

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 rely 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-

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tional reaction channel for the monoterpenes oxidized by ozone, which lead to ELVOCs. We use an ELVOC molar yields of 7 % for ozonolysis of monoterpenes containing an endocyclic double bond (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 $J(O1D) = 2.9 \times 10^{-3} \text{ s}^{-1}$ 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.

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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:

$$J=A*[\text{ELVOC_nucl}]$$

$$J=A*[\text{H}_2\text{SO}_4]$$

$$J=K*[\text{ELVOC_nucl}]^2$$

$$J=K*[\text{ELVOC_nucl}]*[\text{H}_2\text{SO}_4]$$

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$$J=K*[H_2SO_4]^2$$

J = Constant (if UV-light is on)

The ELVOC_nucl concentration will be modeled with the following equation:

$$d[ELVOC_nucl]/dt=y_{OH}*k_{OH}*[VOC]*[OH]+y_{O_3}*k_{O_3}*[VOC]*[O_3]-$$
$$(Q/V+CS+k_{wall})*[ELVOC_nucl]$$

Here [VOC] either represents the concentration of individual monoterpenes 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.

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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 3:

“One of the main results of this study is that sulfuric acid is one of the critical compounds in the nucleation process. This is probably true, but it can not be verified using simulations made in this study. Both nucleation mechanisms used in the model require that there is sulphuric acid, otherwise there will be no nucleation making it a critical compound. It would be useful to test if organic nucleation mechanisms that do not require sulphuric acid (see e.g. Paasonen et al., 2010) would succeed or fail simulating particle formation in these conditions.”

Yes, we agree. We will also 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) (See answers to all reviewers at the top)

“Another main result presented in the abstract is that reversible gas-wall partitioning must be considered in the model. This has already been established by Matsunaga and Ziemann (2010) and confirmed by more recent studies.”

Yes we are aware of this and will refer to these studies in the text and use the theory

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from Matsunaga and Ziemann, 2010.

“Page 27980: It is said that OH oxidation product ELVOCOH was used in Equation (2). This choice has not really been justified in the text. Ehn et al. (2012) have suggested that also ozone oxidation of biogenic volatile compounds produces extremely oxidized compounds that can play a role in new particle formation. Why was ELVOCO3 omitted in the nucleation calculation?”

ELVOCO3 was omitted because we did not find good correlation between the modeled and measured formation rates if ELVOCs involved in the new particle formation event primarily are formed from ozonolysis of monoterpenes. As mentioned in the answer above we will extend the new particle formation analysis with more possible mechanism that also involve ELVOCs formed from ozonolysis of terpenes.

“Page 27981: ELVOC and SVOC yields have to be given for Equation (3) (see comments by Referee 1)”

Yes, we will clearly specify all assumptions including the ELVOC and SVOC yields in the revised manuscript.

“Page 27982: It is unclear how the parameter values in Equation (4) were determined and how it was verified that with these values the observed reversible wall losses were captured.”

Yes we agree that the analysis and description of how the reversible wall losses were chosen need to be improved. We will do this in the revised manuscript (see answer at the top)

“Page 27983: Why were “only 4 lamps used on the remaining days”?”

I (Dr. Roldin) was not involved in the measurement myself and do not know the answer to this. We will add an explanation to this in the revised manuscript.

“Page 27983: How were the concentration values for inorganic compounds deter-

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mined? How sensitive are model results to these choices.”

NO is emitted from plants (Wildt et al., JGR, 102, 5919-5927, 1997). Schimang et al., Atmospheric Environment 40, 1324–1335 (2006) observed a background NO concentration of 300 ppt during measurements with plants in the Jülich plant chamber. We will evaluate how sensitive the model results (e.g. SOA formation) are to different NOx concentrations in the input in the range 0.1-1 ppbv and NO3 in the range 0-1 ppbv. The values of the SO2 and O3 concentrations in the inflow were set in order for the modeled H2SO4 and O3 to agree with the observations. In the revised version we will not include emissions of O3 but use the measured O3 concentration as input to the model. The CO concentration should correspond to the approximate background level in the atmosphere.

“Page 27985: I don't understand the explanation for using 80 % increase in the UV-light. What was this extra sink for O3? Why was it necessary to model O3 concentrations if the main purpose of this study was to investigate new particle formation? Measured O3 concentrations could have been given as an input for the model as it was done for H2SO4. This way, there would have been fewer sources for uncertainty in the simulations and the analysis of factors affecting new particle formation and growth would have been more straight forward.”

We will use the measured O3, OH and H2SO4 as model input in the revised version (see answers to all reviewers at the top).

“Figure 14: What does the term “total volume fraction” mean?”

It should be volume fraction and not total volume fraction. The bars gives the volume fraction of the different compounds in each size bin.

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

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