Response to Reviewers' Comments to Manuscript acp-2019-964 "Observations of speciated isoprene nitrates in Beijing: implications for isoprene chemistry" by Reeves et al.

Reviewers' comments are in black upright font.

Our response is in blue italic font.

Referee #1

This data set is likely interesting.

We believe the data are very interesting and our view is supported by reviewer #3 who says "This makes this a highly unique and useful data set for chemically coupled species, and does indeed represent a great opportunity for testing the mechanism for isoprene photooxidation, and studying the impact of isoprene chemistry on the fate of NOx, and for production of ozone and particulate matter.".

However, this paper is long, data rich and is not succinct in its analysis. It is very hard to tell which conclusions are unambiguously supported by the observations and which depend on assumptions about transmission and sensitivity.

On reflection, we agree that the paper is too long and not succinct in analysis and more clarity is required regarding which conclusions are unambiguously supported by the observations.

We have created a much-shortened revised version, in part by removing the simple model analysis completely and section 6.6. We have added uncertainties, and we have rewritten the abstract and conclusions to highlight the key findings.

It is not currently accessible to a general reader of ACP. I recommend it be rejected. Only the most determined reader will be able to wade through this and find the important information and three years from now, no one will be able to identify key ideas that should stand the test of time from ideas that are momentary arguments about different rates constants in a version of MCM and W2018. Today, no one not deeply steeped in the isoprene chemistry will be able to read it and recognize the ideas being tested.

There are many papers published on isoprene chemistry, demonstrating widespread interest in the subject. Many of these papers are themselves very detailed including several published in ACP. This paper identifies areas of uncertainty in mechanisms that can then be addressed through further research. Publishing these results are an important way to advance science.

In shortening the revised version, we have also aimed to make it more accessible to the general ACP reader.

It would greatly benefit from editing in collaboration with someone who is not as engaged in the details. I recommend it be rewritten with many fewer figures. The figures that remain should be chosen to demonstrate how the observations test competing ideas for the behavior of these nitrates.

In shortening the revised version, we have reduced the number of figures from 21 to 9. We have done this combining some figures, reducing the number of things plotted, removing some plots altogether and moving others to the Supplementary Information. We believe key scientific points are now more clearly illustrated.

In addition, the sections on MCM should be more clearly motivated–are there choices MCM has made that are in conflict with W2018. If so is there a logic to them or is MCM just not updated to be consistent with W2018 yet?

The MCM is a widely used chemical mechanism. There is a logic to the choices made, which for isoprene are primarily described in Jenkin et al (2015). Wennberg et al (2018) does consider some more recent findings, but both mechanisms are based on many assumptions, often with few constraining observations. We, therefore, believe it is important to test both against new observations.

Referee #3

The paper by Reeves et al. describes measurements of speciated organic nitrates that are produced from both OH and NO_3 reaction with isoprene. Using a GC/MS approach, they were able to identify and quantify seven different “isoprene nitrates”, specifically, two ïA¸c´-hydroxy nitrates, four ïA¸d’-carbonyl nitrates, and propanone nitrate, in Beijing during the winter of 2016 and summer of 2017. Isomers were generally (not always) identified by injections of samples of the individual synthesized isomers, and quantified with reasonable time resolution (it appears to be hourly, but that is not stated clearly in the manuscript; that should be clarified). What resulted was a highly unique data set for these compounds, in an isoprene-impacted urban environment, with very good supporting chemical measurements, including isoprene, NOx, HOx, RO_2, NO_3, HONO, and HCHO. Many of these measurements are highly challenging. This makes this a highly unique and useful data set for chemically coupled species, and does indeed represent a great opportunity for testing the mechanism for isoprene photooxidation, and studying the impact of isoprene chemistry on the fate of NOx, and for production of ozone and particulate matter. This paper then should be published, and will be high impact, I believe, ……

We appreciate the reviewer recognising the importance of this data set and its value in testing the isoprene photooxidation mechanisms and potential for high impact.

The measurements were made approximately hourly. We have clarified this in the revised manuscript.

…… once one major flaw in the paper is repaired. Specifically, while the data are compared to simulations using MCM chemistry, for both absolute concentrations and ratios of coupled species, these comparisons are extremely difficult to interpret because there is no uncertainty analysis done for these seven compounds. And that lack of detailed uncertainty analysis is a problem in this case because of all the assumptions made, e.g. that sensitivities are the same for the 4,3-IN and the 1,2-IN, and because of issues related to losses of the compounds, e.g. on valves and other surfaces, that clearly have an impact, and these impacts can be different for different isomers, as the authors recognize. So, while they discuss that looking at ratios of isomer concentrations can remove the complexities of boundary layer dynamics, dilution, and ventilation, there is no discussion of the uncertainties of the ratios presented in the various analysis, discussed at length for figures 5, 6, 10, 13, 14, and 15. So, it is possible that the analyses of the these ratios and comparisons to the models are meaningful, but also possible that they contain systematic errors that make the comparison problematic. With no error bars on any of the data, it is impossible to know if the discussions and conclusions are meaningful. Given the likely very large (impressive!) effort in acquiring these data, this is an unfortunate oversight, and needs to be repaired before this paper is published. I recommend a section that does a detailed error analysis for measurements of each isomer, and presents a calculated uncertainty (which could be concentration-dependent) for each one, and also calculates the uncertainty for the ratios that are compared to MCM. The figures could include representative error bars, either on some points, or use shading to reflect the uncertainties, or some other approach. With this added information, this can be a great paper. I note that the last sentence in the paper says “Our interpretation is limited by the uncertainties in our measurements and relatively small data set, but highlights areas of the isoprene chemistry that warrant further study, in particular the NO_3 initiated isoprene degradation chemistry.” This is good to recognize, but the reader has no idea what are the uncertainties in the measurements.

