Anonymous Referee #1

Received and published: 20 February 2019

In the manuscript "Photolytically-Generated Sulfuric Acid and Particle Formation: Dependence on Precursor Species", the authors Hanson et al. present a set of well carried out flow tube experiments of sulfuric acid formation and new-particle formation. The experiments, accompanied by model simulations, are explained very well, and the analysis and interpretation of the obtained data is convincing (though I feel could be streamlined a bit). I especially like the good level of detail in section 2 ("Methods"). The paper concludes with a comparison of the experimental results to existing literature and discusses the effects mainly of adding base compounds (ammonia and dimethylamine) to the system – not only in the authors' experiments, but at this kind of new-particle formation experiments in general. In total, I think this is interesting work that deserves publication. I did find several points where the manuscript could be substantially improved or at least clarified. I think that overall these "main comments" concern details of how the results are presented, but I believe they need to be considered prior to acceptance. Finally, although this is a convincing, interesting and detailed study of flow tube SA nucleation (and including an interesting application of the authors' model, which seems to work out quite well), I have found that scientifically it eventually "only" corroborates our existing understanding, at least mostly. I.e. it has remained unclear to me what aspects of the study ultimately contribute "new knowledge". The authors may in general want to better work out where such added value (to the community) exactly lies.

Comment [R1]: We agree with this point and believe this reviewer detailed this issue in their comment at the bottom of C4 regarding a more systematic presentation of the results. Indeed, we consolidated three size distributions into 1 figure (moving the majority of the data in these 3 distribution plots to the supplement) and we also consolidated two data sets into one figure where Np is plotted vs Q4.

Comment [R2]: We have a new title (see next comment) and reworked the abstract to better summarize the added value of this work.

Main comments:

A central topic of the Title, i.e. the role of precursor species in H2SO4 new-particle formation, seems not well represented in the introduction. I suggest better guidance here (in the intro) for the reader as to where the paper will be heading to (hopefully, presuming at this stage, to the role of precursor species). Indeed, it kind of remains unclear, at first, what is actually meant by 'precursor' (e.g. after reading the abstract). And the word 'precursor' actually only appears once in the entire text, referring (I believe) to involved in the reactions leading to the formation of H2SO4. But it hasn't been clear to me until quite a bit into reading the manuscript, if this was the (only) kind of 'precursor' the authors had in mind with the title. ... Finally, after reading the manuscript, I actually doubt that the title is appropriate, as I don't actually see the "dependence on precursor species" in both SA and particle production as a main topic of the work as a whole. Maybe that will change in a revised manuscript. But essentially, I am seeing a study of SA formation and subsequent particle formation, with most of the work going into explaining what drives particle formation and growth rates. It is certainly carefully carried out and explained (and almost throughout nice to read), but ends up mostly confirming the community's understanding of the underlying processes. 'Dependence on precursor species' is part of this, but I feel it is not the overall "new thing" here.

Comment [R3]: New title: "H2SO4 and particle production in a Photolytic Flow Reactor. Chemical modeling, cluster thermodynamics and contamination issues "

Fig. 2 would benefit from a discussion, better (if possible) display of, uncertainty estimates. E.g., the authors themselves mention large corrections applied in case of small particle sizes (section 3.1, 2nd paragraph).

Comment [R4]: We added a paragraph on uncertainties in Supplement S4. The bottom line is that random uncertainties are small and scatter is likely due to (small ?) temperature fluctuations. This comment also prompted us to add a section (S1.0) to the Supplement showing raw data from a typical run and a table that shows the correction factors.

Page 6, line 5 & Fig. 2: Has the change in particle size distributions (PSD) between 2/23 and 5/15 (Fig. 2b) occurred gradually? With only those two chosen dates shown in Fig. 2b, one wonders how reproducible the PSD were overall, also considering substantial variations in 'baseline' total number concentrations (Fig. 2a).

Comment [R5]: We were prompted to examine more data and we finalized and thus added data to the paper: from mid-May through June 20. We therefore added several distributions to the former Fig. 2a, added a second figure for the new data and moved them both to the Supplement. The distributions do not show a clear secular trend outside the scatter. There are time periods with unique characteristics in N_p and D_{le} (in the new Fig. 2 a nd b) but we now state that, within the scatter, there is not a substantive change since the mesh was installed.

Fig. 4: The legend of panel (a) needs some explanation. The last sentence of the caption misses a verb or something.

