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Interactive comment on “Modelling the contribution of biogenic VOCs to new particle formation in the Jülich plant atmosphere chamber” by L. Liao et al.

Anonymous Referee #1

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General Comments

This paper describes results of modeling particle measurements in stirred-flow reactor chamber experiments consisting of dark and light-induced reactions of organic compounds emitted from plants (BVOCs) in the presence of ozone, SO₂, and NO_x. The model used a relatively detailed atmospheric mechanism to represent the gas-phase reactions with additional lumped organic reactions to represent particle formation and with a nucleation and particle growth model. Effects of different assumptions regarding the relative importance of H₂SO₄ and condensable organic products in the nucleation model were examined. Fair fits were obtained to the particle number and volume data,

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though parameters had to be adjusted to fit these data. The subject matter may be appropriate for publication in this journal, though as discussed below the irradiation experiments are not good representations of atmospheric conditions.

Unfortunately, this paper is not suitable for publication in its present form because of inadequate discussion of experimental conditions and important aspects of the model used and because some of the conclusions they make are not supported by the data presented. There are also some technical issues regarding the presentation that need to be addressed. These are discussed below.

Specific Comments

The paper correctly points out that there are many uncertainties in our understanding of nucleation processes and the mechanisms for formation of particle precursors in the gas-phase reactions of biogenic compounds. Nevertheless it shows generally good fits of model predictions the overall magnitudes of measured particle numbers and volumes in the experiments, even though there are discrepancies as discussed in the paper. The relatively good fits had to be the result of at least some adjustments of uncertain aspects of the mechanism and model inputs being made, but the paper was not exactly clear on what was adjusted. There was much discussion of effects of making alternative assumptions concerning the relative importance of H₂SO₄ and low-volatility organic products in nucleation and some discussion of adjustments to the light intensity input, but nothing about other adjustments that must also have been made, such as adjustments made total yields of condensable BVOC products required to obtain the relatively good fits to the particle volume data as shown in Figure 12. In order to evaluate the significance of the model results and implications of good and poor fits, the reader must have a clear idea of exactly what adjustments were made to fit the data. Maybe some of the adjustments were made in previous work to fit other data, but this was not made clear. A clear discussion is needed of exactly what adjustments were made using the data in this work and what adjustments from previous work to fit other data were used, if any.

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In the "Air Chemistry" section they state that they base the gas-phase reactions of the BVOCs on how they are represented in the MCM, but they do not clearly indicate if any information from the MCM was used to predict formation of condensable organic products. In the "Aerosol Dynamics" section they give lumped reactions such as "VOC + OH \rightarrow ELVOC(OH) + SVOC(OH)" (Equation 3), implying they used such lumped reactions to predict ELVOC and SVOC, not the MCM itself. Equation 3 as given implies that they assumed 100% yields of ELVOCs and SVOCs in all the VOC reactions, but I doubt very much that this is the case because it is known from published data that total yields of condensable products are much less than 100% at least for isoprene and terpenes. Presumably they used less than 100% yields of EOVLCS and SVOCs in these lumped reactions, with magnitudes adjusted to fit these or previously published chamber data. This is important to how one interprets the significance of the model predictions and needs to be clarified.

There are other aspects of the discussion of the model for ELVOCs and SVOCs from the BVOCs that need to be improved. What is meant by using "compounds as the representatives of the ELVOC(OH) and SVOC(OH)"? Does this mean how they came up with gas-phase rate constants for them or something else? They gave the name of the MCM model species APINAO₂, BINA₂O₂, and NAPINAO₂ as "representatives" used for "stable products", but the MCM website indicates that these model species actually represent peroxy radicals, not stable products. Why did they choose not to have ELVOC's from NO₃ reactions?

Although not clear from the discussion in this manuscript, the paper Mentel et al (2009) cited for details on the facility indicate that the UV light source they employ in the reaction chamber has significant UV intensity well below the 300 nm cutoff for normal sunlight, making it unrepresentative of tropospheric conditions. Many gas-phase compounds in these experiments, particularly organic carbonyl and nitrate products, would photolyze at much higher rates with light sources at these short wavelengths that would occur normally in the troposphere, and this would affect gas-phase reactions and prod-

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uct yields. Presumably the rapid decline in O₃ when the lights are turned on is due to loss of O₃ due to photolysis forming O₁D at rates much more rapid than occur in the troposphere, but this was not stated. No discussion is given concerning how the MCM photolysis rates were calculated in their model. Did they use a spectral distribution appropriate for their light source to calculate appropriate photolysis rates for their light source using absorption cross section and quantum yield data one can obtain from the MCM web site, or did they just use pre-calculated atmospheric photolysis rates multiplied by factors based on the experimentally measured or adjusted light intensity? If the former they should give the spectrum in the supplementary materials or at least state the wavelength cutoff, and if the latter they should point out that they are not using the correct photolysis rates for this light source.

