

## ***Interactive comment on “Secondary organic aerosol formation during June 2010 in Central Europe: measurements and modelling studies with a mixed thermodynamic-kinetic approach” by B. Langmann et al.***

**B. Langmann et al.**

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Answers to J.R. Pierce: In total, 6 comments remain to be addressed after the first iteration.

1) First iteration:

Reviewer: 1b. How are the authors actually doing “SOG nucleation”. They say that their nucleation scheme is Vehkamäki et al. (2002); however, this nucleation

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scheme is a H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O binary scheme (that only predicts nucleation under cold, free-tropospheric conditions in most models... not in the boundary layer).

Authors: The parameterisation for sulfuric acid-water nucleation of Vehkamäki et al. (2002) has been developed for tropospheric and stratospheric conditions, valid for a temperature range from 230.15–300.15 K, relative humidities of 0.01–100% and total sulphuric acid concentrations of 10<sup>4</sup>–10<sup>11</sup> cm<sup>-3</sup>. As aerosol microphysical parameterisations of the regional model REMOTE (Langmann et al., 2008) are based on those of ECHAM5-HAM (Stier et al., 2005), it is the basic nucleation scheme of the model, despite potential limitations.

Reviewer: Thus, it is not clear how the authors are doing SOG nucleation. I have thought of two possibilities of what they might be doing: (1) They are treating LV-SOG as the same as H<sub>2</sub>SO<sub>4</sub> and using [LV-SOG]+[H<sub>2</sub>SO<sub>4</sub>] as an input to Vehkamäki et al. (2002) as opposed to just [H<sub>2</sub>SO<sub>4</sub>]. However, there is no basis for this method.

Authors: In recent years, the awareness that nucleation parameterisations involving only H<sub>2</sub>SO<sub>4</sub> (and water) do not yield satisfying results triggered the development of nucleation parameterisations including organic vapours. Paasonen et al. (2010) (and Kerminen et al. (2010)) proposed eight different empirical nucleation parameterisations derived from combining data from four measurement sites. Inspired by these ideas, the simple assumption applied in the current manuscript is to use the scheme of Vehkamäki et al. (2002) for two nucleation pathways: 1. H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O nucleation and 2. LV-SOG+H<sub>2</sub>O nucleation. For the second pathway H<sub>2</sub>SO<sub>4</sub> concentrations were replaced by LV-SOG concentrations in the nucleation scheme. We certainly agree with the reviewer that such an approach represents a simplification (maybe even an oversimplification), as e.g. interactions between H<sub>2</sub>SO<sub>4</sub>-SOG nucleation are not considered. Nevertheless, we would like to emphasize that – even in a simple way – nucleation of organic vapour is taken into account in the model simulations presented in the manuscript.

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Second iteration:

Reviewer: Thanks for this clarification. However, since there is no experimental or theoretical basis as to why replacing H<sub>2</sub>SO<sub>4</sub> with LV-SOG in the Vehkamäki scheme would give realistic nucleation rates (even though we know that LV-SOG can participate in nucleation), this needs to be clearly discussed in the manuscript. It's ok for us modellers to be creative with our approaches (I'm sure I've done crazier approaches than this), but we need to do our best to be clear about when we are making our own approximations and what the potential limitations of these approximations are.

Authors: To clarify the approach and associated limitations, the following sentences are added to the manuscript: 'The simple assumption applied in the current manuscript is to use the scheme of Vehkamäki et al. (2002) for two nucleation pathways: 1. H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O nucleation and 2. LV-SOG+H<sub>2</sub>O nucleation. For the second pathway H<sub>2</sub>SO<sub>4</sub> concentrations are replaced by LV-SOG concentrations in the nucleation scheme. This approach should be understood as a zero-order approximation to conduct sensitivity studies, as experimental evidence for interactions between LV-SOG and H<sub>2</sub>SO<sub>4</sub> is not considered and no adaptations for LV-SOG have been incorporated into the scheme of Vehkamäki et al. (2002).'

