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:

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(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*[ELVOC_nucl]

J=A*[H2SO4]

J=K*[ELVOC_nucl]^2

J=K*[ELVOC_nucl]*[H2SO4]

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J=K*[H2SO4]ˆ2

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 sesquiter-penes 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 sˆ-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 sˆ-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. frag-mentation to more volatile compounds) and the loss of [ELVOC_nucl] because of the new particle formation.

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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 2:

"In this paper Liao et al. present results from real plant BVOC emission and SO2 oxidation followed by new particle formation and growth. Gas phase reactions are represented with high level of details using Master Chemical Mechanism. However, quite heavy approximations are needed to simulate the condensational growth of particles. In order to achieve agreement between measurement and modelling results, some assumptions are made. The topic of the manuscript fits the scope of ACP and is timely important and the results presented might have some importance, although I do not see too much new information. Because the measurement setup is described in other manuscript (Dal Maso et al, 2014), I concentrate here on modelling part of the study where I have some serious criticism. Major revisions are needed before the manuscript can be accepted for publication."

We agree with the reviewer that we used quite heavy- and not well-justified approximations when modeling the condensation growth. See the answer to all reviewers on how we will improve the manuscript with respect to this.

"Abstract: If SO2 measurements are missing, how can it be a merit that measured and modelled H2SO4 concentrations agree as it is only based on guessing the input

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concentration?"

Yes, you are correct. We will remove this statement from the abstract. In the revised manuscript we will focus more on the particle growth mechanisms and less on the modeled gas-phase chemistry. We will remove figure 5 and only use the measured H2SO4 in the model.

"Abstract: "The modelled total monoterpene concentration was in line with PTR-MS observations, and we provided the distributions of individual isomers of terpenes, when no measurements were available." To whom and for what purpose these there provided?"

We will remove this sentence.

"Abstract: "The aerosol dynamic results supported the hypothesis that H2SO4 is one of the critical compounds in the nucleation process." This is not a new result, and I do not see how this is supported by the results presented. Did you test some nucleation mechanisms without H2SO4?"

Yes, you are correct. We will remove this sentence from the abstract. No we did not test any nucleation mechanism without H2SO4. In the revised manuscript we will test to run the model with a fixed new particle formation rate during the UV-light on periods. We will also focus more on the particle growth mechanisms and speculate less about the actual new particle formation mechanism.

"Abstract: "We classified the VOC oxidation products into two sub-groups including extremely low-volatility organic compounds (ELVOCs) and semi-volatile organic compounds (SVOCs)". This sounds like everything is classified, but what actually is done based on the page 27981, some oxidated compounds are chosen to represent ELVOCs and SVOCs. This should be rephrased."

Yes you are correct. We will rewrite the whole model description section (Sect. 2.2) and change the way we model the SOA formation (see answer at the top).

"Overall, I would like to see more clearly in the abstract what is the main result of

this study. Is it that after some assumption made the model skill to simulate particle formation is highest when ELVOCs are taken into account, or is it that wall losses are actually the critical point in chamber measurements. In the case of the first one, all assumptions should be explained and their effect on modelling results should be discussed. If the case of wall losses, then a more careful analysis of previous studies is needed. Also clear difference between this and Dal Maso et al. (2014) should be made."

Yes, we agree. We will reformulate the abstract and focus on our revised model simulation results, which model parameters are most uncertain and most influential, how do wall losses, the VOC volatility distribution and potential particle-phase oligomerization reactions influences the modeled particle growth.

"Page 27976, lines 9-10: At the moment there is too much speculation in the modelling setup to really quantify the role of ELVOCs and SVOSs on SOA formation. So this should be rephrased."

Yes, we will do that. In the revised version of the manuscript it will be exactly clear to the reader what ELVOC and SVOC yields and properties which we use when simulating the SOA formation.

"Page 27982: Is the choice of saturation vapor pressures of ELVOC and SVOC affecting the results and on what are the chosen values based on?"

Yes, the saturation vapor pressures of both the ELVOCs and the SVOCs are affecting the model results and the chosen values are not well justified. In the revised manuscript we will give detailed information about the molecule properties of the SVOCs (MCM compounds) and the ELVOCs that contributes to the particle growth. Their saturation vapor pressures will be estimated using the boiling point and vapor pressure extrapolation methods from Nannoolal et al. (2004, 2008). We will also test to represent the condensable compounds using a simplified VBS parameterization where we can easily vary the VBS spectrum with the ambition to find the optimum volatility distribution that

gives the best possible agreement between the modeled and measured SOA volume concentration.

