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Comment

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.

baerbel.langmann@zmaw.de

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Answers to anonymous referee #2:

Reviewer: This study presents a modeling case comparing the thermodynamic-kinetic to the pure kinetic approaches and compares predictions to measurements at a site in France in June 2010. First of all, I concur with the comments from the first reviewer. While the study is useful, the manuscript has general lack of clarity. I recommend major revisions with careful accounting of my several detailed comments below before

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the manuscript can be considered for publication.

Authors: Please note that the manuscript compares a thermodynamic-kinetic approach with a pure thermodynamic approach - it seems there is a typing error in the reviewers comment.

Reviewer: 1. Abstract: I disagree with the last sentence based on results shown in the manuscript. I do not see a huge improvement in modeled SOC aerosol mass concentration with the thermodynamic-kinetic approach compared to the pure thermodynamic approach. Figure 7 shows small differences in number concentrations of accumulation mode particles for aged air masses. Please also see my comment number 10 below.

Authors: Please note that the last sentence of the abstract of the ACPD manuscript is 'Comparison with a thermodynamic SOC aerosol formation approach shows a huge improvement in modelled SOC aerosol mass concentration with the thermodynamic-kinetic approach for SOC aerosol formation.' Mass SOC concentrations, however, are presented in Fig. 4, not in Fig. 7. Fig. 4 indicates an increase of up to a factor of 6 in SOC aerosol mass concentration (light blue line: thermodynamic-kinetic approach, green line: thermodynamic approach), which represents a huge increase. The reviewer should not look at Fig. 7 when talking about SOC mass concentrations.

Reviewer: In addition, any comparison for SOC mass should include LV-SOG in both approaches. Including LV-SOG in just thermodynamic-kinetic approach, but not in the pure thermodynamic approach is not a consistent comparison, since LV-SOG is formed by aging of semi-volatile organic vapors.

Authors: To reply on this comment we would like to refer to Fig. 1 of the manuscript. When the thermodynamical approach is used, where only partitioning between MV-SOG/MV-SOC and SV-SOG/SV-SOC is considered and no aging, no low volatile secondary organic gas LV-SOG and secondary aerosol component (LV-SOC) are produced, so that their concentrations equal to zero. Even when only the first aging step from MV-SOG to SV-SOG is considered, LV-SOG and LV-SOC concentrations remain

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equal to zero, as those are only generated by the second aging step. For this reason LV-SOG and LV-SOC concentrations are not included in the pure thermodynamical approach.

Reviewer: 2. P 26764 Lines 1-5: Prior to Jimenez et al. 2009, the aging of organic vapors producing less volatile organic vapors was implemented in 3D model by Robinson et al. [2007] and Shrivastava et al. [2008]. Please include reference to these studies too. In addition, Jimenez et al. 2009 also demonstrated the concept of fragmentation reactions which may lead to increase in volatility of organic vapors. Recently, Shrivastava et al. [2013] demonstrated that including fragmentation reactions in a 3D model improved model-measurement agreement compared to mechanisms that neglect fragmentation reactions. The one-way decrease in volatility of organic vapors is less realistic based on several studies [e.g., Cappa and Wilson, 2012; Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2010; Kroll et al., 2011; Lambe et al., 2012]. The authors should at least acknowledge the limitations of ignoring fragmentation reactions. In the study of Shrivastava et al. [2013], the role of fragmentation (considered only in gas-phase) was chiefly to reduce the amount of condensable organic gas precursors. In the consideration of threshold values on page 26768 (Lines 1-5), it should be further discussed that fragmentation also reduces the amount of condensable organic vapors. I suggest that the authors cite the relevant recent studies (e.g. Shrivastava et al. [2013]) in addition to Jimenez et al. [2009].

