

Interactive comment on “Organic condensation – a vital link connecting aerosol formation to climate forcing” by I. Riipinen et al.

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The authors thank the reviewer for the constructive and insightful comments that we think will improve the manuscript. Our point-by-point answers are as follows:

Major Comments:

1. The abstract can be improved better. Please be more specific and bring more points of the results into the abstract. Since this manuscript does not have conclusion section, the authors may extend the abstract so that readers can take important messages of this study more easily.

We have modified the abstract of the revised manuscript according to the Reviewer's suggestions (see the following for details).

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- The expression "state-of-the-science" is not a common word and ambiguous (At least I could not find this word in the dictionary. Did authors mean state-of-the-art?). Please be more specific. For example, authors can say "We demonstrate that the thermodynamic models fail...".

We have replaced "state-of-the-science" with "state-of-the-art models that assumed instant equilibration of the aerosol with the gas phase" in the revised manuscript.

- What modeling approach is that which is consistent with measurements?

We have added a sentence where we state that assuming roughly half of the condensing organics to be effectively non-volatile and distributing the rest to the pre-existing organic mass gave the best agreement between the measured and the modeled growth, but that there was a relatively large variability between the analyzed days.

- "The large sensitivity of climate forcing" is too far to conclude by this study. The authors indeed showed the increase in aerosol number concentration by organic condensation, but did not "demonstrate" any change of climate or radiative forcing. I think "discuss" is a fair word to use here.

We agree, and have replaced "large sensitivity of climate forcing" with "large sensitivity of the CCN number concentrations" and added a sentence where we state that the effect to the climate forcing is discussed.

2. The description of microphysics models are not enough and it is hard to see how authors did simulations presented in Fig. 5-8 exactly. The authors provided only rough and qualitative information of the models. The authors should specify/clarify at least some key equations, parameters, and assumptions used in both thermodynamic and kinetic models. If the authors do not want to disturb the flow of the discussion, the authors may put them in the appendix or supplemental information.

We have added more detail on the modeling approach to the revised manuscript, as requested by the Reviewer (see the following for details). In particular, we have added

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equations describing the rate at which low-volatile and semi-volatile SOA condenses onto each size.

- For kinetic model results of Fig .5, did the authors assume mass accommodation coefficient of 1? If so, please explicitly mention this. I expect the kinetic model results are very sensitive to this parameter. Did the authors do any sensitivity tests?

Yes, we assumed the mass accommodation to be unity in the model calculations. It is correct that the results are relatively sensitive to the parameter. However, it does not really change our conclusions on the fact that we need to assume that a significant portion of the condensable organics is distributed proportional to the aerosol surface area rather than the pre-existing organic mass. For our simplistic approach (where the aerosol phase constituents were assumed to be non-volatile) lowering the mass accommodation would in fact result in this fraction being even larger. Since in reality lowering the mass accommodation coefficient would naturally slow both condensation and evaporation, it has a complicated effect on the results. We are testing the mass accommodation coefficient extensively in our future work on this topic. We have added discussion on the impact of the mass accommodation coefficient to the revised version of the manuscript.

- The authors use the sentence "organic mass flux condense kinetically" quite often. But what do you mean exactly? Do you mean that all molecules colliding to surface are taken up by particle? In reality, anyway molecules collide kinetically to the surface, whether you treat them thermodynamically or kinetically. Therefore, I am wondering if the way authors present (50% kinetic + 50% thermodynamic) are really appropriate way.

We agree that the "kinetic condensation" is a loose term and the Reviewer is correct that in reality there is always a kinetic component in the flux of molecules to a particle surface. In this paper the "kinetically-controlled condensation" is equal to the assumption that the kinetic collision rate is the only process limiting the uptake of the vapor

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molecule, i.e. that once it hits the particle surface it does not evaporate (and its saturation vapor pressure is effectively negligible). We are aware that in reality this is not the case (at least for many of the molecules condensing in the atmosphere), but we think that separating the condensing organics to two classes, one whose condensation is mainly limited by the kinetic collision rate and other whose condensation is limited by its partitioning to the pre-existing organic material in the particles (i.e. its effective saturation concentration) is a reasonable first step – particularly as the identities and thermodynamic properties of the organic vapors condensing on ultrafines are not known. We are already working on the next step, i.e. an approach that would allow for a more realistic description of the properties of the compounds growing the smallest atmospheric aerosols.

- Although the authors call the model used in Fig. 5(d) very general name of "kinetic model", it seems that the authors did not resolve any chemical kinetic processes (i.e., chemical reaction on surface and in bulk), but consider only a part of the physical kinetic processes (i.e., collision and condensation, and also gas phase diffusion?, but not bulk diffusion). I would suggest calling this model "kinetic condensation (collision) model", for example.