"Page 27982, lines 2-4: "In order to not systematically underestimate the total particle volume concentration, the formation of the five condensable compounds were multiplie with a fixed correction factor of two." Where is this factor of two coming from? Based on figures 10 and 11, the modelled aerosol size distributions look totally different than the measured ones. Could it be that the factor should be different for ELVOC than for SVOC? It would change how Figure 14 looks like and based on this it would be impossible to say how different compounds contribute to SOA formation. I see this as a major weakness of this study. Although MCM provides good chemistry, it does not produce compounds with low enough volatility. So why to use such a mechanism to study SOA formation?"

In the revised manuscript we completely change the way we simulate the SOA formation (see answer at the top). We will evaluate if MCM produces compounds with low enough volatility or not and if the recently found ELVOC formation mechanism from ozonolysis of monoterpenes (Ehn et al., 2014) may help to explain the observed particle growth. We will also run sensitivity tests with a simplified VBS model to see if we can find a VBS spectrum which makes it possible to capture the particle growth and SOA volume formation during the entire experiment.

"Page 27983, lines 1-2: Is sulfuric acid condensing on the walls?"

Yes in the MALTE-BOX we used a first order loss rate of H2SO4 to the chamber walls. In the revised version model simulations we will not try to simulate the sulfuric acid concentration but instead used the measured H2SO4 concentration as input to the model. Thus, we will not consider any wall losses of H2SO4. In the revised manuscript all gas- and particle wall losses considered in the model, will be described.

"Page 27983, lines 24-26: I cannot see a clear diurnal pattern in Figure 3. Was there a period with lights totally off?"

No.

"Page 27984: Why is the measured condensation sink used to calculate the condensation of sulfuric acid and nitric acid if modelled total number and volume distributions agree with measured ones? If the shape of particle size distributions totally differs, does it mean that properties of condensing compounds are not representative of actual compounds? If there is no ammonia, is nitric acid even condensing?"

In the revised version we will only use the modeled condensation sink. No if there is no base (e.g. NH_3) which can neutralize HNO_3 it will not condense. ADCHAM which we will use for the revised model simulations contain a detailed thermodynamic model which allow use to study ammonium nitrate formation, however since the NH_3 concentration in the chamber probably was very low (not measured) we don not expect to see any substantial contribution from HNO_3 to the particle growth. We will test if low levels of $NH_3(g)$ $\sim$100 ppt in the inflow to the reaction chamber may contribute to the formation of ammonium nitrate. We will remove the last sentence of Sect. 2.2.4.

"Page 27985, lines 14-15: What does this UV intensity correction mean? Is the correction 80% within every day so that correction is 0% when UV-lights are turned on every day, and growing linearly to 80%, or is it 0% in the day1 and grows to 80% on day4?"

The correction which we applied was a correction from 0 to 80 % for each day.

"Page 27986: If SO2 concentration measurements are missing, why to speculate reasons for differences between modelled and measured sulfuric acid concentrations?"

Yes we agree and for the revised model simulations we will always use the measured H_2SO_4 concentration as input to the model.

"Page 27989: There is discussion on "Sub-3 nm particles", but in the text and figures it is stated that concentrations are total for particles larger than 1.6nm. It should be made clear what is meant here."

Thank you for pointing this out. The title of the section is confusing. We will change this

title. Both figure 7 and 8 gives the total number concentration and not the sub-3 nm particle concentration. We will remove figure 8 from the manuscript and replace sub-3 nm particle number concentration with total particle number concentration in the text.

"Page 27991: What makes such a big difference between modelled total aerosol particle volumes when only nucleation method is changed? Still the total SOA should be approximately the same."

The SOA volume formation is sensitive to the condensation sink if the wall losses of VOCs and the dilution are substantial. At the start of the new particle formation event the condensation sink is very small and most of the condensable organic compounds will not go the particle phase as would have been expected at gas-particle equilibrium. Instead they will be lost to the walls or removed in the outflow from the chamber. Therefore, the modeled SOA volume concentration depends on the new particle formation rate. In the revised manuscript we will illustrate this effect more clearly and during which conditions the new particle formation rate has large influence on the SOA volume concentration.

"Page 287992: Why is SVOC contribution to aerosol total volume much lower on day 4 than on day 3?"

We are not sure about this. As mentioned in the beginning we will redo all model runs with a more detailed mechanism for SOA formation and hope that the results will be more convincing and clear.

"Figures: Figures 8 and 13 are difficult to read and all information is actually in Figures 7 and 11, so these could be removed."

Yes we will remove these figures.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 27973, 2014.

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