2) First iteration:

“maximum threshold of reactant concentration” Reviewer: “To further simplify the approach of Yu (2011) we determine the mass conserving transformation rate of MV-SOG → SV-SOG and SV-SOG → LV-SOG by prescribing a maximum threshold of the reactant concentration being available for oxidation. This way we avoid determining the saturation vapour pressure of the oxidized SOG compounds, which greatly simplifies the procedure proposed by Yu (2011). Results with 1% and 10 % threshold values (in the latter case an additional requirement is that OH concentrations exceed 0.1 ppt thereby excluding night-time aging processes) are presented in Sect. 4.2.” I'm not exactly sure what the authors are doing here. My best guess is that if “k” is the aging

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rate constant, they are predicting  $d[\text{LV-SOG}]/dt$  by...  $d[\text{LV-SOG}]/dt = k[\text{OH}](0.1[\text{SV-SOG}])$  for the 10% threshold or  $d[\text{LV-SOG}]/dt = k[\text{OH}](0.01[\text{SV-SOG}])$  for the 1% threshold rather than  $d[\text{LV-SOG}]/dt = k[\text{OH}][\text{SV-SOG}]$  (and similar for the aging of MV-SOG to SV-SOG). However, if this is the case, isn't this the same as scaling the aging rate constant down by 10% and 1%. I'm not sure what the basis of this would be. My only guess is that perhaps the un-scaled rate constant created chemistry too fast for their modelled time step (causing negative concentrations under some conditions) and rather than reducing the timestep, they reduced the rate constant. However, I am only speculating because I really don't follow the reasoning for the maximum threshold. Also, why does this procedure avoid determining the saturation vapor pressure of the oxidized SOG components? The authors have these pure-value vapor pressures in Table 1 for SV and MV (and the authors can calculate the sat vap pressures over a mixture from partitioning theory), and LV the authors assume to be non-volatile, so I'm not sure why the authors need to avoid determining them. And I also don't know why this max threshold would allow the authors to avoid determining the saturation vapor pressures. The discussion of the “maximum thresholds” needs to be clarified.

Authors: The reviewer understood the concept of thresholds correctly regarding the introduction of the threshold value in the aging reaction equations. However, we strongly reject speculations about a too large time step and negative concentration – both do not appear in the model simulations described in the manuscript. The reason for the implementation of thresholds is a conceptual one. As LV-SOG represents the lowest volatile SOG, further aging is not considered (see Figure 1 of the manuscript), and the concept with maximum thresholds is only applied for MV-SOG and SV-SOG aging. The concept with maximum thresholds for MV-SOG and SV-SOG aging has been introduced into the model, to take into account that only a fraction of the respective SOG's will reach saturation vapour pressures low enough to move into the next category (MV-SOG into SV-SOG and SV-SOG into LV-SOG). As the oxidation products are represented by only one component in each category, this way the spread of saturation vapour pressures of different oxidation products is implicitly considered. Other authors

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limit the category jump by e.g. assuming that each OH oxidation adds one oxygen atom and reduces C\* by 1.5 decade (Yu, 2011) or introduce C\* bins and determine the mass yields of products in each C\* bin (Donahue et al., 2006). We will clarify the concept of thresholds in the aging equations in the revised manuscript according to the above written explanations and also by better pointing out that this empirical approach makes use of the Puy-de-Dôme measurements (shown in Fig. 6 of the manuscript) for scaling.

Second iteration:

Reviewer: Ok, this explanation is much better. I think the concept of “the fraction of oxidation products that have a volatility low enough to move to the lower volatility class” is solid, and it is fine for publication once it is explained clearly as you describe here.

Authors: To clarify the approach, the following sentences are added to and modified in the manuscript: ‘The reason for the implementation of thresholds is a conceptual one. It has been introduced into the model, to take into account that only a fraction of the respective SOG’s will reach saturation vapour pressures low enough to move into the next lower volatility category (MV-SOG into SV-SOG and SV-SOG into LV-SOG). As the oxidation products are represented by only one component in each category of the model, this way the spread of saturation vapour pressures of different oxidation products is implicitly considered. Results with 1% and 10% threshold values (in the latter case an additional requirement is that OH concentrations exceed 0.1 ppt thereby excluding night-time aging processes) are compared in section 4.2 with measurements thereby empirically pointing to a reasonable threshold value of 10 %.’