Comment [R6]: Fig. 4a is moved to the Supplement and its caption was better explained.

Section 3.2.2 (varying SO_2) First (page 9, line 5 & Fig. 5, I suggest to also show the model case excluding the HO_2+SO_2 reaction be in Fig. 5. That would quickly illustrate how model results improve and also make this paragraph easier to understand.

Comment [R7]: This is now done and there is a clear difference in the model runs. Note also that we updated the model to use thermodynamics better suited for 52% RH which greatly affects predictions for the binary system. See the next comment for more details.

Then, I am not sure I completely follow the matter of the NH_3. 70 pptv of NH_3 at inlet were assumed in the modeling (also lines in Fig. 5), but do I understand correctly that no NH_3 was added for the experimental data shown, and NH_3 is assumed as contaminant? Especially, as later in this section the potential role of ppq levels of dimethylamine is discussed, I'd be curious to see how the model would play out in the absence of any contaminant (i.e. also without NH_3). That would maybe lead to the question: How much dimethylamine would be needed INSTEAD of NH_3 to _fit the experimental data? Again, I might have run into a misunderstanding, in which case some clarification would benefit the section...

Comment [R8]: This comment prompted a hard look at this issue. (1) We realized that the 16 % RH thermodynamics we had used poorly represents the binary kinetics at 52 % RH. Thus a new set of H_2SO_4-H_2O thermodynamics for 52 % RH was developed using the methodology outlined in Panta et al. 2012. A new section in the Supplement (S8) contains a description of this process and lists the new 52% RH and the (old) 16 % RH cluster free energies.

Comment [R9]: The binary (absence of contaminant) model results are significantly lower than the experimental work. We had pointed out in the previous version that 5 ppqv of dimethylamine gave the same Np as 70 pptv ammonia, a finding that has not changed. We are preparing a new section in the paper **(3.3. Modeled Contaminant levels**; the current 3.3 will be renamed 3.4) that presents these comparisons in detail. This section will focus on characterizing the type and amount of possible contaminant in PhoFR.

Fig. 6: The legend of panel (b) needs some explanation. (Cf. comment on Fig. 4 above.) Same issue also in Figs. 9 and 10.

Comment [R10]: Fig. 6(a) was also moved to the Supplement and its caption was fixed. The Np information from the distributions in Figs. 9 and 10 are plotted in Fig. 4a and one distribution is plotted in Fig. 4b. Figs. 9 and 10 are included in the supplement (S3.2).

Comparing Figs. 6b and 4a, and as per the related discussions in section 3.2, it looks like the addition of NH_3 makes the leading-edge mode easier to fit, as the <10-nm minimum is more pronounced. This is in agreement with the model simulations (Fig. S1). However, in Fig. 2b (and discussion), the less pronounced minimum had been attributed to more contaminants contributing to new-particle formation in the earlier (vs later) times of spring. (Actually, Fig. 2b vs. Fig. S1 is already discussed in section 3.1 also.) So from that, one could conclude at least that "contaminant" 6= NH_3. But following the CLOUD works and others, it seems most likely however that NH_3 or other base compounds (amines) would be the primar suspects as for the kind of contaminant suspected. So I see a contradiction here. To resolve that, I suggest the authors discuss somewhere, how purported contaminants would make that minimum (_2.4nm) less pronounced, whereas if bases ("contaminants") were added upstream the opposite would be observed. (And, if applicable, if effective contaminants to blame for Fig. 2b could be something other than bases.) Is it merely the different spatial distribution of contaminants vs. added bases in the flow tube? But if so, does the model manage to simulate those observations, and how does that align with my comment on (understanding of) section 3.2.2 above?

C3

Comment [R11]: This was a temporal minimum as discussed above in R5.

Comment [R12]: We agree.

Comment [R13]: It is also the type of contaminant: added DMA at the top gives a differently shaped distribution than added NH_3 at the top. We have greatly expanded the S1.3 Model results in the Supplement to show this. The new section 3.3 in the paper, discussed in R9 above, will discuss these issues.

Section 3.2.3, last paragraph: Is the DMA simulation (I assume it is simulation results) shown somewhere? What is "experiment base"? Not sure I understant that sentence. And maybe as a consequence, I am also not sure I understand the follow-up sentence (page 10, line 1). In any case, I think the sudden introduction of amides and some not-more-closely defined "strength" is confusing.

