

Interactive comment on “Observations of speciated isoprene nitrates in Beijing: implications for isoprene chemistry” by Claire E. Reeves et al.

Anonymous Referee #3

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The paper by Reeves et al. describes measurements of speciated organic nitrates that are produced from both OH and NO₃ reaction with isoprene. Using a GC/MS approach, they were able to identify and quantify seven different “isoprene nitrates”, specifically, two α -hydroxy nitrates, four β -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, NO_x, HO_x, RO₂, NO₃, 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 NO_x, and for production of ozone and particulate matter. This paper then should be published, and will be high impact, I believe, 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

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our measurements and relatively small data set, but highlights areas of the isoprene chemistry that warrant further study, in particular the NO₃ initiated isoprene degradation chemistry.” This is good to recognize, but the reader has no idea what are the uncertainties in the measurements. 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)? Line 43 – The observed relationship. . . Line 53 – should say “from” the observed.

Line 92 – This key issue should be explained mechanistically, e.g. showing an example of an alkoxy radical that can decompose, releasing NO₂.

Line 167 – sentence needs a period.

Section 3.2 – what do you know about the desorption efficiency from the Tenax trap? Since INs are olefinic, and there is lots of O₃, what do you know about ozonolysis during sampling? 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? Lines 204 – 208 – how do these assumptions impact your calculated uncertainties? Line 278 – what exactly is the “large uncertainty”? Without these estimates, comparing to model results is an empty exercise.

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

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 NO₃; 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.

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

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

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

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

Line 417 – how does $4 \times 10^{-5} \text{ s}^{-1}$ compare to the magnitude of the calculated chemical reaction loss? (since you assume here that all the loss is uptake)

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.

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.

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.

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?

Line 552 – delete “the” before “using”.

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

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.

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

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

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

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

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