Reviewer: Can you explain better how this “greatly simplifies the procedure proposed by Yu (2011)”? It seems like the procedures are similar, but you just scale your production rates by 0.01 or 0.1.

Authors: Please note that Yu (2011) writes the following: ‘To determine  $\xi_{MV \rightarrow SV}$  and  $\xi_{SV \rightarrow LV}$  is a challenging task.’ . . . ‘ $\xi_{MV \rightarrow SV}$  is the fraction of each MV-SOG that

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can be oxidized to become the corresponding SV-SOG, and  $\xi_{SV \rightarrow LV}$  is the fraction of each SV-SOG that can be oxidized to become LV-SOG.’ ‘To account for the spreading of saturation vapor pressures around the averaged values, we represent each SV-SOG or MV-SOG group with a normalized distribution . . .’ ‘The volatility change within each group is taken into account by assuming that the log-normal distribution of each SOG category is always maintained after a fraction of the SOG in the left-tail . . . of the log-normal distribution has been moved down to the next category.’ We do not describe the whole approach of Yu et al., (2011) here, but invite the reader to refer to this manuscript for more detailed information.

3) First iteration:

Reviewer: P26767 L7-9: Why couldn’t the authors apply the quasi-steady-state approximation here? Please clarify.

Authors: P26768? The equilibrium approach assumes that the secondary organics in the particle phase and gas phase are always in instantaneous equilibrium. This represents a good approximation for organics with relatively high saturation vapour pressure. However, when ignoring secondary organics in the gas phase during transport, and only transporting the organics in the particle phase, the approach is better valid for low volatile species with only low gas phase concentration. Therefore, we argue that for both, secondary organics in the particle phase and gas phase, transport processes should be taken into account, because otherwise the mass of secondary organics in the gas phase is lost (see Fig. 4 of the manuscript (green line)).

Second iteration:

Reviewer: Yes, 26768, sorry. I’m still confused here. The quasi-steady-state approximation is not the same as assuming instantaneous equilibrium (the quasi-equilibrium approach). In the paper you say quasi-steady-state approximation, but in the response, you only mention equilibrium. The quasi-steady-state concentration of a species will be out of gas-particle equilibrium if there is net production or loss of that species (but mass

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transfer is balancing production, so you get essentially a constant concentration in the gas phase). In general the quasi-steady-state approximation is used for species with low-vapor pressure such as sulfate (e.g. Pierce, J.R., Adams, P.J., A computationally efficient aerosol nucleation/condensation method: Pseudo-steady-state sulfuric acid, *Aerosol Science and Technology*, 43, 216-226, 2009.). In the case of low-volatility material, there is not much in the vapor phase for transport. Thus, I'm not sure why QSS wouldn't work. Did you mean to say "quasi-equilibrium approximation" in the manuscript? If yes, than things make sense to me.

Authors: Sorry for the confusion. Indeed 'quasi-equilibrium approximation' was meant. The correction will be made in the manuscript.

4) First iteration:

Reviewer: Reviewer: P26767 L19-21: Vehkamäki et al. (2002) is just for H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O, not SOG. Why not Metzger et al. (2010), which actually accounts for LV-SOG concentrations?

Authors: see answers above

Second iteration:

Reviewer: When you add the description of how LV-SOG to Vehkamäki, can you add discussion of why you chose to do this method rather than using Metzger?

