

We thank the reviewer for their comments, below are point-by-point responses referencing the adjusted manuscript. The line number reference line numbers in the “track changes” document.

Major comments:

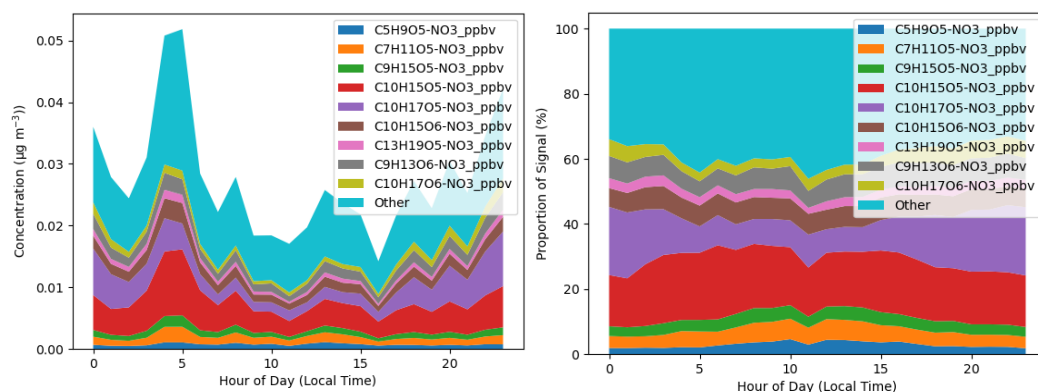
1. I suggest the title to be changed to “The global Importance of Gas-phase Peroxy Radical Accretion Reactions for Secondary Organic Aerosol Loading ” or “.....Secondary Organic Aerosol Budget”. The term “formation” suggests an emphasis on the process, and therefore I thought I would read a lot of content in nucleation, aerosol growth etc...but what the paper primary studies is the impact on aerosol mass and radiation.

As requested, the title has been changed to refer to ‘Aerosol Loading’ as opposed to ‘Formation’.

2. One important piece of information I did not find is how accretion product signals in CIMS were selected. Are they ions with more than 10 carbon? Besides, what signals contribute to the spike at 5 am in Figure 3, and can those species provide insights in the potential source of model-measurement disagreement? Is it possible to do some sort of species-to-species or groups of species comparison with MCM-Accr, even just on molecular formula? There may be some useful information that haven’t been sufficiently utilized in box modeling to address some of the uncertainties and characterize the importance of reaction pathways.

The means by which accretion product signals were selected is outlined in Section 2.2. Specifically, the reported ion masses were compared against species from the MCM-Accr mechanism, and any model masses for which accretion products made up an overwhelming fraction of the mass were selected for comparison. This certainly omits some measured accretion products, but the aim of the filtering was to avoid comparison with signals that may include large amounts of non-accretion products which are not accounted for in the box model’s aerosol partitioning calculations.

Regarding the signals contributing to the measured I-CIMS signal, we have produced the figure below for the interest of this reviewer. As can be seen, the average contribution of the top 9 measured signals (from the subset selected for the accretion product comparison) shows little variation over the course of the day, including during the 5 am spike.



While it would be interesting to investigate trends in individual signals further, it is difficult to make specific comparisons given the uncertainty of sensitivities for individual species/signals. This is why we limited our discussion in the manuscript to demonstrate

that the bulk accretion product concentrations of the model are in-line with the measurements. As noted in previous review responses, we regret that we are not able to be more quantitative in this section but believe that this paper should act as motivation for increased and updated measurements to inform future model representations.

3. Did the AMS use a PM_{2.5} inlet in the field campaigns? The authors may want to clarify, because some AMS measure PM₁, some measure PM_{2.5}, and this may affect the analysis results here.

Both of the AMS datasets used (Amazonia and South-eastern USA) measured sub-micron aerosol. This has been clarified in the manuscript by the addition of the following text:

Line 165 has been changed to read: “Submicron OA measurements from this campaign, measured by aerosol mass...”

Line 168 has been changed to read: “...the AMS measured submicron OA during the GOAMAZON campaign.”

4. In Figure 2 and 3, the diurnal variation in SOAS seems stronger in modeled results than in measurements. In the modeled results, the peak concentration at night can be more than 3 times higher than day-time concentration, but such contrast is less in measurements. What could be the possible reason?