Authors: The references to Robinson et al. (2007) and Shrivastava et al. (2008) are added to the manuscript. Please note, that the applied parameterisation for aging with maximum threshold values used in the model is an empirical one, which is now mentioned in the revised version of the manuscript: '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 %.' Therefore, fragmentation (and oligomerisation – see reviewer comment 3 below) are

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implicitly, but not explicitly taken into account. Nevertheless, the role of fragmentation in reducing the amount of condensable organic gas precursors with a citation to Shrivastava et al. (2013) is included in the revised manuscript in the conclusion and outlook section together with the importance of oligomerisation reactions (see the following comment 3 of the reviewer) as follows: 'Furthermore, a deeper understanding of chemical mechanism contributing to the aging processes of secondary organic gases, such as fragmentation or oligomerisation reactions (Shrivastava et al., 2013), will be necessary to improve aging parameterisations for three-dimensional modelling.'

Reviewer: 3. Another major point which the authors ignore is the importance of oligomerization reactions. Shrivastava et al. [2013] have discussed how rapid particle phase oligomerization reactions could transform semi-volatile organics to low volatility compounds, and showed that this transformation causes large spatial and temporal distributions in predicted SOA loadings. Given the potentially large impact, some discussions are needed as to how would oligomerization reactions influence the modeling approach proposed by the authors.

Authors: Please see answers to comment 2 above. The additional text is: 'Furthermore, a deeper understanding of chemical mechanism contributing to the aging processes of secondary organic gases, such as fragmentation or oligomerisation reactions (Shrivastava et al., 2013), will be necessary to improve aging parameterisations for three-dimensional modelling.'

Reviewer: 4. P 26768 L14-16: Treating LV-SOG nucleation without its condensation to H₂SO₄ nuclei is clearly unrealistic. This could be a pedagogical case, however, the authors should consider adding the H₂SO₄+SOG nucleation similar to Metzger et al. for completeness. In addition, the authors should better describe their replies to the first reviewer comments clarifying how they treated nucleation of LV-SOG in the manuscript. On my first read of the author's replies, I thought they were considering 2 different nucleation pathways which were mutually exclusive. On reading the manuscript I realized this was not the case. Their nucleation pathway includes H₂SO₄+LV-SOG+H₂O, but

they neglect interactions between LV-SOG and H₂SO₄.

Authors: Thanks for the advise in the first sentence. In Fig. 1 of the manuscript the condensation of LV-SOG to form LV-SOC,ns was missing, which is corrected in the revised manuscript. The corresponding text in the revised manuscript reads as written below and hopefully clarifies how LV-SOG nucleation is treated in the model. Please note, that now we state that the LV-SOG nucleation study represents only a sensitivity study. 'The number of nucleated particles and the mass of nucleated LV-SOG is determined using the homogeneous nucleation parameterisation of Vehkamaeki et al. (2002). 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 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 H₂SO₄ is not considered and no adaptations for LV-SOG have been incorporated into the scheme of Vehkamäki et al. (2002). Future studies with REMOTE should consider interactions between LV-SOG and H₂SO₄ as proposed by Kerminen et al. (2010), Metzger et al. (2010) and Paasonen et al. (2010).'

Reviewer: 5. P 26772 last paragraph: The description is very confusing. Also the caption to Figure 6 says Model simulations correspond to those shown as light blue line in Figure 4. Do all model simulations shown in Figure 6 correspond to the light blue line in Figure 4? But line blue line in Figure4 corresponds to 1% aging. Figure 6 shows both 1% and 10% aging. I also do not understand how light blue line for 1% aging shown in Figure 6a generates more semivolatile SOA than 10% aging (red line). The last paragraph on page 26772 says the semi-volatile SOA is sum of modeled MV-SOC and SV-SOC. Does this mean that semi-volatile SOA is lower in the 10% aging case (red line in Figure 6a) because it is moved to the low volatility (shown in Figure 6b)? If this is the case, please explain this better.

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Authors: Thanks for the hint. The colours in Fig. 6 have been adapted to those used in Fig. 4, so that model simulation results correspond to those shown as black and light blue line in Fig. 4. Assuming 1 % aging, more semi-volatile SOG (MV-SOG + SV-SOG) is produced as the formation of LV-SOG is more limited compared to 10 % aging.

