Author response are in blue.

Referee 1

This paper remains a rambling unfocussed document. As I said in my previous review it lacks the organization that would let any but the most determined reader identify what, if anything has been learned. I recommend it be rejected. It started too far from acceptable to have had a proper open review. I don't see how it could become acceptable in one or two more revisions.

We have reorganised the paper substantially. There no longer separate sections on the observations and model results. Instead, they have been combined with much of the description of the observations removed such that the text is far more focussed on the interpretation and so on what is learnt.

I recommend the paper create a new figure or figures with the specific set of rate constants (or ratios of rate constants) the paper is testing. That the figure should guide the reader to thinking about what is already known and what is new in this paper.

This paper is based on field observations, some of which are the first of their kind, and we compare them with a model using a chemical mechanism that is widely used around the world to help evaluate understanding of the isoprene nitrate chemistry. The mechanism is complex and involves many reactions that contribute together to the model outputs and is well-documented elsewhere (Jenkin et al., 2015). We have added a diagram (Fig. 5) specifically to illustrate some of the key reactions in the formation of the IHN to help the reader particularly when thinking about the ratios. In the introduction we have made more reference to the existing Fig. 1 to help the reader understand the aspects of the chemistry that we are examining.

Some other specific comments follow. I have not taken the time to be complete in my suggestions. There are just too many places where this paper is in need of editing and focus.

We can only address the comments that the referee has made.

1) The abstract is 4 paragraphs. We do not consider this to be a problem, but in the rewrite this has been reduced to 3. The last one is inappropriate in an abstract. We are not sure why it is inappropriate, but it has changed in the rewrite. One in the middle includes the phrase, "although the correlation is weak due to their being only a few data points." That paragraph should be removed. It sets the tome for the rest of the paper as a rambling collection of facts and not an attempt to distill what has been learned into some key conclusions. This paragraph has been rewritten and hopefully now reflects the rest of the paper that is more focussed on what has been learnt.

2) All of the discussion in the paper that refers to their being too few data points to draw a strong conclusion should be deleted.

Our field observations are limited by the number of data points we have, but we believe that the relationships that they show, even if not strong, are important as there are virtually no other data of this kind available. They also point to where further research can improve understanding. Referee 3 seems to agree with our view stating, "The measurements made were difficult, and, with the uncertainties added in the revision, represent useful ambient data.".

3) The introduction reads like it was written years ago. I recommend it start with W2018 and articulate key current uncertainties. Going back to papers that quote 4%IN yields that no one following the literature believes any more is not helpful to the reader.

The introduction has been shortened to make it more focused and reference to much of this older research has been removed.

4) The paper would be better if it started with the model predictions and then articulated which aspects of the model predictions the observations are able to test.

We have adopted this approach.

5) If the winter data is unusable, remove discussion of that from the paper.

We have removed all comments about the winter campaign.

6) Section 4.2.1 mixes up a description of what was measured with a comparison to models and other locations. The paper would be clearer if these were completely separated.

This section has been removed in the reorganisation and tightening of focus. We have also reduced the comparison with previous research where comparison is of less relevance.

7) Line 243. The opposite of not surprising, is expected. I recommend the authors describe their results as what was expected. This has been removed when addressing point 6.

8) Line 251, starting the discussion with non-detection of chemicals (and reporting that non-detection is expected) is not a good beginning. The discussion should start with observations that can teach us something. I believe the referee means lines 241. I agree that this is not the most positive of starts. Non-detection can still teach us something and discussion of this is now presented later in the paper.

9) Lines 260-270 there are so many differences in chemical concentrations between these observations and those of SOAS that a direct comparison is not meaningful. The reviewer's point 11 below seems at odds with what they say here. We have however, removed much of this in tightening the focus of the paper.

10) Line 311-313. In what way do these comments about OH advance the theme of this paper. The fact that OH was observed at night is important as it shows that OH initiated oxidation of isoprene can be a source of isoprene nitrates at night, i.e. not just NO_3 initiated oxidation. However, in tightening up the paper this has been removed.

11) Line 315-325 I recommend moving all of the comparison to SOAS to a single location in the paper. We have not done this, largely because much of this comparison has been removed in response to point 9 above.

12) Lines 429-435 and similar paragraphs should be deleted. There is no justification for removing this paragraph, unless this relates to comment 2 above. I have responded to that already. Furthermore, the mention of "few data points" is just one aspect to this paragraph and to say that this paragraph and all like it should be deleted is unwarranted.

13) Line 490-496 lacks a clear focus This was rather descriptive. Much of this text has now been removed in the rewrite.

Referee 3

We appreciate the constructive comments that this referee has provided. They are useful in improving the manuscript.

The paper by Reeves et al. has been significantly improved. The authors have carefully addressed the main issues raised, in my judgement. I feel that the revised paper is a significant contribution to the literature, given the speciated organic nitrate measurements reported here, from isoprene chemistry. The measurements made were difficult, and, with the uncertainties added in the revision, represent useful ambient data.