Comment [R14]: The DMA simulations will be presented in different contexts in new section 3.3 and in the supplement. The variation with SO_2 and contaminant as DMA was mostly speculative and the paragraph at the end of 3.2.2 will be removed. The DMA model results are discussed in terms of the shapes of the size distributions and how they differ from the NH_3 model results.
The word base in 'experiment base' was a mistake and it should be 'experiment '.

Section 3.2.6, DMA additions: It is stated that Np increases _linearly with [DMA]. Could be good to show, similarly to Fig. 8? (In the Supplement possibly.) Same for D_le. Actually, there is reference to a Np-vs-[SA] figure in the Supplement, but again it is very hard to find it.
Not sure how that would work out, but maybe there could be unified plots of N_p vs. [X] (and of D_le vs. [X]), i.e. showing all X in one figure. In general, the various effects

Comment [R15]: With the new organization of the data, this section is now largely re-written. We back off of using linear to describe the behavior of Np with DMA level (only three data points).

of changing inputs on N_p and D_le are presented somewhat inconsistently. E.g., N_p vs [NH3] is shown (Fig. 7), but N_p vs [DMA] is not, neither is D_le vs [NH3] (whereas D_le vs [HONO] and D_le vs [RH] are shown). Another example is maybe Fig. S9 in the Supplement: It shows model results together with experimental data for some cases but not for others. I could imagine that the paper would benefit from a more systematic presentation of the various results.

Page 13, line 27 vs. line 10 & Fig. 11: First (and Fig. 11), it says that the H2SO4-power dependence here was close to those by Yu et al. and the findings from CLOUD. Then, a H2SO4-power dependence from CLOUD of 2.6 is mentioned to be somewhat lower than the one found here. Why this difference (apparent contradiction)?

Minor comments:
Page 2, paragraph starting at line 12: Instead of only listing the questions approached by the community in recent years, I think it would be more instructive to also shortly summarize the state-of-the-art in our ability to answer the listed questions.

Page 2, paragraph starting at line 18: Not clear, what levels of contaminant base compounds were (a) determined or estimated to have been present in the cited past studies vs. (b) suggested to have played a role in altering the outcome of the respective results.

Page 3, line 4: Though clarified later, I was confused here, if the results presented in the paper were all obtained with that Teflon screen in place, or only some? Anyway though, how was the "jetting" from the inlets manifest, so that it was decided to include the screen? In other words, why was it decided to put the mesh there?

Page 7, line 18: I am unfamiliar with the meaning of "truncated" here.

Fig. 5: Caption mentions orange lines, but plots are B&W.

Page 9, line 31: Please indicate more precisely where in the Supplement the information is. I couldn't actually find the place for certain.

Page 10, line 5: Don't see red squares in Fig. 7.

Page 10, line 8: Again, would prefer a more specific reference to where in the Supplement.

Page 13 & Fig. 11: As the Sipila et al. (2010) results are discussed, it could be nice to present them also in some way in Fig. 11.

Page 13, line 33 (and before/after): I can't quite follow these sentences, pitching the Glasoe et al. data against various other datasets (including the present one). Please clarify. To accompany the discussion of the effects of NH3, it may be illustrative to show a figure similar to Fig. 11 (i.e. comparison to literature results) but showing J-vs-[NH3].

Fig. 9 has two sets of data for DMA = 0 pptv (one denoted as "0", the other as "0.0" in the caption). Is there a difference or where these just repeats?

Fig. 11, including caption: Explanation of the dotted line and the marking "xˆ3.7" is missing. It would also be good to be more precise with the citations in the legend. (E.g., "Kurten, 292K" doesn't assure me I'll be ending up with the correct work if I decide to check it out.)

Fig. S5 misses a caption.

Fig. S9 as well.

Comment [R16]: Figs. 4 and 6 have the data consolidated in such a manner. The D_le for the Fig 2a data is plotted in 2b just below the Np data. The consolidation within the paper and supplement we believe has led to a more systematic line of reasoning.

Comment [R17]: Line 10 is referring to the binary system and line 27 refers to the added ammonia cases. We will provide a reference for the CLOUD 2.6 power dependency.

Comment [R18]: We have significantly re-worked this paragraph and the following, listing the state of the art information and also categorizing these uncertainties: known and somewhat quantifiable and truly unknown.

Comment [R19]: We added phrases to answer these questions and to further clarify these statements.

Comment [R20]: Another reference to the date Feb. 23 has been added. There is an indicator in Fig. 2a at this date.