This is correct. The approach now only considers the gas phase kinetics related to the condensation process. We have clarified this in the revised manuscript and followed the Reviewer's suggestion on renaming the approach.

- Is the simulation result shown in Fig. 5(b) gas diffusion limited or mass accommodation limited?

It could be both. In the simulation we have taken the mass flux to the nucleation mode from the AMS and distributed according to either 1) the pre-existing organic mass or 2) the surface area of the aerosol. The latter is consistent with both gas-diffusion limited and mass accommodation limited growth, but again we feel that for the purpose of demonstrating that the condensation kinetics need to be accounted for in large scale

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models, we do not need to make this distinction at this point. We have clarified this in the revised manuscript.

- In the thermodynamic model, it seems that the authors consider only absorptive partitioning, but not adsorptive partitioning (is this correct?). If yes, probably it is better that authors call this model "thermodynamic absorptive model" for clarification, as adsorptive process is not included. If the authors include adsorptive partitioning in their model, do the authors get better results than Fig. 5(b)? Are authors sure that adsorptive partitioning is a minor process?

This is an excellent point. We cannot exclude adsorptive partitioning based on the results. However, that too, would result in the condensing mass being distributed proportionally to the aerosol surface area rather than the bulk mass. We have clarified this in the revised manuscript, added adsorption as a potential explanation for our observations, and followed the Reviewer's suggestion on renaming the thermodynamic approach.

- P399, L13: Why the authors are sure that these assumptions do not change any conclusions?

In the following we give our reasoning to why we think that the assumptions given in p399 and numbered from 1 to 5 do not change the overall conclusion that semi-volatile SOA that instantaneously reaches thermodynamic equilibrium and partitions to pre-existing mass cannot explain nanoparticle growth observed on the analysed nucleation days. (1) We assumed that the organic mass flux measured by the AMS represents a major part of the overall flux. This is usually a good assumption knowing that the total organic aerosol mass fluxes to >20 nm particles as calculated from the AMS data ranged from 0.02–0.2 $\mu\text{gm}^{-3} \text{h}^{-1}$ for spring 2007 in Hyytiälä. The mass required to grow the nucleation mode particles is thus usually less than 10

3. The authors suggest that the 50%-50% ratio of LV- and SV-OOA corresponds to the ratio of the organic mass to condense on the aerosol. I think LV-OOA can be formed

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mostly in the condensed phase reactions and it may be difficult to form such high mass and very low volatile organic compounds by gas phase reaction. Since the presented models (both thermodynamic and kinetic models) seem to consider only gas phase oxidation but no surface or condensed phase reactions, how the authors can connect thermodynamic and kinetic partitioning to LV- and SV-OOA?

This is an interesting point, and we fully agree with the Reviewer that it is possible that the LV-OOA and actually also our "kinetic" SOA as well could be produced in particulate phase reactions. We do not think, however, that there is a problem assigning the "kinetic" SOA with the LV-OOA: in our simplistic modeling approach we treat the "kinetic" SOA as completely non-volatile – sticking to the particle when it hits the particle surface. We think that it is not unreasonable to assume that this approach is roughly in line with particle-phase reactions making the aerosol constituents effectively non-volatile once they get to the condensed phase. For instance oligomers or organic salts can behave as effectively non-volatile after being formed in the particles.

4. The authors use the word "climate forcing" both in the title and abstract. However, there is actually not much discussion about climate forcing. Is it possible for authors to provide a figure of for example "increase in radiative forcing (W m^{-2}) due to ultrafine aerosol growth" analogous to Fig. 9-11?

This is a good point, and it would indeed be desirable to have robust calculations on the climate forcing resulting from the ultrafine aerosol growth. However, currently large uncertainties exist in the conversion of aerosol number concentrations to cloud droplet number concentrations. We are therefore reluctant to draw any more specific conclusions than the generic $> 1 \text{ W m}^{-2}$ that is given now in the current version of the paper (p.404). This number is based on the simple calculation following the procedure presented by Seinfeld and Pandis (2006) in equation 24.43.

We agree with the Reviewer that in the current version of the manuscript the climate forcing is over-emphasized. We have softened the corresponding statements and

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shifted to focus more towards the impact of organics on aerosol number size distributions.

Minor Comments:

- P.395, L14: *What does EUCAARI stand for? Better to put a reference of EUCAARI project.*

We have added a reference to the EUCAARI project to the revised manuscript.

- P.399, L11: *It should be "the fraction of semi-volatile. . ."*

We have corrected this to the revised manuscript.

- P.400, L16: *Please give references for large uncertainties in the emissions of SOA precursor gases in all atmospheric models, if you have.*

We think that Hallquist et al. (2009), is an appropriate reference to demonstrate these uncertainties. We have added citation to it to the place suggested by the reviewer.

- *Nel, 2005 is missing in the reference list.*

We have corrected this to the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 387, 2011.