorly formatted and difficult to read. It may be helpful to remove the references and list them numerically with a list of numerical references in supplementary information (similar to the style adopted for Figure 2 perhaps).

Response: We agree, the table formatting, which was done to match ACP standards, has made some of the presented information difficult to read. We have made an effort to improve the formatting, borders and spacing of all tables to make them more readable.

8. Numerous acronyms are used without definition. This review may be particularly useful to graduate students and researchers new to the area, and definitions should be provided at the point of first use to aid those researchers. A glossary would also be helpful.

Response: We thank the reviewer for this suggestion. A glossary of acronyms and common chemical formulas has been included at the end.

9. Page 3, line 24: Terms such as 'enormous' should be avoided, quantify the statement or at least provide a relative comparison to anthropogenic emissions.

Response: Agreed. "enormous" has been replaced by "large".

10. Page 4, line 6: Should this be 'alkenes'? The reactions of NO3 with alkanes are very slow.

Response: The review is right. This has been corrected in the revised manuscript.

11. Page 7, lines 17-19: Are the two statements regarding isoprene rate coefficients contradictory? If *the results from different studies for isoprene differ by over a factor of two, how is the IUPAC recommendation precise?*

Response: The reviewer is correct that the statements are contradictory. The first sentence has been modified to state that BVOC with multiple NO_3 rate constant studies have been evaluated by IUPAC to produce recommended values. The sentence now reads as "The most emitted/important BVOC have been subjected to several kinetic studies, using both absolute and relative methods, which are evaluated to determine recommended rate constants by IUPAC".

12. Page 16, line 4: '. . . was investigated in the context of. . .', perhaps a brief discussion of the results of this investigation?

Response: We have added a second clause to this sentence to briefly describe the results of Draper et al: "This difference among monoterpenes was investigated in the context of the competition between O_3 and NO_3 oxidation (Draper et al., 2015), in which shifting from O_3-dominated to NO_3-dominated oxidation was observed to suppress SOA formation from α-pinene, but not from β-pinene, Δ-carene, or limonene."

13. Page 16, line 8: 'at conditions' to 'under conditions'.

Response: Modified.

14. Page 16, line 11: '. . . fairly constant. . .', please quantify.

Response: The sentence is modified to "Recent experiments showed that the particulate organic nitrates formed from β-pinene-NO_3 are resilient to photochemical aging, while those formed from α-pinene-NO_3 evaporate readily".

15. Page 16, line 27: 'reaction' to 'reactions'.

Response: Corrected.

16. Page 17, line 18: '. . . observed a tight correlation. . .', provide the correlation coefficient.

Response: The correlation coefficient was 0.99 ($r^2 = 0.98$) and has been added to the text.

17. Page 17, line 21: Remove 'the' in '. . . the nucleation and . . .'.

Response: Corrected.

18. Page 20, line 18-19: 'Our present understanding. . .', please provide a reference.

Response: We have added Hallquist et al (ACP, 2009) and Tsigaridis et al. (ACP, 2014) as references.

19. Page 21, line 20: Please clarify the term 'oxidized once', what does this mean? A single oxidation step?

Response: The phrase has been clarified to read "… undergo a single reaction with NO_3."

20. Page 21, line 26: '. . . effectively limit rate. . .' to '. . . effectively limit the rate. . .'.

Response: Corrected.

21. Page 22, line 1: 'a phase transition' or 'phase transitions'.

Response: The sentence is changed to "…..owing to a phrase transition…".

22. Page 23, line 23: lower case 'u' in undec-10-ene-1-thiol.

Response: Corrected.

23. Page 25, line 11: Provide a definition for 'SOx-'.

Response: The sentence is changed to "….. SO_x^- *(sulfur-containing radical anions)*…".

24. Page 25, line 14: Perhaps 'in situ' in place of 'instantaneous'?

Response: Phrase has been changed to "measured in-situ"

25. Page 25, line 30: Can the rate coefficients used in CAPRAM be linked to those recommended by IUPAC?

Response: Unfortunately, there are no IUPAC recommendations for the aqueous phase available right now. However, this task is currently ongoing. In the future, all measured CAPRAM rate coefficients will be linked to IUPAC data. At current, CAPRAM has to be considered as a database with carefully evaluated kinetic data for aqueous phase reactions.

26. Page 27, line 10: 'similar rate constants'.

Response: Corrected.