Comment [R21]: We did flow visualization experiments, as discussed in our much earlier work in Ball et al. (sentence added on p. 6.)

Comment [R22]: This word was not used in the revised text.

Comment [R23]: They were orange in a draft version, which we overlooked upon editing. Caption is fixed.

Comment [R24]: The 3 ppqv DMA data was erroneously listed here; should have been noted as 5 ppqv (Fig. S9). This text will be included in the new section 3.3: Modeled Contaminant Levels.

Comment [R25]: They are black in the submitted version (they were once red in a draft.) In the revised figure they will be red again. And the data at lower Q4 will be yellow.

Comment [R26]: This was Fig. S8 and its new designation will be inserted here.

Comment [R27]: Yes, now included.

Comment [R28]: This is a delicate point and we were too careful in our wording. It will be expanded in the new version. We are pessimistic but will explore the possibility of a comparison figure including results from other experiments.

Comment [R29]: There were repeats: just before and just after DMA was added. These plots will be moved to the supplement (S4).

Comment [R30]: We have heavily re-worked Fig. 11 and its caption; it will likely be Fig. 9 in the revised manuscript.

Comment [R31]: Added. Now it is called Fig. S3.2.

Comment [R32]: Captions are now added for former figures S8 and S9.

Anonymous Referee #2

Received and published: 28 February 2019

The paper by Hanson et al. reports on measurements made with a photolytic flow reactor (PhoFR). The PhoFR is used for nucleation studies where new particle formation is initiated from reactions involving mainly sulfuric acid and water. Additional measurements were made by adding base molecules, i.e., either diluted ammonia or dimethylamine are added to the flow reactor. The sulfuric acid is generated from the photolysis of HONO and further reactions involving SO2, O2 and H2O. After a reaction time of approximately 30 s the particle size distribution is determined with a nano-differential mobility analyzer and a condensation particle counter using diethylene glycol. The measured size range covers diameters from approximately 2 nm to the largest sizes the particles can reach after the short reaction time, i.e., _10 nm. The particle number from integration of the size distribution is used to derive new particle formation rates. C1 With this information, the values from the present study are compared with other experiments and especially for the binary experiments (sulfuric acid and water); the data from the present study agree well with other data from the literature. For the ternary experiments involving ammonia, some discrepancy is reported. Further results are presented that show the variation of the integrated particle number and the particle size with the concentration for different gases. Results from a model involving various gas-phase reactions and the photolysis of HONO are shown for a comparison. Hanson et al. are also suggesting that a reaction between HO2 and SO2 could be relevant for forming sulfuric acid for the conditions of their flow tube experiment. I mainly agree with the conclusions drawn by the authors and the experimental data are mostly carefully evaluated and discussed. However, there is one major concern I am having regarding the experiments that involved ammonia (see below). After this point is addressed in a revised manuscript, I recommend publication in ACP.

(1) The bases (either ammonia or dimethylamine) are added from a sidearm into the flow reactor. The concern I am having is that this geometry does not ensure proper mixing and homogeneous distribution of the base. This possibility should be discussed and ideally, it should be evaluated in how far the mixing is homogeneous and if incomplete mixing could have influenced the results. For example, the results shown in Figure 7 suggest a relatively weak dependency of particle formation with the ammonia mixing ratio that is not consistent with other studies cited by the authors. Could this be related to the way the base is introduced into the flows? Another factor that can have an influence on the ammonia concentration is the mesh that is present in the flow reactor. It seems that the diluted NH3 needs to pass that mesh before it can contribute to new particle formation. Almost certainly, some of the ammonia will be lost on the surfaces of the mesh, especially since its surface is acidic (as it has been soaked in a dilute sulfuric acid solution). More discussion related to these questions is required in the revised manuscript.

Further comments:

C2

P4, L4: Please use the correct spelling for some of the references (e.g., Sipilä et al. but also others). In addition, the references should be checked; for some of them, the year is not correct in the list or has not been cited correctly in the text

P3, L8: μmol / mol ?

P3, L12: I think the word “additions” should be deleted

P4, L12: The year is missing here for the reference to Lovejoy et al.; this is the case also for other references in the main text

P5, L4: Does the outcome of the model depend on the flow setting? What mode is the “correct” one?

P5, L14: As can be seen from Fig. 1a the base is added from a sidearm at the end of the conical glass piece. Based on the geometry and the rather low flow rates it seems unlikely that the base is equally distributed over the whole cross section of the reactor. Has the possibility of inhomogeneous mixing been examined?