We accept these criticisms.

In the revised manuscript we have included a detailed uncertainty analysis (section 3.3), providing uncertainties for both concentrations and ratios, and included errors bars in the figures. We have modified the discussions and conclusions of the comparison with the model to reflect these uncertainties.

Other comments and relatively minor issues are listed below, in the order they arose in the paper. Comments/issues, in order

Abstract – line 32 could say isoprene-derived organic nitrates (the first time)?

Added

Line 43 – The observed relationship. . .

Corrected.

Line 53 – should say “from” the observed.

Corrected.

Line 92 – This key issue should be explained mechanistically, e.g. showing an example of an alkoxy radical that can decompose, releasing NO_2.

The Wennberg et al (2018) paper is cited and more information is given already in the Supplementary Information (section S1.3), so in the interest in shortening the paper, we decided not to add further explanation here.

Line 167 – sentence needs a period.

Corrected.

Section 3.2 – what do you know about the desorption efficiency from the Tenax trap? Since INs are olefinic, and there is lots of O_3, what do you know about ozonolysis during sampling?

The reviewer is correct to point out that olefinic compounds can be affected by trapping with oxidants, however in our instrument paper (Mills et al 2016, Atmos. Meas.Tech., 9, 4533-4545, doi: 10.5194/amt-9-4533-2016, 2016.) we have demonstrated that our trapping methods are unaffected by ozone or NO_2.

Is the metal valve the only surface on which INs can be (differentially) lost? How do (will) all these things affect your calculated analytical uncertainties? When you knew you had some loss on the valve, did you apply any correction for this? If not, do you have asymmetric error bars?

Regarding differential losses, the inlet and column are not substantially different from the analytical columns and conditions used by CalTech (e.g. Vasquez et al, Atmos. Meas. Tech., doi: 10.5194/amt-11-6815-2018, 2018) so any differential losses in these parts of our system are likely to be similar and very small, consistent with the Caltech group not reporting any such losses. Only the trap and metal valve are significantly different. The metal valve clearly had significant differential losses and we have stated in our experimental section that we have indeed applied corrections for these losses. We have included the uncertainties for these corrections in our uncertainty analysis.

It is possible that the glass sample trap may cause differential losses. For the IHNs we measured in Mills et al (2016), these are accounted for in the overall sensitivity from calibrations of single isomer samples, however we could not do this for the ICN. We used two different sample traps and fittings towards the end of the campaign (with the plastic valve in place), and did not notice any obvious changes in the nature of the data, but this was in a period when we were doing calibrations etc and so there was a period of many hours between the air samples on the two different traps. As far as desorption from the Tenax trap, that is also covered in the Mills et al (2016). Whilst we do not know the exact desorption efficiency or losses, they must be consistent and vary little as the instrument linearity and precision demonstrated in that paper are good and there is no observable carry-over to a subsequent blank.

Lines 204 – 208 – how do these assumptions impact your calculated uncertainties?

The assumptions the reviewer refers to here are regarding ion counts for IN that we were unable to directly calibrate for. We have included these in our measurement uncertainty analysis (section 3.3).

Line 278 – what exactly is the “large uncertainty”? Without these estimates, comparing to model results is an empty exercise.

We have now provided an uncertainty analysis and adjusted the text of this section accordingly.

Line 295 – should be “of” the summer campaign.

Corrected.

Line 322 – since you mention the “appreciable concentrations of OH at night”, and there is a lot of interest in that subject, can you include some representative error bars in Figure 7? The same goes for NO_3; I would like to repeat that there is some really lovely data in this paper, but it would help the reader to know things like LODs and uncertainties.

We have added information on the uncertainties of the supporting data in the Supplementary Information. Measurement uncertainties for OH have been added as error bars to Fig. S2 (old Fig. 3) and shaded areas representing ±1 s.d. in the variability of values for each hour of the day have been added to Fig. 4 (old Fig. 7).

Line 357 – the ratio E-1,4 to E-4,1 is not in Figure 6.

Yes, this was an error in the text. Corrected.

Line 365 – yes, but we don’t know what the uncertainties are!

Addressed in the revised manuscript with the addition of the uncertainty analysis.

