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Atmospheric Chemistry and Physics Discussions

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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Answer to J. R. Pierce

Reviewer: 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 re-

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Interactive Discussion

Discussion Paper

visions 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 a 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.

Authors: We would like to thank the reviewer for his comments on the manuscript. We are happy to enter into the on-line discussion of the manuscript now. We believe that this is the right time and place during the review process for manuscripts to be published in ACP where e.g. techniques described in the manuscript can be clarified or more references can be added. According to the guidelines for the review process in ACP, technical corrections can be suggested (typing errors, clarification of figures, etc.) before publication in ACPD. However, further requests for revision (e.g. clarification of methods) of the scientific contents are not allowed. They shall be expressed in the interactive discussion following publication in ACPD. In our opinion, these guidelines help to avoid modifications of the original ACPD manuscript, so that the published ACPD manuscript only reflects the author's opinion (although this might need revisions), and not already that of the reviewers. However, by insisting to stick to these rules, we never questioned the value of the reviewer's comments and appreciate the time and effort the reviewer has spent to read the manuscript and provide constructive comments to improve the manuscript. Below we address the major and minor comments in detail.

Major comments:

1. SOG nucleation

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

Authors: Thanks for this advice. In the revised manuscript we will for sure remove the sentences 'To our knowledge, three-dimensional modelling studies on SOG nucleation are not yet available.' in the introduction and '. . . but to our knowledge they have not yet been evaluated in three-dimensional atmosphere-chemistry aerosol model simulations.' in the conclusions. Please note, however, that nucleation is not the primary focus of the manuscript, considering that nucleation events at Puy-de-Dôme were rare during the investigated period.

Reviewer: 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 H2SO4+H2O 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 104-1011 cm-3. 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

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thought of two possibilities of what they might be doing: (1) They are treating LV-SOG as the same as H2SO4 and using [LV-SOG]+[H2SO4] as an input to Vehkamäki et al. (2002) as opposed to just [H2SO4]. However, there is no basis for this method.

Authors: In recent years, the awareness that nucleation parameterisations involving only H2SO4 (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. H2SO4+H2O nucleation and 2. LV-SOG+H2O nucleation. For the second pathway H2SO4 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 H2SO4-SOG nucleation are not considered. Nevertheless, we would like to emphasis that – even in a simple way – nucleation of organic vapour is taken into account in the model simulations presented in the manuscript.

Reviewer: (2) They are using Vehkamäki et al. (2002) as just H2SO4+H2O, 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 (H2SO4+H2O) 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

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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.

Authors: As outlined above and hopefully described in a more clear and understandable way, nucleation of organic vapour is taken into account in a simplified way in the model simulations presented in the manuscript. Condensation of LV-SOG is considered in addition (see Fig. 1 of the manuscript).

2. “maximum threshold of reactant concentration”

Reviewer: “To further simplify the approach of Yu (2011) we determine the mass-conserving trans-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]*[SVSOG]

(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

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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 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.

Reviewer: 3. Beyond the references missing with respect to "SOG nucleation" mod-

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elling 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 nonvolatile species that are growing the ultrafine particles must be less than 1E-3 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 Shiaiwa paper).

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

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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.

Authors: Thanks for these references. We oversaw these recent papers. Nevertheless, we would like to note, that in particular in the introductory section, we included quiet a number of references to describe the research topic studied in the manuscript in a broad context. We agree, however, with the reviewer that referencing in section 4.2.2 is sparse and should better take into account the existing literature. This will be done in the revised manuscript.

Specific comments:

Reviewer: 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.

Authors: see answers above

Reviewer: 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 coagula-

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tion.

Authors: Condensational growth will be added as explanation in the revised manuscript.

Reviewer: 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.

Authors: SOC aerosol mass concentration increased by a factor of up to 6. This will be added in the revised manuscript.

Reviewer: P26764 L9-10: More than 2 products are used in Yu (2011). GEOS-Chem has 2 products for several different species classes (e.g. 2 for monoterpenes, 2 for isoprene etc)

Authors: Yu (2011) uses the abbreviation N x 2p + A/C for his approach, implying that N parent components are used in the two-product model (2p) for successive oxidation aging of SOGs and kinetic condensation of low-volatile SOGs on atmospheric particles (A/C). In the revised manuscript we will replace ‘two compound thermodynamical gas-particle partitioning’ by ‘two product thermodynamical gas-particle partitioning of a number of parent compounds’.

Reviewer: 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).

Authors: As already written above, more references will be added to the revised manuscript regarding the discussion on size distribution.

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

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Authors: see answers above

Reviewer: 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.

Authors: see answers above

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

Authors: Scavenging is treated independent of size with scavenging efficiencies based on Kasper-Giebl et al. (2000) distinguishing between soluble and insoluble aerosols dependent on cloud liquid water content (see P26767 L1-3). We will replace line 1-3 on page 26767 with the above sentence.