27. Page 27, line 11: 'well correlated', provide the correlation coefficients.

Response: The correlation of OH and NO_3 rate expressions and statistical analysis data calculated from kinetic data of hydroxyl radical and nitrate radical of the reactions with organic compounds for the various compound classes are given in Table SI-3 of the Supplement. We have made this clear in the revised manuscript.

28. Page 29, line 13: How long is 'long path', the 5 km referred to above?

Response: Quotations around long path have been removed, and the typical path length on the order of several km for the active techniques has now been specified.

29. Page 30, line 3: Perhaps worth noting that a single wavelength measurement is more difficult to identify potential interferences?

Response: This depends on how the measurement is done. For NO_3, with chemical titration by NO combined with 662 nm detection, the measurement is quite specific. The phrase has been modified to include "specificity can be achieved through chemical titration with NO (Brown *et al*. 2001)."

30. Page 31, line 2: Please provide some information regarding the 'Langley-Plot method'.

Response: The Langley-Plot method is now defined in the text. "… by the Langley-Plot method (Noxon et al., 1980), which takes advantage of the different dependence of tropospheric and stratospheric NO_3 slant column density on the Lunar Zenith Angle."

31. Page 32, line 11: Note that DOAS is also an absolute technique.

Response: We agree that DOAS is absolute, but the paragraph in question is not about DOAS, but rather about potential wall losses in CEAS or CRDS instruments with closed sample cells. Since DOAS does not fall in this category of instruments, it is best left out of this list.

32. Page 33, line 17: Quantify the statement 'less good'.

Response: We add a sentence at Page 33, Line 19: “Whereas differences between N_2O_5 measurements were less than 20% in the absence of aerosol, measurements differed up to factor of 2.5 for highest aerosol surface concentrations of $5x10^8$ nm^2cm^{-3}. Also differences between NO_3 measurements showed an increasing trend (up to 50%) with increasing aerosol surface concentration for some instruments.”

33. Page 40, line 6: What was the integration time associated with the 6 ppt detection limit?

Response: Unfortunately, the integration time is not given in the Golz et al. (2001) reference.

34. Page 44, line 1: Superscript in Rˆ2, note that ‘R’ has been quoted elsewhere, it would be good to maintain consistency throughout.

Response: Superscript has been corrected, and the manuscript has been checked to ensure that R^2 is used for correlations throughout.

35. Page 46, line 6: ‘K-puszta’ to ‘Puszta’?

Response: K-puszta is the name of the field station.

36. Page 46, line 29: Why not maintain consistency and use either LO-OOA or SV-OOA throughout?

Response: We note that LO-OOA has been used consistently throughout the manuscript. LO-OOA is used instead of SV-OOA as multiple studies have found that the degree of oxidation of OA does not necessarily correlate with its volatility.

37. Page 48, line 15: Please briefly outline the potential fates of RO2 radicals and how these each impact nitrate formation and the nitrate yield.

Response: The potential fates of the RO_2 radical are listed on page 47, line 28 (they are reaction with NO_3, RO_2, HO_2, or NO). Table 5 summarizes the nitrate yield in current models by RO_2 fate which is sometimes identical for all RO_2 fates. The yield spans from 0 to 100% (page 48, line 6-7). Observed organonitrate yields are covered earlier in the manuscript, and Table 2 summarizes observed organonitrate molar yields.

38. Page 48, line 31: ‘k’ in italics.

Response: Corrected.

39. Page 48, line 33: Multiplication symbol in equation rather than letter ‘x’ (and in following *equations). Units for these equations should be presented in a consistent way with those elsewhere in the manuscript (e.g. in Table 1).*

Response: Multiplication sign has been corrected, and units have been standardized to cm^3 molecule^{-1} s^{-1} throughout

40. Page 60, line 3: 'the SOAS campaign'.

Response: Corrected.

41. Page 60, line 4: Remove the brackets around the reference.

Response: Corrected.

42. Page 66, line 12: Inconsistency between 'modeling' and 'modelling' throughout the manuscript.

Response: This is the only place where "modelling" is used. We have changed it to "modeling" to be consistent with the rest of the manuscript.

43. Page 76, line 22: Space in 'BVOCchemistry'.

Response: Corrected.

44. References: Chemical symbols – some use subscripts, others don't, while some display markup language formatting instructions (e.g. page 92, line 25 onwards).

Response: The subscripts in the references are now properly formatted.