Comment [R33]: We have added two sections in the Supplement (S3 and S7.1) explaining the findings from our previous publications on this topic and we present results from model simulations that mimic inhomogeneous mixing (Figures S7.1).

Comment [R34]: Yes, data are not consistent with calculations based on the thermodynamics derived from some of our previous data. One of our conclusions in this paper is that the Glasoe et al. ammonia data may have been affected by small amounts of amines that were carried in with the ammonia. For the present experiments, base was introduced in a similar manner as was doen for Glasoe et al. We were very careful in the present experimental work to never expose the ammonia dilution system to any other base species.

Comment [R35]: We have clarified in the text and in Fig. 1 that the mesh is upstream of the base addition port.

Comment [R36]: We apologize for our poor attention to detail in our reference list. Many have been fixed and we discovered we had missed some in the list.

Comment [R37]: Yes.

Comment [R38]: Correct.

Comment [R39]: Done.

Comment [R40]: Good questions and a new section in the Supplement was added, S7.2. The modeled Np depends only slightly on which radial profile is selected. The distributions do change significantly between plug and laminar shown in S7.2. We present evidence that laminar flow is expected.

Comment [R41]: This issue is important (also brought up in R1) as it goes to how well the model can be compared to experiment. Our previous CFD work (Hanson et al. 2017) was a 3D model and thus could explicitly take mixing into account. In that work we also detailed the model used here (called 2D-LFR in that work) and presented an alternative way that base could be introduced in the model that would mimic - in part and maybe good enough - the inhomogeniety of the mixing. This mimic was to confine the base into the middle 1/4 of the mass flow. We add such simulations here and present them in the supplement (S7.1) with a reference to this section in the main text.

P5, L27: ". . . data were binned . . ."; please check the whole manuscript and use plural when using the word data

Comment [R42]: Thank you.

P6, L7: In the SI a detailed definition for the leading edge is provided; it would be good to provide a reference here to the SI regarding this exact definition

Comment [R43]: Will do.

P7; L23: A definition for Z is missing

Comment [R44]: We took out this text. It was replaced by text describing a similar point.

P8, L10 to L11: The process described here (scavenging of H_2SO_4 on the particles) is particle growth by condensation, which should be linear with the concentration of the condensing vapor (see, e.g., Nieminen, T., et al., 2010 ACP). Therefore, I do not understand this argument.

Comment [R45]: We no longer discuss the departure from linearity as it applies to only about 5 data points. Yet we want to clarify: we were arguing that as particle surface area grows, it begins to become a significant loss process compared to wall loss. So no longer would H_2SO_4 be linear with HONO.

P9, L1: It would be good to include also curves from the model that do not include the $HO_2 + SO_2$ reaction in order to see the difference.

Comment [R46]: Done.

C3

P9, L6: ppmv instead of pptv?

Comment [R47]: Correct.

P9, L12 to L16: I might have missed this but how exactly is the nucleation of particles modeled? The model needs to include evaporation rates for the smallest clusters. How are they obtained?

Comment [R48]: The thermodynamics of the clusters largely determine their evaporation rates and they are included in the model. Please see Hanson et al. 2017. Note we also added a section in the Supplement with cluster free energies.

P9, L28 to L30: In this context, it should be noted that the factor of a 100 refers to the ratio of experiments with several hundred pptv and 4 pptv (which is the estimated contaminant level at 292 K in the Kürten et al. (2016, JGRA) study). For lower baseline (contaminant) NH_3 the enhancement factor is very likely much larger.

Comment [R49]: Lines 26 and 27 are very much in line with this assertion. However, the sulfuric acid levels were very much different between those experiments and the CLOUD study and we feel we cannot draw the conclusion suggested here no matter how reasonable it is.

P9, L32: Is the conclusion then that the contaminant ammonia level is _70 pptv for the set-up of the present study? This higher contaminant level (relative to the CLOUD experiment) could possibly explain the differences between the present and the Kirkby et al. (2011, Nature) study (Fig. 11).

Comment [R50]: The contaminant is consistent with 70 pptv NH_3. This seems a rather high level to not be depleted by simple evaporation. And the simulations with DMA at ~0.005 pptv shows that gas-phase DMA gets depleted by clusters and variation with HONO doesn't match experiment. So we consider other base species like amides that are of intermediate strength in nucleation. We are adding discussion of the model simulations in a new section (3.3) in the paper.

