

## ***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.***

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In this paper, the authors evaluate aerosol mass and size distributions predicted by a regional model over Europe against measurements from Puy-de-Dôme during 2 weeks of June 2010. Specifically, they test assumptions about the partitioning and condensational properties of SOA. The authors conclude that an approach that uses aging of organics towards low-volatility SOA (treated as non-volatile) gives the best agreement for mass, and somewhat better agreement for the size distributions.

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The paper has several points that are confusing (e.g. the “maximum threshold of reactant concentration” and the “SOG nucleation”) as well as claims that this paper is the first to evaluate SOG nucleation. I requested clarification of these issues as well as citation of the previous modelling work that included SOG nucleation during the quick review (pre-ACPD) stage. The authors chose to not make any of these revisions at the quick review stage even though \*none\* of these changes were scientific (beyond clarification of techniques), changed the conclusions of their paper, or would have taken much time to revise. Yet, these changes would have (1) enhanced my ability to review the paper in this round by allowing me to better understand their approach and (2) prevented the authors from falsely claiming they were the first to consider SOG nucleation in a model. Because I will need to consider what the authors are actually doing with the “maximum threshold” and “SOG nucleation” approaches once they have been explained to me more clearly, I will require at least 1 more set of reviews (or maybe this could be done by iterated responses on the ACPD discussion site).

Otherwise, while I have a decent number of revisions, I feel that they are generally on the “minor” side of things in that I don’t think new model simulations are required.

Major comments:

1. “SOG nucleation”

1a. First, there are at least 2 papers that have included SOG nucleation in global modelling studies:

- The Metzger et al., 2010 paper that the authors already cite has global modelling showing the impact of organics on nucleation globally.

- Scott, C. E., Rap, A., Spracklen, D. V., Forster, P. M., Carslaw, K. S., Mann, G. W., Pringle, K. J., Kivekäs, N., Kulmala, M., Lihavainen, H., and Tunved, P.: The direct and indirect radiative effects of biogenic secondary organic aerosol, Atmos. Chem. Phys. Discuss., 13, 16961-17019, doi:10.5194/acpd-13-16961-2013, 2013.

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Please remove the claims that no one has tested this before and cite/discuss their work.

1b. How are the authors actually doing "SOG nucleation". They say that their nucleation scheme is Vehkamäki et al. (2002); however, this nucleation 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). 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. (2) They are using Vehkamäki et al. (2002) as just H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O, but since they are condensing LV-SOG onto the nucleation mode, they are calling this "SOG nucleation". However, this latter approach is not SOG nucleation at all, it is binary (H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O) nucleation followed by condensation of LV-SOG to already-nucleated, stable aerosols. If this is the case, the authors should not be calling this SOG nucleation at all. Furthermore, this would be in no way novel as many papers have used condensation of non-volatile SOA onto freshly nucleated particles (see any global aerosol microphysics modelling paper out of the following groups since about 2008 or 2009: Ken Carslaw, Dom Spracklen, Risto Makkonen, Peter Adams, Jeff Pierce... there are probably ~25 papers that already do this... furthermore Riipinen et al. 2011 is entirely about how important this initial LV-SOG condensation is in new-particle growth).

I'm curious as to why the authors did not just use the scheme published in Metzger et al. 2010 for SOG nucleation that explicitly has SOG in the scheme? This seems like the easiest way to have SOG nucleation in a model at this time.

Before the paper can be published in ACP, this "SOG nucleation" needs to be clarified (or removed if it is not actually SOG nucleation).

2. "maximum threshold of reactant concentration"

"To further simplify the approach of Yu (2011) we determine the mass-conserving trans-

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formation 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 oxidised 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 rate constant, they are predicting  $d[LV-SOG]/dt$  by...

$d[LV-SOG]/dt = k*[OH]*(0.1*[SV-SOG])$  for the 10% threshold or  $d[LV-SOG]/dt = k*[OH]*(0.01*[SV-SOG])$  for the 1% threshold rather than  $d[LV-SOG]/dt = k*[OH]*[SV-SOG]$

(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.

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3. Beyond the references missing with respect to “SOG nucleation” modelling studies, there is a large amount of other recent and relevant papers missing from the literature review in the introduction as well as for use in comparing how the size distributions change due to the SOA scheme. These all have looked at the interplay between the volatility of SOG/SOA and its affect on the predicted aerosol size distributions.

a. Riipinen, I., Pierce, J. R., Yli-Juuti, T., Nieminen, T., Hakkinen, S., Ehn, M., Junninen, H., Lehtipalo, K., Petaja, T., Slowik, J., Chang, R., Shantz, N. C., Abbatt, J., Leaitch, W. R., Kerminen, V.-M., Worsnop, D. R., Pandis, S. N., Donahue, N. M., and Kulmala, M.: Organic condensation: a vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, *Atmospheric Chemistry and Physics*, 11, 3865-3878, 2011.