Reviewer: 6. Since the authors describe SOC and OC results please indicate what factors were used to convert from OM to OC? Most models predict OM rather than OC.

Authors: Please note that all mass concentrations of organic compounds are given in [$\mu\text{g}/\text{m}^3$] in the manuscript and not in [$\mu\text{gC}/\text{m}^3$]. Therefore, conversion of modeled concentrations from [$\mu\text{g}/\text{m}^3$] to [$\mu\text{gC}/\text{m}^3$] or vice versa was not necessary for the results presented in the manuscript. To clarify this, the abbreviation SOC is replaced by SOA throughout the revised manuscript.

Reviewer: 7. Table 1: If the authors are not using the saturation vapor pressures to describe MV-SOC and SV-SOC what is the utility of Henry's law coefficient shown in the table? Is it used only in their dry and wet scavenging parameterizations? Please explain.

Authors: Henry's law coefficients shown in Tab. 1 are used for the calculation of the thermodynamic partitioning between SV-SOG/SV-SOC and MV-SOG/MV-SOC, which is calculated using Henry's Law equilibrium according to Anttila et al. (2010).

Reviewer: 8. P26774 Lines 10-15: Why do fresh air masses show more particles in the Aitken mode using the pure thermodynamic approach? The curvature effects should cause less particle growth of nuclei to the Aitken mode in this approach compared to the thermodynamic-kinetic approach.

Authors: Different to e.g. Riipinen et al. (2011) and Yu (2011), nucleation events in the boundary layer were rare at Puy-de-Dôme, France during late June 2010. Therefore, in the model simulation using the mixed-thermodynamical-kinetic approach the contribution of nucleation mode particle number concentrations that could contribute to the

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formation of Aitken mode particles, was low - see also Fig. 9. Aitken mode particles result mainly from primary particle emissions (see page 26773/26774, last sentence/first sentence). Under these conditions, Aitken mode particle growth is more pronounced with the mixed-thermodynamical-kinetic approach compared to the thermodynamical approach, explaining the higher load of Aitken mode particles in the simulation with the thermodynamical approach.

Reviewer: 9. Why are the differences in the pure thermodynamic and the thermodynamic-kinetic approach much so small for aged air masses? The authors suggest that a faster growth occurs in the thermodynamic-kinetic approach during aging. Would these differences increase if the aging rate from SV-SOC to LV-SOC were increased?

Authors: Please note that with the mixed-thermodynamical-kinetic approach larger particles in the accumulation mode (and more) are produced in the aged air masses compared to the thermodynamical approach (Fig. 7). In addition, Fig. 7 shows a comparable distribution for accumulation mode particles in the aged air masses as modelled with the mixed-thermodynamical-kinetic approach considering both, the first and second aging step, and considering only the first aging step. The simulation with the first aging step only does not generate LV-SOC (see explanation to the first reviewers comment above), indicating that increasing the aging rate from SV-SOC to LV-SOC would have no effect.

Reviewer: 10. Lines 20-22: I find this statement very less useful: “Generally, the thermodynamic-kinetic approach can more realistically reproduce observed data than pure thermodynamic-kinetic approach in particular in fresh air-masses”. The model resolution of most global models is even coarser than the 0.5 degrees used by authors. This implies that air masses are already aged in these coarse grid models. In that case the author’s results imply no large improvement in predicted distribution of CCN relevant accumulation mode particle numbers by using the thermodynamic-kinetic as compared to the pure equilibrium approach. Am I missing something here? Please

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explain.