P9, L33: Delete the word "base"

Comment [R51]: Thank you.

P10, L5: Replace "red squares" with "open squares"

Comment [R52]: We now have red and yellow open squares in the new figure.

P10, L10: The slope in Fig. 7 seems to be closer to 0.5 than to 1. How can this be explained?

Comment [R53]: The reviewer must have thought this was a log-log plot? The data were represented by a fitted line in that plot. But this plot is superseded by the new figure 6 which is a semi-log plot and includes more data. The whole discussion on the linearity of this data has changed.

P11, L24: Delete the word "and"

Comment [R54]: Replaced with a comma.

P13, L33-L34: This is one possibility; however, further discussion regarding the uncertainties of the present study is necessary. First, how would inhomogeneous mixing (of NH_3) influence the outcome of the present study? Second, is it possible that NH_3 is lost on the Teflon screen between the conical and the cylindrical glass pieces? It is mentioned that the screen was soaked in a dilute H_2SO_4 solution. Therefore, it could be that a significant fraction of NH_3 was lost on the mesh, which could lead to lower Np in comparison to the previous studies (Glasoe et al., 2015 JGR and Hanson et al., 2017 JPhysChemA).

Comment [R55]: Loss on the mesh and inhomogenieties are not issues as discussed in R1,R3 and R9 above.

C4

P22, Fig4, L4: Please include "the CPC" before "raw count rate"

Comment [R56]: No longer applicable in this plot but in the new Fig. S1 CPC was added.

P23, L4: "orange line", please check

Comment [R57]: Done.

SI:
P6, S5.2: The PTrMS is mentioned here. In terms of checking the homogeneity of NH_3 in the flow through the reactor, this instrument could possibly be used to measure ammonia at the outlet of the reactor when the lights are off.

Comment [R58]: Since ammonia is lost on the wall, very little makes it to the end of the tube. This was also the case for the Glasoe et al. experimental work. The model assumes diffusion limited loss to the wall and there is less than 1 % of the added ammonia that exits the flow reactor. More important, the model suggests that the diffusion-limited-wall-loss radial profile for ammonia is established after a length of about 15 cm. Please see the two figures below.

P7, L3 to L4: References are missing here and the last sentence is incomplete.

Comment [R59]: These are fixed. Note: we re-confirmed the analysis and present equations to derive photolysis rates from the isoprene photoxidation results. There is no substantive change in the calculated photolysis rate.

P7, end of section S5.2: It should be explained why exactly this is consistent with expectations.

Comment [R60]: True. This data is now shown in a separate plot (Fig. S5.2 right) and it was analyzed in the text as well.

P7, S6, end of first paragraph: It is mentioned here that Np increases with time for a set NH_3. If this is the case, how are the results with ammonia exactly obtained? Were the data only evaluated after a long enough waiting time? How long was this period and did the Np level off eventually for all measurements?

Comment [R61]: An increase in Np with time was noticed only when 2000 pptv was added and it was particularly dramatic on the second consecutive day as can be seen in the figure. For all the other base-added measurements, counts were generally stable after an initial surge in Np (e.g. 20 min) upon introduction of the base-addition tube into PhoFR. This initial surge can be seen in Fig. S1 in the new S1.0 section with raw data plotted vs. time.

P8, Table 1: The model does not seem to include the photolysis of NO_2. This can lead to an increased NO concentration and in turn increase OH (from HO_2 + NO). Photolysis of H_2O_2 can further enhance the OH level. When these reactions are implemented, is there still a need to include the HO_2 + SO_2 reaction? Furthermore, is the presence of HNO_3 further considered? It could possibly also be taken up by the aerosols.

Comment [R62]: These are astute comments and we agree that this chemistry occurs. We think those reactions are negligible though, compared to the first-order photolysis of HONO and reaction of HO_2 with NO. NO_2 photolysis would occur but less than 10 % would be depleted over the course of the reactor: we will test adding this photolysis in the simulation. H_2O_2 photolysis at 350-380 nm would be extremely slow. HNO_3 uptake is possible but would not explain any SO_2 dependence for the total number of particles. The reactions suggested in this comment would not be affected by the level of SO_2.

Note that the 10 and 15 cm profiles have the same shape, whether ammonia was introduced at -5 cm uniformly across the reactor (top plot) or multiplied by 4 and confined to the middle 1/4 of the mass flow (bottom plot).