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Reply on RC1

Michael S. Taylor Jr. et al.

Author comment on "Modelling ultrafine particle growth in a flow tube reactor" by Michael S. Taylor Jr. et al., Atmos. Meas. Tech. Discuss.,
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Author Responses to Reviewer Comments

We thank both reviewers for their comments, which give us direction of how to better communicate the goals, results, and conclusions of this work. First, we focus on two key points that appear to be at the center of concern for both reviewers. Specific replies to individual reviewer comments appear after these general comments.

Key point #1: Modeling seems to be incomplete and/or oversimplified.

We see how confusion has arisen over this topic as there are two different types of "modeling" described in the paper, each with a very different intention that also affects how complete they are with respect to detailed models in the literature. First is the SOA formation model (condensation of nonvolatile compounds; oligomerization of semivolatile compounds that have partitioned into the particle phase). This modeling is meant to illustrate the complexity of growth kinetics inside the flow tube, even though we are not able to directly measure it. Think of this model as a simulated growth experiment that we wish to interpret. Second is the model referred to in the title of the manuscript – which is a generic model to interpret flow tube growth data when we don't know the detailed physicochemical processes and parameters needed to accurately calculate SOA formation. Hopefully, these concepts will become clearer in the remainder of this comment.

The goal of this study is to investigate how best to represent complex particle growth kinetics within a flow tube reactor. In a typical flow tube experiment, one measures the input and output conditions to determine a time-averaged measure of growth, which may be difficult to interpret if the growth kinetics change as particles transit through the flow tube. In this work, we use a simplified single-particle growth model for secondary organic aerosol (SOA) formation to illustrate how complex growth kinetics inside a flow tube can arise (Section 2). We then develop and assess a generic interpretive model to represent these complex growth kinetics when the details of SOA formation (chemical reactions on or inside the particle, molecular diffusion within the particle, etc.) are unknown (Section 5).

The SOA formation model used in this study is not meant to be a detailed chemical model of any specific system, but rather to simulate complex growth kinetics in a flow tube. The

model we use is inspired by SOA formation from alpha-pinene ozonolysis since this system is so well studied in the literature. Accordingly, the essential features of this model are a surface-limited process (condensation of nonvolatile material), a volume-limited process (dimer formation in the particle phase that transforms partitioned semivolatile compounds into nonvolatile dimer products), and a range of volume-limited reaction pathways and rates relative to the surface-limited process (multiple semivolatile gas-phase mixing ratios and volatilities that influence their concentrations in the particle phase and hence the dimer formation reaction rate). In the revision, we will provide literature backup for this approach. Of course, a detailed model for alpha-pinene SOA would include a broader range of ozonolysis products and particle phase reactions along with relevant physicochemical properties, for example hindered molecular diffusivity in the particle phase – all of which would affect how much growth occurs due to dimer formation. However, such a detailed model is not needed to draw basic conclusions.

We will rewrite parts of the abstract, introduction, and modeling procedure sections to emphasize the above points about the SOA formation model. Again, please think of this as the simulated data we use to test the interpretive model discussed below.

A related change we will make is to replace the term “growth yield” with “growth factor”. It is still represented the same way in the modeling equations (i.e. a product “yield” for ozonolysis of the precursor compound), but we hope that the change of wording will further emphasize that we’re not trying to perform detailed modeling of a specific SOA reaction, but rather to define a parameter that empirically describes particle growth when no such detailed model exists.

The “modeling” referred to in the title is the second type of modeling, which is used to interpret flow tube data as described in Section 5. This interpretive model calculates a growth factor based on the particle diameter change between the inlet and outlet of the flow tube as simulated by the modeling procedure of Section 2. This interpretive model assumes that the growth factor is constant inside the flow tube. However, the SOA formation model (simulation) shows that even under simplified reaction conditions, the growth factor is NOT constant as particles move through the flow tube. So, the question arises (and is answered by the results): How closely does the growth factor from interpretive modeling correspond to the actual range of growth factors inside the flow tube?

Key point #2: Consolidation of figures will more effectively convey the significance of this work.

We plan just five figures for the revision. These are described below along with significance.

Figure 1 – This figure will consist of slight reformatting of Figures 1a and 1b in the original paper. This figure introduces the concept of growth factor in the context of particle growth under atmospheric conditions. Growth factor summarizes the net amount of the reacted precursor that goes into the particle phase during a specific time period – whether it irreversibly condenses, reversibly partitions, or irreversibly/reversibly forms dimers.