Authors: For explanations the following sentences are added to the manuscript: 'The simple assumption applied in the current manuscript is to use the scheme of Vehkamäki et al. (2002) for two nucleation pathways: 1. H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O nucleation and 2. LV-SOG+H<sub>2</sub>O nucleation. For the second pathway H<sub>2</sub>SO<sub>4</sub> concentrations are replaced by LV-SOG concentrations in the nucleation scheme. This approach should be understood as a zero-order approximation to conduct sensitivity studies, as experimental evidence for interactions between LV-SOG and H<sub>2</sub>SO<sub>4</sub> is not considered and no adaptations for LV-SOG have been incorporated into the scheme of Vehkamäki et al. (2002). Future

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studies with REMOTE should consider interactions between LV-SOG and H<sub>2</sub>SO<sub>4</sub> as proposed by e.g. Kerminen et al. (2010), Metzger et al. (2010) and Paasonen et al. (2010).'

5) First iteration:

Reviewer: P26772 L21-25 and Figure 6: Are the authors comparing the modelled LVSOA to the measured LV-OOA and comparing the modelled SV-SOA+MV-SOA to the measured SV-OOA? I didn't find this explicitly stated. The authors should use some caution here because OOA in the AMS can be aged POA. Since the model doesn't have aged POA in this comparison, this could be a source of error.

Authors: As written in the manuscript, we compare modeled LV-SOC to measured low-volatile SOC and the modeled sum of MV-SOC and SV-SOC to measured semi-volatile SOC (page 26772 lines 21-23). We will correct the y-label of Fig. 6 (SOC instead of SOA) and add the above description to the figure label as well. Concerning POC, we agree with the reviewer, that AMS measurements may include aged POC, however, this contribution cannot be separated from SOC. We will add a sentence about this source of uncertainty to the revised manuscript.

Second iteration:

Reviewer: The AMS technically doesn't measure SOC (or SOA), what you are using, I believe, is the SV-OOA and LV-OOA (oxidized organic aerosol) or the carbon-only portion of these (SC-OOA and LV-OOA). I assume you equating SOA and OOA. This is why I said "I didn't find this explicitly stated" because it wasn't clear what the "measured SOC" was. Please also describe this explicitly along with the aged POC that you mentioned.

Authors: We agree with the reviewer, that AMS measures oxidised organic aerosol (OOA). For clarification and to avoid misunderstandings, we modified the abbreviation SOC to SOA throughout the manuscript, as we present and discuss the whole

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SOA mass concentration and not the carbon-only fraction. As written by the reviewer, we are indeed equating SOA and OOA, which we think is reasonable as the aging processes are producing oxidised organic compounds from which SOA aerosols are produced. The following sentences are added to the manuscript for clarification: 'It should be noted that from C-ToF-AMS measurements oxidised organic aerosol (OOA) concentrations are determined, which we equate with modelled SOA concentrations. In addition, C-ToF-AMS measurements may include aged POA, however at Puy-de-Dôme, this contribution was not separated from SOA.' In addition, the colours in Fig. 6 are adapted to Fig. 4 and the above mentioned additions from the first iteration are added to the figure label.

6) First iteration:

Reviewer: L26772 L28: Why wasn't 100% aging tested? I assume this would be the same as Yu... but this goes back to me not understanding the "maximum thresholds".

Authors: see answers above

Second iteration:

Reviewer: Would 100% aging be the same as Yu? I'm thinking yes, but the "greatly simplifies the procedure proposed by Yu (2011)" comment in the methods section makes me think that perhaps something else changed.

Authors: No, 100% aging would not equal to the approach used by Yu (2011), as also Yu (2011) considers that 'In the real atmosphere, all SOGs should react but only a fraction of SOGs in the category (MV-SOG, SV-SOG) has saturation vapor pressure low enough to be moved to the next category.' 'To account for the spreading of saturation vapor pressures around the averaged values, we represent each SV-SOG or MV-SOG group with a normalized distribution ...' 'The volatility change within each group is taken into account by assuming that the log-normal distribution of each SOG category is always maintained after a fraction of the SOG in the left-tail ... of the log-

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normal distribution has been moved down to the next category.' In the manuscript we cannot describe the whole approach of Yu (2011) in detail but invite the reader to refer to this manuscript for more detailed information.

References:

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