The paper could be further improved, if there is one more round of edits by again paying less attention to the tedious details (e.g. telling the reader about all the information that is in W2018) and focusing on what is new.

We have made extensive changes to the organisation of the paper to make it more focussed and removing many of the tedious details. References to W2018 in the main text are rather few. However, we have included a summary of the isoprene nitrate chemistry in the supplementary information (SI), much of which is based on W2018. Perhaps this is what the referee refers to. We have included it in the SI to help the more general reader who might not be determined enough to find this information in W2018, which is an extensive paper. We also note that the referee makes minor comments below (19 to 22), which include additions to this section. It is therefore not clear whether they want this removed or not. As it is in the supplementary information, we don't see any need to delete it.

In particular, the Conclusions just repeat what is said in the paper, implying that it wasn't said well enough in the paper. The Conclusions section is an opportunity to paint the big picture as to – what did we learn that is new? A list of the points made in the paper is relatively dull. It would be better to focus on what new understanding was obtained, and at least equally importantly, what needs to be done next (which is there to some extent). Are there suggestions for improved measurements? Better time resolution? Are there laboratory studies that need to be done? What could be done to better understand the fate of nitrooxy-peroxy radicals, etc. I note that with all those standards, it would be trivial to measure all the hydrolysis rates, and information about hydrolysis lifetimes vs aerosol pH and structure are badly needed.

We have rewritten the conclusions to make them more of a synthesis rather than a repetition of points made earlier in the paper. The emphasis is on what was learnt, and we have added more comments on further areas of research required.

Minor edits I would recommend are listed below, in the order they arose in the paper.

1. Line 123 – We used a chemical…
   Typo eliminated in the rewrite.
2. Section 4.1 is not needed, it can be incorporated into the results and discussion, as needed.
   The text about the winter campaign has been deleted in response to comment 5 by reviewer 1. The sentence describing the air quality conditions during the summer campaign has been incorporated into section 3.1 where a brief overview of the campaign is provided.
3. Line 244 – during the Southern Oxidant…
4. Typo eliminated in the rewrite.
5. Line 261 – why would that be? Please speculate. Is O3 highest in the high NO2/NO condition, and is OH highest at that time? Perhaps you can examine the product [OH][isoprene]xGamma.
   We took a look into this, but with nothing conclusive and in tightening the focus of the paper, this comment has been removed.
6. Line 402 – are you assuming that all species are mixing with clean air? This is an assumption that cannot be justified for all species equivalently. Some longer-lived species such as propanone nitrate will likely have significant concentrations in the residual layer, and mix down as the BL height grows, leading to overestimation of the dilution in such a case, if you are treating all species the same. This should be discussed wherever you discuss the mixing issue (e.g. line 579, 592).
   The mixing is dealt with using a loss rate constant and does not make any specific assumptions about the concentrations of the species in the entrained air. However, we do assume the loss rate constant is the same for all species, which in reality will change for the reasons stated by the referee. I thought we had addressed this comment in the last revision with the inclusion of the comments on lines 575 to 578 and again in lines 590-593. We have now added a further comment on this at the end of section 4 and at the beginning of section 5.3.
7. Lines 424 and 425 – this implies that for some days, model and data compare better? If so, say so

We have added this (section 5.1).

8. Lines 426 and 427 – could there be greater evening production or slower loss?
   Yes. Added to section 5.1.
9. Line 432 – than observed…
   Typo corrected.
10. Line 434 – delete comma after that
    Typo corrected.
11. Line 485- this assumes that transport to the surface is not the rate limiting step for deposition of "sticky" species. If you have reason to believe that, say why.
    We do not have a strong reason for saying this so have deleted the paragraph. We have added a comment to the conclusions regarding this being an area that requires further study.
12. Line 525 (paragraph) – I think it would help the discussion to plot the average measured [NO3][isoprene] in Figure 8.
    The model is constrained by observed concentrations of NO_3 and isoprene, so the model diagnostic for the production term of δ-nitrooxy peroxy radicals (INO_2) is $[NO_3][isoprene]k$. We discuss this modelled production term in the text (section 5.2) and do not feel there is any need to include $[NO_3][isoprene]$ to the figure.
13. Line 624 – specify the ratio being discussed.
    Done.
14. Line 638 – comma after 7
    Added.
15. Line 665 – "Our interpretation is limited by the uncertainties in our measurements" – how so?
    This was a rather general comment, but we have added a comment on the need for a more accurate calibration of (1-OH, 2-ONO_2)-IHN. We also note the need for more measurements, which, although not specifically a measurement uncertainty, contributes to the standard deviation in hour of day means.
16. Figure 3 – The two colors in panel c are hard to distinguish. Could you plot radiation on those plots? It would help the reader with the discussion of daytime v. nighttime sources of propanone nitrate.
    We have changed the colours. The vertical gridlines are at each midnight, which we now point out in the figure caption. Note this figure is now Fig. 8.
17. Figure 4 – I think you need legends in the figure – the colors won't work well in the published version.
    The figure caption has been expanded explain the colour coding. Note this figure has now been moved to the supplementary information (Fig. S4).
18. Figure 6 – use a color other than yellow?
    This has been changed. Note this figure is now Fig. 4. We have also changed the colours of Fig. 3 to make it consistent with the colours used in Fig 4.
19. Figure 7 – Why not add a line to panel F that represents the best fit to the data in panel E, for ease of comparison of measured and modelled data (esp. since the scales are different)?
    Lines based on the mean β-IHN ratios for bins of NO have been added to both panel E and F to ease comparison. Note this figure is now Fig. 6.
20. S1.1 – state which values for the branching ratio you used for each ISOPOO.
    This is not very straight forward because, as discussed in this section of the supplementary information and in the main paper, the reactions of these adducts with O_2 to form ISOPOO are reversible and so lead to a redistribution of the ISOPOO which will change as a function of NO. However, we have added the branching ratios that we used for the initial formation of the adducts (Jenkin et al, 2015) for comparison with those recommended by W2018.
21. S1.2 – first line – it should be nitrooxy, I think.
    Typo corrected.

