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Discussions

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

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Answer to all reviewers:

We thank the reviewers for the thorough review, which certainly will help us to improve the manuscript. Because Dr Liao that finished his PhD in December 2014 has left science towards the non-academic world I (Dr. Roldin) have taken over the main responsibility to improve the manuscript in accordance with the reviewers comments.

Based on the comments from all three reviewers, we summarize the major weaknesses of the manuscript as:

(1) The model setup used to simulate the condensation growth (SOA formation) is not well described (e.g. ELVOC and SVOC SOA yields) and the modeled condensation growth relay on heavy approximations.

(2) It is not clear from the manuscript how the model estimates the photolysis rates of the MCM compounds and the 80 % increase of the UV-light during the UV-on period is not well justified.

(3) The assumptions and effects of the reversible VOC gas-wall partitioning is not described and justified.

(4) The influence of different new particle formation mechanisms is not evaluated in enough detail to conclude about which mechanism that is most likely and shows best agreement with the observations.

We totally agree with the reviewers that these aspects of the manuscript need to be improved. For this reason we are currently redoing all model simulations using a different model called ADCHAM (Aerosol Dynamics, gas- and particle-phase chemistry model for laboratory CHAMber studies), which has been constructed explicitly to be used for smog chamber experiments (Roldin et al., Atmos. Chem. Phys., 14, 7953–7993, 2014). ADCHAM also uses the MCM gas-phase chemistry but also includes a more detailed module for reversible gas-wall partitioning, particle chamber wall losses and a detailed particle-phase chemistry model that includes the AIOMFAC activity coefficient model. The particle condensation growth will be simulated using the non-radical MCM terpene oxidation products with vapor pressure less than 0.01 Pa at 289 K (in total 535 compounds). We have estimated their pure liquid saturation vapor pressures with the boiling point and vapor pressure extrapolation methods from Nannoolal et al. (2004, 2008). Their gas-particle partitioning will be simulated considering the curvature effect and using Raoult's law corrected for non-ideal mixing with the activity coefficients calculated with AIOMFAC. In order to address the contribution of ELVOCs to the particle formation and growth, we will modify the MCM gas-phase chemistry by adding an addi-

tional reaction channel for the monoterpenes oxidized by ozone, which lead to ELVOCs. We use an ELVOC molar yields of 7 % for ozonolysis of monoterpens containing an endocyclic double bound (alpha-pinene and delta-3 carene). This yield is based on the alpha-pinene ELVOC yield derived from measurements in the JPAC chamber by Ehn et al. (2014). As an alternative to the use of the MCM gas-phase mechanism VOCs for the condensation growth, we will also test to simulate the SOA formation using a simplified VBS approach, where the VBS compound concentrations are calculated based on the amount of reacted monoterpenes and sesquiterpenes in the MCM gas-phase chemistry code. We will clearly describe which mass and molar yields that we use for the VBS parameterizations, and will compare these parameterizations with VBS parameterizations found in the literature.

The photolysis rates are simulated using the quantum yields and absorption cross sections reported at the MCMv3.2 web site. The light spectrum in the reaction chamber is estimated using the measured spectrum for the Discharge lamps (HQI 400 W/D; Osram, Munich, Germany) in the wavelength range 280-650 nm and with a single UV-light peak at 254 nm representing the UV-spectrum from the Philips, TUV 40W lamp. The light spectrum used in the model will be given as a supplementary material.

We agree with reviewer 1 that it is most unlikely that the UV-light intensity varies to a large extent due to contamination on the UV-light source. In the revised model simulation we intend to use a constant UV-light source intensity corresponding to a $J(O1D)$ = 2.9×10^{-3} s^{-1} as specified by Mentel et al., Atmos. Chem. Phys., 9, 4387–4406, 2009 and Dal Maso et al., Atmos. Chem. Phys. Discuss., 14, 31319–31360, 2014. We will use the measured OH, O3 and H2SO4 concentration as input to the model. Thus, the focus of the revised manuscript will be entirely on the new particle formation and particle growth and not on the ability of our model to simulate the inorganic gas-phase chemistry (i.e. the OH, O3 and H2SO4 concentrations). However, we will clearly state the reason why we decided to use the measured and not the modeled OH, O3 H2SO4 in the revised manuscript.