They state that they make a relatively large adjustment to the total light intensity and assume it varies with time in order to fit their model to some of the data, and attribute this to contamination. It does not seem particularly reasonable to me that contaminants on the light surface would have such a large effect on UV light intensity or cause it to change so much during the relatively short UV-on periods. However, if there is indeed so much contamination that it causes such a large effect on light intensity, one might expect it may also introduce contaminants into the reactor that may affect particle formation and nucleation. This possibility needs to be discussed and needs to be ruled out in order for this work to be publishable. No data were presented or discussed concerning background particle formation in this chamber during irradiations.

The measurement data on Figure 7 indicate very similar particle numbers are formed from day to day during the irradiations, except for the initial spike that was lower on day 3 and missing on Day 4. As noted in the paper, this disagreed with the predictions of the kinetic nucleation (H₂SO₄-dominated) model that increased with each day following the H₂SO₄ measurements, but it also disagreed with the organic nucleation model that predicted a decrease with day, following the decline in BVOC inputs as shown on Figure 3. This suggests that the real nucleation source may be something other

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than H₂SO₄ and organics – something that is more constant from day to day than either of these. Could contaminants be contributing as discussed above? Because of this uncertainty, I would not use these data to make conclusions about the relative validities of the two nucleation models.

In their discussion of the data on Figures 9-11, they make the statement "Comparing with the modelled particle number size distributions without tracking the SVOC gaswall-partitioning, it is conclusive that a substantial amount of SVOCs adsorbed on the JPAC reaction chamber walls during the measurement campaign, and the desorption of SVOCs from the walls significantly contributed to the growth of the freshly formed particles." I do not understand this statement at all, and why the data they show on Figures 10 and 11 provide any evidence one way or other about the role of wall-absorbed SVOC in particle formation. Neither model fits the data on these figures very well, and the differences between plots (b) and (c) are far less than the differences between these and the data on plots (a). I would think that aerosol volume data such as shown on Figure 12 would have more of a test on whether wall desorption of SVOC is important, but they do not show this effect on their calculations. They need to explain the reasoning behind their conclusions in this regard better, or remove it from the discussion, conclusions and abstract. Maybe showing the effects of this on model performance of particle volumes would be more convincing? They say in the conclusion section that desorbed SVOC affected model predictions of particle volume, but gave no data to back this.

They state that increased measured OH from day to day as shown on Figure 4 may be the reason for the day-to-day increase in H₂SO₄ because of the OH + SO₂ reaction. However, the increase on OH on Figure 4 was not nearly enough to account for the amount of measured H₂SO₄ increase on Figure 5.

The model underprediction of the reductions of isoprene and terpenes when the lights are turned on showed in Figure 6 could be due to the flow conditions in the reactor not being exactly as predicted using a CSTR model. They state that incorrect OH+BVOC

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rate constants may be causing this discrepancy, but I doubt they be far enough off for this to be a reasonable explanation.

Technical and Editorial Comments

Dal Maso et al (2014), which is indicated as submitted to APCD, is cited as the reference for the chamber measurements. The citation was not found at the APCD web site, which I believe shows papers under review. If it exists, it should be accessible to the reviewers so they can evaluate the suitability of the measurements for publication. If it has not yet been submitted the citation should be changed to "in preparation" or deleted, and relevant information should be given in the manuscript.

If they state the input concentrations for NO₃, SO₂, O₃, and CO in the text where they give the input NO and NO₂, then Table 2 would not be needed. The flow rates are not relevant if the concentrations refer to the concentrations once diluted in the reactor. If they refer to the concentrations in the injectors then this needs to be clearly stated, along with the total flows into the reactor.

They need to define all the terms used in Equation (4) and give the values of the parameters used.

I had to go to the Mentel et al (2009) to obtain important model input information concerning CSTR conditions related to total flow rates and residence time. These should be given in the "Model Input Parameters" section.

The scatter plots on Figures 8 and 13 don't seem to contribute much to the paper and can be deleted. The information in Figures 7 and 12 are sufficient to show model performance.

I don't understand what is meant by (SVOC+ELVOC)(OH or O₃) means on Figure 9. If they are totals they should be higher than SVOC on the wall, but they are much lower. Or are they gas-phase concentrations? In that case, wouldn't gas-phase ELVOC be negligible?

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