Figure 2 – This figure will consist of Figures 4a and 4b in the original paper, which simulates how particles are growing in the flow tube. Key points are: 1) one must use much higher mixing ratios than ambient conditions in order to obtain measurable growth over the short time period of the flow tube, and 2) growth factor changes over the time period of particles in the flow tube, illustrating the complexity of growth kinetics. This complexity arises from rapid partitioning of material to the particle phase when the

particle first enters the flow tube, and the changing rates of surface-limited vs. volume-limited growth processes as particles move through the flow tube.

Figure 3 – This figure will consist of Figure 6a in the original paper. The idea here is that the high mixing ratios of reactants in the flow tube cause the kinetics of particle growth (volume vs. surface-area limited) to be much different from that in the atmosphere. As the reactant mixing ratios increase, surface-limited growth begins to win out over volume-limited growth.

Figure 4 – This figure will consist of Figure 9 in the original paper. This figure illustrates how aerosol liquid water can enhance particle growth, and in particular shows that even just a few monolayers of water on the surface of an effloresced particles have the ability to substantially increase the growth rate.

Figure 5 – This figure will be a modified version of Figure 10 in the original paper. This figure compares the growth factor obtained from interpretive modeling of particle growth based on inlet-outlet change in particle diameter (Section 5) to the average growth factor associated with the simulated kinetics inside the flow tube (Section 2) as embodied by the Figures 2-4 in the revision. Interpretive modeling is found to be a robust way of describing particle growth when the changing growth kinetics within the flow tube are unknown. It can be used, for example, to empirically quantify the differences in particle growth due to changing precursor mixing ratios (Figure 3) or different amounts of aerosol liquid water (Figure 4).

Specific Responses to Reviewer 1 Comments

Comment: I find the concept [growth yield] and its value a little difficult to grasp.

Response: Hopefully, the above discussion provides clarity (renaming to growth factor; improved discussion of the motivation for the modeling approach used). We will also revise section 2.3 to indicate why we introduce this term – specifically, one cannot directly compare growth rates (nm/hr) in flow tube experiments if the condensation sink changes from one experiment to the next. Therefore, we need to define a new parameter that takes condensation sink into account.

Comment: Model was not applied to any measurements in this paper... I worry that because of the complexity of most reaction systems that it is difficult to constrain the model.

Response: Hopefully, the above discussion provides clarity (the SOA “model” is meant just to simulate complex growth in the flow tube). As we stated above, working with actual data requires too much of an expansion of the paper, making it unwieldy. Besides, we still would not know how the growth kinetics change inside the flow tube.

Specific comment 1: Why don't the more volatile SVOCs contribute to the growth yield?

Response: For the simplified SOA formation model we use, we find that they don't contribute substantially to the growth we calculate, so we don't include them. It is conceivable that a more detailed SOA formation model would cause more highly volatile SVOCs to contribute to growth.

Specific comment 2: How well are the rates of loss of products to the walls understood, and how does this impact the modeling?

Response: We will add some discussion of this point, but actually it is beyond the scope of this paper. In our experimental work, we switch back and forth between two sets of conditions in a manner that keeps the wall condition the same.

Specific comment 3: What happens to the model when dimer formation is treated as reversible instead of irreversible?

Response: Hopefully, our general comments above clarify why we don't use a more sophisticated SOA formation model for this work. If we were to include reversible dimer formation in the simulation, it could reduce the amount of growth one observes depending on the timescale of dimer dissociation relative to the timescale of the experiment. The result would be a lower growth factor for both the simulated flow tube data and the interpretive modeling, but the conclusion would be the same – that interpretive modeling gives a robust measure of growth kinetics (Figure 5 of the revision).

Specific comment 4: Isn't water likely to affect the dimer formation process?

Response: Yes, it is likely that dimer formation reactions are somewhat different in organic and aqueous media. The goal of this work is not to accurately represent that, but simply to show that the volume associated with a few monolayers of water on the particle surface have the potential to substantially enhance SOA growth. We will add clarifying text to the manuscript on this point. We include this in the paper because it is not intuitively obvious that a small amount of surface water could have such a large effect.

Response to technical comments: Problems noted by the reviewer in lines 157 and 190 will be corrected.