The reversible gas-wall partitioning of the VOCs will be modeled using the method proposed by Matsunaga and Ziemann (2010). For the ELVOCs we will use the JPAC first order loss rates estimated by Ehn et al. (2014). For SVOCs we will use the theory from McMurry and Grosjean (1985) which has recently been applied by Zhang et al., PNAS, 111, 5802–5807 (2014) , McVay et al, Environ. Sci. Technol., 48, 10251−10258 (2014) and Zhang et al., Atmos. Chem. Phys. Discuss., 14, 26765–26802, (2014).

The VOCs deposited by gas-wall partitioning or particle deposition is included as an effective wall pool of VOCs which based on their estimated individual pure liquid saturation vapor pressures will evaporate from the walls in variable amount (theory from Matsunaga and Ziemann, 2010). We will run several sensitivity tests in order to evaluate how sensitive the model results are to the reversible gas-wall deposition loss rates, particle deposition loss rates, condensable compound volatility distribution and possible particle-phase oligomerization. For this we will either use the MCM gas-phase mechanism VOCs as condensable compounds or a more simplified VBS approach. With the later approach we will search for an optimum VBS distribution that can describe the SOA volume formation during the entire experiment.

In the revised manuscript we will not claim that we have found the optimum new particle formation mechanism but make a more thorough analysis of possible mechanism. We will run model simulations where we test how well the new particle formation can be represented by a new particle formation mechanisms which involves extremely low volatility organic oxidation products (ELVOC_nucl). The mechanisms we will test in the revised manuscript are:

$J = A \cdot [\text{ELVOC\_nucl}]$

$J = A \cdot [\text{H2SO4}]$

$J = K \cdot [\text{ELVOC\_nucl}]^2$

$J = K \cdot [\text{ELVOC\_nucl}] \cdot [\text{H2SO4}]$

J=K*[H2SO4]^2

J = Constant (if UV-light is on)

The ELVOC_nucl concentration will be modeled with the following equation:

d[ELVOC_nucl]/dt=yOH*kOH*[VOC]*[OH]+yO3*kO3*[VOC]*[O3]–(Q/V+CS+k_wall)*[ELVOC_nucl]

Here [VOC] either represents the concentration of individual monoterpens or sesquiterpenes or the total concentration of monoterpenes and sesquiterpenes in the reaction chamber.

kOH is the VOC specific OH reaction rate

kO3 is the VOC specific O3 reaction rate

yOH is the molar yield of VOCs reacting with OH that form ELVOC_nucl

yO3 is the molar yield of VOCs reacting with O3 that form ELVOC_nucl

CS is the condensation sink

Q is the outflow from chamber (31 lpm)

V is the chamber volume (1450 l)

k_wall is the first order wall loss rate. (We will use the observed ELVOC loss rates of 0.011 s^-1 from Ehn et al., (2014) in the JPAC chamber). With this wall loss rate the dilution effect is almost negligible and the condensation sink is always smaller during the experiment. CS reaches a maximum value during the first day of ∼0.005 s^-1. Thus, during most conditions the ELVOC_nucl concentration (at steady state) will be nearly proportional to the chemical formation rate.

In this equation we have neglected chemical degradation of ELVOC_nucl (e.g. fragmentation to more volatile compounds) and the loss of [ELVOC_nucl] because of the new particle formation.

We will test to run the mechanism where ELVOC_nucl is formed both from VOCs reacting with OH and O3, only OH or only O3.

We will also extend the analysis of which VOC properties and growth mechanism that are required in order for the model to capture the observed particle number size distributions. We will evaluate how the model results depend on the initial size, surface tension and chemical composition of the formed particles and how particle phase dimer formation (e.g. through reactions between aldehydes and organic hydroperoxides forming peroxyhemiacetals (Shiraiwa et al., PNAS, 11746–11750, 2013 and Roldin et al., Atmos. Chem. Phys., 14, 7953–7993, 2014)), may contribute to the particle growth.

Specific answers to reviewer 1:

"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."