It should be noted that Figure 2 compares the box model results to the GEOS-Chem output, not measured data. As such, the reviewer is instead noting that the box models produce a stronger diurnal than both the GEOS-Chem output and the I-CIMS measurements.

The diurnal profile will be sensitive to the representation of physical processes in the box model, such as varying boundary layer mixing, which can strongly influence species concentrations at the surface. Such physical processes are difficult to represent in box models, particularly for long-lived stable species. We have attempted to represent such processes in this work by accounting for both deposition (scaled by boundary-layer height) and ventilation (scaled based on a reference compound of MVK), which is more complex than the approach taken in many ambient box modelling investigations and has been validated in previous work (Mayhew et al. 2022). Nevertheless, it is not unexpected that the box models are unable to capture the diurnal profile perfectly because of the complexity of representing physical processes.

This has been noted in the paper by adding the following text. This text focuses on the comparison to measurements, since boundary layer dynamics have been shown to be a source of error in GEOS-Chem and so it is best to not rely on the GEOS-Chem output as “truth” when focusing on relatively small discrepancies in the diurnal profile.

Line 332: “The diurnal average profile of the measured and MCM-Accr data show similar trends, with higher night-time concentrations. However, the modelled diurnal is stronger than that observed with I-CIMS. This may suggest that the representation of physical processes in the box model are either removing species too quickly during the day, or not quickly enough at night, particularly for aerosol-phase accretion products.”

5. In Figure 2 and S4, the authors attribute the higher accretion products in GEOS-Chem primarily to the overprediction of NO. In Figure S4, GEOS-Chem did a nice job after 10 am. However in Figure 2b, GEOS-Chem's prediction is still higher by several factors (from 10am-5pm for example). This suggests that besides NO, there are other important drivers for the discrepancy that need to be discussed.

The reviewer is correct that the GEOS-Chem simulation offers good predictions of NO in the afternoon period, which does not correspond to accretion product concentrations in line with the box models in Figure 2. However, given the lifetime of the produced accretion products, the increased production from lower NO concentrations (resulting in more $\text{RO}_2 + \text{RO}_2$ reactions and higher night-time RO_2 concentrations) will produce accretion products that are able to persist over the course of the day. Indeed, the OH loss rate constant of $1 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ used in the GEOS-Chem simulations results in a chemical lifetime of over 1 day (assuming $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$). As such, we maintain that higher production at a given time of day can explain the higher concentrations observed over the course of the whole day.

We do also already mention the potential influence of differences in the representation of physical processes between the box models and GEOS-Chem as an additional source of the difference.

6. If the underprediction of NO by GEOS-Chem is (one of) the main reason for overpredicting the accretion products in SOAS, how is this issue in NO underprediction (or NO simulation uncertainty more generally) addressed later when assessing the global-scale impacts of adding accretion products?

The reviewer is right that there may be errors in GEOS-Chem's representation of NO (both under and over-predictions) that could affect the observed accretion product formation. However, GEOS-Chem's ability to simulate NO concentrations is not directly addressed as part of this investigation as there may be numerous causes of poor NO predictions in different global regions, including both emissions and secondary chemical processes shifting NO/ NO_2 partitioning.

In recognition of this limitation, we have added the following statement to the conclusion.

Line 614: "The representation of NO concentrations in global models like GEOS-Chem is important for accurately representing RO_2 loss pathways, as illustrated by the SOAS model results presented here. Uncertainties in global NO predictions could act to either increase or decrease the presented global accretion product concentrations. Future efforts to produce more mechanistic representations of SOA formation will require confidence in the predictions of gas-phase atmospheric species such as NO and HO_2 through their continued validation against measurements collected over long periods in a range of environments."

7. I agree with one of the previous reviewers that the accretion reactions used in the mechanism should be given. Although the authors provided full reactions in "Code and Data Availability", it would be very nice if the authors can provide a subset of the reactions (for example, even just for one key species) in the SI. This will give the readers ideas on how the chemistry is treated. If the readers are interested, they can then dive deep into the full mechanism.

Given the sizes of the mechanisms produced, it is difficult to summarize them in a way that is both succinct and comprehensive. However, to give the reader an idea of the implementation approach in response to this comment, we have included a handful of examples in a new SI table (Table S4). This table is referenced at Line 144:

“A small selection of reactions has also been listed in Table S4 to demonstrate the implementation.”

Minor comment:

8. Please explain “LVOC” when it first appears in Line 147 (instead of in line 257).

The explanatory sentence has been moved, as requested.