This paper uses observed growth of the nucleation mode to determine that at least 50% of the condensing organics condense kinetically as if they are essentially non-volatile. There is also global modeling to show the effect this has on CCN.

b. Pierce, J.R., Riipinen, I., Kulmala, M., Ehn, Petaja, T., Junninen, H., Worsnop, D.R., Donahue, N.M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, *Atmospheric Chemistry and Physics*, 11, 9019-9036, doi:10.5194/acp-11-9019-2011, 2011.

This paper shows that the effective saturation concentrations of these essentially non-volatile species that are growing the ultrafine particles must be less than  $1\text{E-}3 \text{ ug m}^{-3}$ .

c. Donahue, N.M., Trump, E.R., Pierce, J.R., Riipinen, I.: Theoretical Constraints on Pure Vapor-Pressure Driven Condensation of Organics to Ultrafine Particles, *Geophysical Research Letters*, 38, L16801, doi:10.1029/2011GL048115, 2011.

This paper shows what must happen in the gas phase to produce these low-volatility OC (if these species are produced in the gas phase... see the Shaiwa paper).

d. Zhang, X., S.N. Pandis, and J.H. Seinfeld: Diffusion-Limited vs. Quasi-Equilibrium

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Aerosol Growth, *Aerosol Sci. Technol.*, 46, 874-885, 2012.

This paper looks at how the evolution of the size distribution is different between diffusion-limited (kinetic) and quasi-equilibrium (thermodynamic) net-condensation of SOA.

e. Shiraiwa, M. et al.: Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation, *PNAS*, 2013.

This paper shows that the kinetic growth of particles during SOA condensation may be due to particle-phase chemistry.

f. D'Andrea, S. D., Hakkinen, S. A. K., Westervelt, D. M., Kuang, C., Levin, E. J. T., Leaitch, W. R., Spracklen, D. V., Riipinen, I., and Pierce, J. R.: Understanding and constraining global secondary organic aerosol amount and size-resolved condensational behavior, *Atmos. Chem. Phys. Discuss.*, 13, 18969-19007, doi:10.5194/acpd-13-18969-2013, 2013.

This paper uses observations of the aerosol size distribution to determine the amount and condensational behavior of SOA, similar in ways to the current manuscript.

Specific comments: P26762 L9-11: This has been tested in models, and it is not clear that SOG nucleation is actually being tested in this manuscript, see above.

P26762 L17-19: Are the authors sure that coagulation of nucleation-mode and Aitken-mode particles is the dominant mechanism for generating new accumulation-mode particles? Unless nucleation-mode and Aitken-mode concentrations are extremely high (much higher than shown in Figure 7), condensational growth of the Aitken-mode generates many more accumulation-mode particles than coagulation.

P26762 L22-25: Please quantify the improvements. If the authors are going to claim “huge”, it should be quantified at least somewhere in the paper.

P26764 L9-10: More than 2 products are used in Yu (2011). GEOS-Chem has 2

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products for several different species classes (e.g. 2 for monoterpenes, 2 for isoprene etc)

P26764 L10-11: While most bulk aerosol models use thermodynamic approaches, many (perhaps most) aerosol microphysics models generate non-volatile SOG with a fixed yield, a 100% kinetic approach (most recent global modelling work out of Ken Carslaw's, Dom Spracklen's, Peter Adams's and Jeff Pierce's groups have done this). In terms of how this assumption affects the size distribution, it has been shown to be far superior to thermodynamic approaches (see D'Andrea et al. 2013 above).

P26764 L24-25: Yes they have, see above.

P26765 L3: Again, not sure if the authors consider nucleation of low-volatility SOG. Yu (2011) did have condensation of LV-SOG onto the freshly nucleated particles, so if that is what is being done in this manuscript (without actual SOG nucleation), there is no difference.

P26767 L3: "Size dependent scavenging has not been taken into account until now." How is size-dependent scavenging being done now?

P26767 L27 - P26768 L7: See above.

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

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?

P26772 L10-12: Why would the authors total mass concentrations be sensitive to nucleation? I guess there may be some minor feedbacks due to shifts in the size distribution and small changes in removal rates due to size-dependent scavenging. However, these effects are generally quite small.

P26772 L21-25 and Figure 6: Are the authors comparing the modelled LV-SOA to the

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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.

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".

Figure 7 and Figure 4: Can the authors make the line colors the same between the 2 figures?

Sections 4.2.1 and 4.2.2: Can the authors quantify the differences between the model and measurements?

P26774 L4-5: Did the authors remove the nighttime data from the measurements too? This should be done for an apples-to-apples comparison.

Conclusions: Please remove comment about this being the first study to consider SOG nucleation.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 26761, 2013.

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