Line 400 – I’ll just note that alpha is not known to even two significant figures.

Whilst we agree with the reviewers comment this value is taken from MCM which is given to 3 significant figures. However, we have removed the simple model analysis, so this has been deleted anyway.

Line 415 – Is it known that the -OH group has no impact? What is the uncertainty here?

We use the photolysis rates in the MCM. Without measurements of the photolysis rates of some of the larger VOCs, the MCM uses measured rates for some of the smaller VOCS to represent those of the larger VOCs following the protocols set out in Jenkin et al (1997) and Saunders et al (2003). Jenkin et al (2015) updated the degradation scheme for isoprene, and although the photolysis rates of the higher generation nitrates with carbonyl groups were revised on the basis of work by Muller et al (2014; 2015), no changes were made to the photolysis rates of the hydroxy nitrates. Whilst we accept that the -OH group may have some impact, we believe that the MCM represents the state-of-the-art in terms of scientific understanding and so it is appropriate to use these rates.

Line 417 – how does 4x10-5 s-1 compare to the magnitude of the calculated chemical reaction loss? (since you assume here that all the loss is uptake)

We have removed the simple model analysis and focussed the paper on the MCM model. This has therefore been removed.

Line 443 – Is the upwind environment chemically comparable on a timescale relevant to the lifetimes of these species? If not, there could be significant advective dilution.

We have removed the simple model analysis and focussed the paper on the MCM model. This has therefore been removed.

Line 460 and Figure 10. Consider that the difference between the simple model and the adjusted model is about 25%. Is the uncertainty in the measured ratio smaller than that? If not then this would not be a useful exercise.

We have removed the simple model analysis and focussed the paper on the MCM model. This has therefore been removed.

Line 472 – I am not sure that your analytical system materials are a good proxy for vegetation or urban materials like pavement. And, at night, is the dominant deposition resistance the aerodynamic resistance? If so, we would expect more or less identical deposition rates for these isomers.

Our analytical system materials may not be a good proxy for vegetation or urban materials, but the evidence that exists (i.e. difficulty of getting (1-OH, 2-ONO_2)-IHN through an analytical system and its fast rate of hydrolysis (W2018)) suggest that, if anything, (1-OH, 2-ONO_2)-IHN is more likely to have a faster deposition than that of (4-OH, 3-ONO_2)-IHN.

Line 504 – doesn't this imply that the glyoxal chemistry is very well known? Are there aromatic hydrocarbons present? Other glyoxal precursors? What is your confidence in the model production chemistry for glyoxal?

A range of aromatic species were measured (including benzene, toluene, ethyl benzene, xylenes and tri-methyl benzenes) and used to constrain the model as well as acetylene which is another important glyoxal precursor. As a further check on the physical loss rate imposed, however, the model was run unconstrained to HCHO using the same deposition rates and was found to reproduce the observed HCHO concentrations that were observed during the daytime, but under-predicted the concentrations at night.

Line 552 – delete "the" before "using".

Corrected.

Line 573 – is there a statistically meaningful diel pattern for the observed ratio? It doesn't look like it to me.

No, there is not. The text here is referring to the modelled rather than observed ratio.

We have clarified this in the text.

Line 638 – it would be good to recognize that in chemically reactive environments, NO_3 chemistry can be equally important in the daytime, if the NO_3 production rate is greater in the daytime.

We do not fully understand the point being made by the reviewer. Equally important to what? Night-time chemistry? OH chemistry? We do say "the production of δ-ICN in the model is mostly during the daytime, despite NO_3 usually being considered to be more important at night.". We think this is a clear message as to the importance of NO_3 chemistry during the daytime, based on looking at the modelled source of the δ-ICN.

Line 647 – please recognize that the dilution term depends on the concentration of the species in the diluent air.

Yes, this is an important point and we have added this to the discussion here.

Figure 19 – this makes it clear that given the broad diel cycle, a lot of propanone nitrat arises from transport, and so likely can't be simulated well.

Whilst transport may play a part, the broad diel cycle may also be due to there being both daytime and night-time sources. The chemical lifetime of propanone nitrate does mean that transport is important making it difficult to simulate the observations with a box model, but it is still useful to gain an insight into the dominant chemical production and loss processes.

Line 703 – is it really mostly nighttime and unimportant? What do you know about the propene concentrations and their diel cycle?

Yes, the source of propanone nitrate produced following the NO_3 addition to propene acts predominantly at night-time. Overall, the model results suggest this to be a relatively small source, however, looking at the fluxes again we can see that at night it is often calculated to be the dominant source, and so some of the night-time peaks in propanone nitrate may not come from isoprene.

The text has been changed to reflect this.

Line 733 – why do you believe it to be anthropogenic? I think Section 6.6 could be dropped.

This section has been dropped.

Conclusions – this section is entirely a summary. Instead of restating what is in the paper, can you draw conclusions about what we don't know that we should work on? What are the areas that warrant further study (your important last line)?

The Conclusions sections has been rewritten highlighting what we do not know and areas for further study as suggested.