In the revised manuscript we will clearly describe all adjustments and motivations with references if possible in order for the reader to clearly judge the significance of our model results. As described above we will model the particle growth by considering the condensation of all non-radical VOCs from MCM with vapor pressure less than 0.01 Pa and not introduce any unclear adjustments. ELVOCs will be formed from ozonolysis of endocyclic monoterpenes with molar yields based on Ehn et al. (2014). We will not draw any definite conclusions concerning the nucleation mechanism and will choose our words more carefully when we discuss possible new particle formation mechanisms.

"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 –> 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."

Yes, thank you for this comment. See answer to all reviewers at the top.

"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 re-

action 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 product 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."

Yes it is correct that a UV-light source with a dominating peak at 254 nm was used to photolyze O3 in order to produce OH. In the model we calculate the photolysis rates using the estimate light spectrum (which we will give as a supplementary material) and quantum yields and absorption cross-sections from the MCMv3.2 web site. We will test how sensitive the model gas-phase chemistry and SOA formation is for the photolysis of VOCs with the low-wavelength UV-light source by performing simulations with or without considering the 254 nm light peak for the photolysis rates of VOCs.

"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."

We agree that it is unlikely the UV-light intensity varies due to contamination on the UV-light source. We do not think that contamination (i.e release of VOCs from the chamber walls not originating from the VOCs released from the trees in the plant chamber) has a large influence on the particle formation and nucleation, but we will discuss it and mention it as a possible bias in the revised manuscript. We are aware of that chamber wall effects have large influence on the results, primarily as a sink of VOCs. Based on the state-of-the-art knowledge about VOC chamber wall losses we will evaluate their potential influence on the results. In the revised model simulation we intend to use a constant UV-light source intensity corresponding to a $J(O1D) = 2.9\times10^{-3}$ s^{-1} as specified by Mentel et al., Atmos. Chem. Phys., 9, 4387–4406, 2009 and Dal Maso et al., Atmos. Chem. Phys. Discuss., 14, 31319–31360, 2014. We will use the measured OH, O3 and H2SO4 concentration as input to the model. Thus, the focus of the revised manuscript will be entirely on the new particle formation and particle growth and not on the ability of our model to simulate the inorganic gas-phase chemistry (i.e. the OH, O3 and H2SO4 concentrations).

"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 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"

We will test to run the model with a fixed nucleation rate during the UV-light on period and compare this with the other nucleation mechanisms. In the revised version we will make a more thorough analysis of potential new particle formation mechanism (see answers to all reviewers at the top). As in any smog chamber experiment we cannot rule out the potential influence from compounds on the chamber walls, and we try to address this with our model runs. But we will be honest and admit that chamber wall effects are not fully understood (e.g. reactions on the chamber walls) and this may influence the new particle formation and growth during the experiments.

"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 gas-wall-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."

We agree that the modeled particle number size distribution is not the best way to

illustrate the potential influence of reversible gas-wall partitioning. In the revised version we will instead illustrate how reversible gas-wall partitioning influences the modeled particle volume concentration. We will clearly describe the assumptions used when modeling the gas-wall partitioning.

"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."

Yes we agree. This statement is not correct and will be removed. The increase in the H2SO4 concentration is primarily due to a decreasing condensation sink.

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

Yes, this is another possibility. We will mention this in the revised manuscript. Another possibility which we will also take up is that oxidation products with similar molar mass as the monoterpenes may also contribute to the unity resolution PTR-MS mass peak which is interpreted as monoterpenes. This effect may become especially prominent at low concentrations of monoterpenes.

"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."

Dal Maso et al., Atmos. Chem. Phys. Discuss., 14, 31319–31360, 2014

"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."

We will give the concentrations in the inflow to the chamber in the text and remove Table 2.

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

Yes thank you we will do that.

"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."

Yes we agree. We will add this information to the revised manuscript.

"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."

Yes we agree and will remove Fig. 8 and 13.

"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?"

Yes they are gas-phase concentrations. No with a concentration on the order of 1E9 molecules cm^-3 the ELVOC and SVOC gas-phase concentrations will not be negligible

for the particle growth. In the revised model simulations we will test if the recently proposed ELVOC formation from ozonolysis of monoterpens are an important mechanism to consider during these experiments.

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