Reviewer: P26767 L27 - P26768 L7: See above.

Authors: see answers above

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)).

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Reviewer: P26767 L19-21: Vehkamäki et al. (2002) is just for H2SO4 and H2O, not SOG. Why not Metzger et al. (2010), which actually accounts for LV-SOG concentrations?

Authors: see answers above

Reviewer: 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.

Authors: Similar to the reviewer, we do not expect a substantial increase in mass when nucleation is taken into account, as written in the manuscript 'SOC mass concentration remains nearly unchanged taking into account nucleation of LV-SOC'.

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

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

Authors: see answers above

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

Authors: Will be done in the revised manuscript. See figure below.

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

Authors: Compared to the thermodynamical approach, SOC aerosol mass concentration increased by a factor of up to 6 with the thermodynamical-kinetic approach. This will be added in the revised manuscript. It is already mentioned in the manuscript (page 26772, line 8-10) that increasing the amount of biogenic VOC emissions by a factor of 5 in the10 % aging simulation leads to a considerable increase in OC aerosol mass concentrations in the range of the measurements (see Fig. 4 of the manuscript). For section 4.2.2 we prefer the qualitative comparison provided by the discussion in section 4.2.2 and Fig. 7 without further quantifications, as the modal size distributions derived from the model are compared to measured size distributions in size bins.

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

Authors: Thanks for this advice. The corrected figure is shown below and resembles the original one pretty much. The major differences are that the observation curves are more noisy and that in the aged air masses, daytime observation show higher Aitken mode concentrations (compared to the daily median), in comparable number concentration as the model results.

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

Authors: The second part of the sentence 'New developments considering heteromolecular nucleation between H2SO4 and organic vapours have been published recently (Paasonen et al., 2010), but to our knowledge they have not yet been evalu-

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ated in three-dimensional atmosphere-chemistry aerosol model simulations.' will be removed in the revised manuscript.

References: Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635–2643, 2006.

Kasper-Giebl, A., Koch, A., Hitzenberger, R., and Puxbaum, H.: Scavenging effi ciency of aerosol carbon and sulfate in super-cooled clouds at Mt. Sonnblick (3106m a.s.l., Austria), J. Atmos. Chem., 35, 33–46, 2000.

Langmann, B., Varghese, S., Marmer, E., Vignati, E., Wilson, J., Stier, P., and O'Dowd, C.: Aerosol distribution over Europe: a model evaluation study with detailed aerosol microphysics, Atmos. Chem. Phys., 8, 1591–1607, doi:10.5194/acp-8-1591-2008, 2008.

Stier, P., Feichter, J., Kinne, S., Kloster, S., Vignati, E., Wilson, J., Ganzeveld, L., Tegen, I., Werner, M., Balkanski, Y., Schulz, M., Boucher, O., Minikin, A., and Petzold, A.: The aerosol climate model ECHAM5-HAM, Atmos. Chem. Phys., 5, 1125–1156, doi:10.5194/acp-5-1125-2005, 2005.

Vehkamaeki, H., Kumala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M., and Laaksonen, A.: An improved parameterization for sulphuric acid-water nucleation rates for tropospheric and stratospheric conditions, J. Geophys. Res., 107, 4622, doi:10.1029/2002JD002184, 2002.

Yu, F.: A secondary organic aerosol formation model considering successive oxidation aging and kinetic condensation of organic compounds: global scale implications, Atmos. Chem. Phys., 11, 1083–1099, doi:10.5194/acp-11-1083-2011, 2011.

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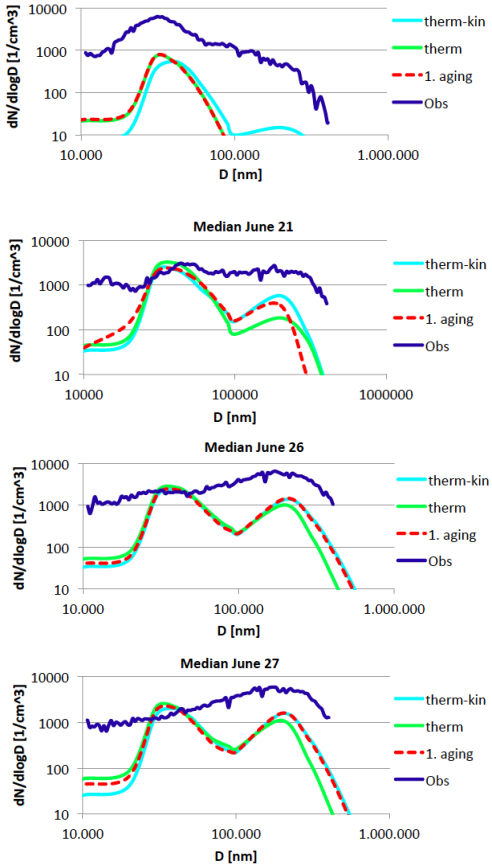

Corrected Figure 7 of the manuscript.

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