Authors: As already mentioned in the answer to the 9th reviewers comment above, model simulations with the mixed thermodynamical-kinetic approach produce larger particles in the accumulation mode (and more) in the aged air masses compared to the thermodynamical approach (Fig. 7). The reviewers statement that air masses are already aged in coarse grid global models are disproved by the results of global model simulations presented e.g. by Riipinen et al (2011) and Yu (2011), who both used a model resolution of $4^\circ \times 5^\circ$ and studied the aging of secondary organic gases, revealing considerable differences when taking into account kinetic processes. One should keep in mind that the aging process of secondary organic gases is a temporal process. Therefore, the statement of the manuscript that model results with the mixed thermodynamical-kinetic approach show improvements compared to the thermodynamical approach remains valid and generally important for three-dimensional modelling studies.

Reviewer: 11. P26775 first few lines: Why is nucleation of increasing importance with increasing height in the thermodynamic-kinetic approach? My understanding is this approach is based on LV-SOG which is nearly insensitive to decrease in temperature with altitude that favors condensation of semi-volatile organics. Please elaborate.

Authors: Please note page 26768, line 16-19 of the manuscript: 'As condensation on pre-existing particles and nucleation of new particles compete for the available LV-SOG, first the maximum amount of condensable LV-SOG on pre-existing particles is calculated. The remaining LV-SOG is available for the nucleation of new clusters.' That means that condensation is the preferential case. However, according to Vehkamäki et al. (2002), Fig. 11 the nucleation rate increases with decreasing temperatures. Therefore, higher particle number concentrations are determined in the free troposphere in the model simulation including nucleation of LV-SOG. Metzger et al. (2010) determine lower particle number concentrations in the free troposphere using a binary homogeneous nucleation approach for H₂SO₄ and organic carbon compounds. However, in

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a long-term study, Boulon et al. (2011) found favoured nucleation at Puy-de-Dôme compared to an adjacent station at lower altitude. Therefore, it remains open if the results presented in Fig. 9 of the manuscript are realistic or not, as vertical profile measurements at Puy-de-Dôme are not available for evaluation during the measurement campaign investigated here. We will add/modify the following sentences to the manuscript: 'As measured vertical profiles of particle number concentrations are not available at Puy-de-Dôme during the period investigated here, an evaluation of the model results was not possible. However, in a long-term study, Boulon et al. (2011) found favoured nucleation at Puy-de-Dôme compared to an adjacent station at lower altitude. Further studies will be necessary to highlight the role of LV-SOG nucleation in the PBL and lower free troposphere and the role of this process for the formation of particles in the size range of CCN particles. Those studies should consider interactions between LV-SOG and H₂SO₄ as proposed by Kerminen et al. (2010), Metzger et al. (2010) and Paasonen et al. (2010).'

Reviewer: 12. Going back to first few lines on page 26765: The authors say that different to Yu et al. (2011), they consider the contribution of anthropogenic SOC to SOC aerosol formation. But in their sensitivity tests (e.g. in Figure 4) they only increase biogenic VOC emissions by a factor of 5. What about the uncertainty due to anthropogenic SOC emissions? Also in the conclusions please comment on the relative importance of anthropogenic vs. biogenic SOA in their study.

Authors: The relative importance of biogenic VOC emissions over anthropogenic VOC emissions during high-pressure periods in summer has been reported for long, e.g. Lamb et al. (1987). In addition, previous studies on the organic aerosol sources at Puy-de-Dôme show a predominate contribution of biogenic sources in summer (Freney et al., 2011). Therefore, the focus of the manuscript, investigating a high-pressure situation during summer 2010 over Europe was on the more important uncertainty of biogenic VOC emissions. For a US biogenic emission inventory with monthly resolution, Lamb et al. (1987) reported an uncertainty of a factor of 3. Therefore, an uncertainty

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of a factor of 5 for the biogenic VOV emissions is in line with the uncertainty estimate of Lamb et al. (1987) considering that the overall uncertainty increases with temporal resolution, which is 5 minutes (the model time step) for the model study presented in the manuscript. The following sentence will be added to the conclusions of the manuscript: 'During high-pressure periods in summer, as investigated here, biogenic VOC emissions play an important role for the formation of SOA.'

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