22. S1.3.1 line 6 and line 13 – you should mention production of the organic hydroperoxides when you mention HO2 as a reactant.
    Added
23. In this section you refer to "reaction rates" throughout, when it should say rate constants.
    We have corrected that in this section and throughout the manuscript.

Editor

Given the concerns of the reviewers I recommend you do a careful and extensive revision of the document. Please take all comments into careful consideration including carefully considering a reorganization of the paper as suggested by one of the reviewers. If the paper is hard to follow for experts (and myself) it will be hard for general readers to benefit from the interesting findings.

In our response above, we hope we have demonstrated that we have carefully considered all of the reviewers' comments.

Editor Response

I have read the manuscript carefully and thought about the issue. Here are my thoughts.

1. The measured data is a valuable addition to existing datasets of isoprene oxidation products.

We agree.

2. The manuscript could indeed benefit from some restructuring as one of the reviewers has suggested. You mention in the title the implications for isoprene chemistry. However, these are not spelled out clearly in the abstract or the conclusion. I think the reason is that the manuscript talks extensively about the individual measurements of an array of isoprene oxidation products. It also presents the model results. Both of these are important but it is hard for a reader, at least for me, to follow and understand where the manuscript is going with this. I think it would be useful to focus on the underlying kinetics/processes that, in my humble opinion, are the ones tied to the implications of your work. In other words, what do your measurements tell us about the underlying processes.

We have restructured the manuscript as described above. To focus on the implications, we have shortened the manuscript, removing some of descriptions of the observations and structuring the paper around the comparison of the observations with the model. We also believe that the implications for the chemistry are now more clearly articulated in the Abstract and Conclusions.

3. I thought about how this could be implemented. I think it would be useful, early on in the manuscript, to lay out the processes that for example lay out the ratios of reaction products, be it the 1,2 vs 3,4 position or others. It is my understanding that the current state of understanding of the processes is reflected largely in the model. This could then be followed by the observations and a comparison with the model results. Perhaps some model results could already be used to detail what processes you are discussing, but I am not sure whether that would be putting the cart before the horse, if that is the correct expression.

Within the results sections, we have used the model results to lay out current understanding of the key processes, often putting this first and then using the observations to test this.

4. The conclusion could then focus on the actual implications of your work. What processes/kinetics show statistically significant discrepancies and what could the causes be, e.g., model inputs such as some constraint that may be erroneous, or some other process be it production or loss that may be

misrepresented. I think all of this is already in the document except perhaps what your findings tell us about causes for discrepancies but is somehow hard to get a good synthesis sense of this.

We have now provided more of a synthesis within the Conclusions.

In summary, the manuscript contains valuable data and analysis, but to make it more comprehensible the focus could be shifted more to the scientific understanding rather than listing observations and model results. I admit that as this is a complex chemistry it is difficult to not have the extensive discussion of observations and model results. It may be useful to add some figures that show the processes determining the ratios of e.g., the IHNs and others. as I think it is very hard to grasp this just from text. I do think having a figure(s) that shows what you are trying to understand and then discussing this could be helpful although I admit the complexity of the chemistry makes this challenging…

By removing descriptive text, restructuring the sections and focussing on the discrepancies between the model and the observations, we believe the paper is more focused on the scientific findings and more comprehensible. We have added a diagram (Fig. 5) specifically to illustrate some of the key reactions in the formation of the IHN to help the reader particularly when thinking about the ratios.

Please, do not understand my suggestions as trying to "tell you what to do". I am trying to help to find a pathway to address one of the reviewers concerns and I think shifting to starting with something like a concrete hypothesis that you then test, discuss, and finally suggest where issues my lie could do this.

Thank you for taking the time to provide these useful suggestions, many of which we have followed.