Reviewer comment on "Evaluation of Isoprene Nitrate Chemistry in Detailed Chemical Mechanisms"

Anonymous Referee #1

Referee comment on "Evaluation of isoprene nitrate chemistry in detailed chemical mechanisms" by Alfred W. Mayhew et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-333-RC1, 2022

This manuscript describes an intercomparison between measured isoprene-derived organonitrate species from a polluted megacity in China and simulated mixing ratios of the same organonitrates from box models with three detailed isoprene chemistry mechanisms. Because isoprene is such a critical volatile organic compound (even in urban areas), and because the removal of reactive nitrogen species via organonitrate formation from VOCs like isoprene can play a crucial role in regulating ozone formation, oxidizing capacity, and particulate formation, the accurate modeling of these processes is highly important for simulations of air quality.

The manuscript is quite clear and well-written, and effectively guides the reader through the process and outcomes of the research topic. Some surprisingly large differences arise between the three state-of-the-art mechanisms, but they are clearly described and their impacts well-enumerated. The sensitivity analysis of the INHE uptake term is particularly compelling. However, some aspects of the model-measurement comparisons remain unconvincing, and in particular, how much the reader should read into certain model-measurement discrepancies isn't clear. The manuscript lacks a quantitative assessment of measurement uncertainties even though that very uncertainty -- or, at least, the potential for instrumental sensitivity to the compounds of interest to vary over time due to varying contributions of isobaric isomers -- becomes a crucial message of the manuscript (and one that I think deserves mention in the abstract). More of the manuscript is devoted to the potential for various model processes to influence results, such as ventilation timescales and INHE uptake, but two factors that seem of critical importance for determining model outcomes -- namely, the aqueous hydrolysis of tertiary nitrates and the potential for model-measurement differences in HO2 and NO to affect RO2 fates -- are not quantitatively discussed, which limits the applicability of these results beyond the confines of the present box-model analysis. More detailed questions on these issues are included in the line-numbered comments below.

Finally, it would be very interesting to know what the models determine the fate of the analyzed organonitrates to be, considering that this determines their major impacts on air quality and atmospheric chemistry. To what extent is NOx recycled back to the gas phase or transported out by ventilation? While this could of course open another proverbial can of uncertainty worms, it might at least be worth a mention, especially if there are differences between the mechanisms or between the species analyzed (i.e. IPNs vs. IHNs vs. ICNs).

L 109-110: Can some discussion be provided here about how much uncertainty is introduced by using a single invariant calibration factor for all organonitrate species in the I- CIMS and, on top of that, one that is derived from a non-nitrate compound? In general it would be helpful throughout to add more discussion of the measurement uncertainties when comparing with the models, so that readers can be aware of instances when the model-measurement disagreement may not be statistically significant. It would also be immensely helpful to show the measurement uncertainty on some of the figures, although I understand this would be difficult to combine with the bounds already shown to represent the standard deviations across days.

L 201-208: The daytime ISOPOOH+IEPOX overestimate is likely attributable in part to the model overestimates of HO2, which therefore emphasizes the RO2+HO2 pathway more than measurements suggests. (However, NO is also overestimated in the afternoon, it appears, so I can't be sure of the balance of these compensating errors). It would be interesting to note here that this also suggests the RO2+NO pathway may be underestimated in the models, which would exacerbate daytime overestimates of IHNs. This leads to two points that I think deserve more discussion:

  - first, it looks like the sum of *all* major isoprene first-generation products are drastically overestimated in the afternoon, when MVK, MACR, IEPOX, ISOPOOH, and the nitrates are combined. Could this just be a result of excess isoprene in the model? I see that model isoprene is constrained to the measurements, but perhaps it is the upwind isoprene, not the in situ isoprene, that matters more here.

  - second, I think the reasoning behind not constraining NO and HO2 to measurements is well-described and sound, but it would be worth at least mentioning how different the product distribution would be if these crucial determinants of RO2 pathway were modeled correctly or constrained to measurements. How much of the afternoon model

overestimate of ISOPOOH or of IHN can be explained by the model overestimates of HO2 and NO respectively?

L 213: Terminal losses of tertiary nitrates to aqueous particles can be very rapid (Vasquez et al, 2020), to the extent that under humid, particle-rich conditions this can be the dominant IHN loss pathway. (The effect on other nitrates, like IPNs and ICNs, is not as well characterized, but could still be significant). It seems that this could be incorporated into the box models here with a similar (or even simpler) method to the INHE uptake parameterization, but even if the goal is to avoid doing more simulations, the potential contribution of this pathway should at least be estimated. To what extent could this hydrolysis correct the overestimate in IHN? If other functionalized tertiary nitrates behave similarly, how might hydrolysis affect the modeled ICN, IPN, and C4H7NO5 mixing ratios? And finally, given that the hydrolysis rates seem so isomer-dependent, how well is an isomer-lumping mechanism (like MCM for the IPNs) able to properly simulate this process?

L 216-217: The IPN isomers (excluding isobaric C51NO3, INHE and dihydroxy-nitrooxy-isoprene) have double bonds, which means they should react with ozone and NO3 fairly rapidly. Is this really not included in any of the models? From the mean nighttime levels of NO3 and O3, can the contribution of these potential losses be estimated?

L 217: The reason given here for the modeled IPN diurnal profile is the lack of nighttime loss processes, but that would have the opposite effect from what the models show, which is a gradual but substantial decrease over the course of the night (after the sunset spike) resulting in a minimum at sunrise. If there are no nighttime loss processes, is this gradual decrease due entirely to the mixing-out lifetime, and why is the rapid loss relatively insensitive to the mixing out rates (Fig S3)? It seems, both here and for IHN in figure 9, that the modeled nighttime loss rates are too high (although this may, of course, be alternatively attributed to nighttime sources being too low) -- how can they be reduced?

L 295-308: This potential diurnal variation in calibration factors is very interesting and potentially important both for the conclusions of this paper and the wider community; I'd suggest including a reference to it in the abstract. The varying calibration factor was not

applied to the I- CIMS measurements reported here, was it? Can any quantitative estimate be provided here for how much difference the application of a time-varying calibration factor would make to the measurements reported here and shown in Figure 9? Also, to what extent might the same issue of variable sensitivity come into play for the other compounds measured and reported here -- e.g., the fact that some species isobaric with IHNs (MPRKNO3, MIPKBNO3...) contain carbonyls rather than hydroxyl groups (reducing sensitivity, I believe), and the fact that some C4H7NO5 species are hydroxy-carbonyl-nitrates while others are PANs, nitrooxy-acids, or hydroxperoxy-nitrooxy-alkenes?

L 319-322: Is there any quantitative estimate of the sensitivity difference that can be provided here? Could it be a big enough difference to bring any of the models into agreement with measurements?

Figure 5: I don't think that ozonolysis in the top section is correct; ozonolysis should break the double bond, which would not result in any C4 fragments. (Ozonolysis of 3-hydroxy-4-nitrooxy isoprene would work here though). Also, why are there no co-reactants on the bottom pathway?

Figure 6: Are the different modeled NO traces overlapping, or are some missing? If they're overlapping, that's probably worth mentioning in the caption just to avoid confusion.

Fig S10: The legend seems to say MVK+MACR where it should say ICN.