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# ***Interactive comment on “Modelling non-equilibrium secondary organic aerosol formation and evaporation with the aerosol dynamics, gas- and particle-phase chemistry kinetic multi-layer model ADCHAM” by P. Roldin et al.***

**P. Roldin et al.**

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Thank you for the relevant and constructive comments on the manuscript. They definitely will help us to improve it.

First of all we want to mention that in the revised manuscript we will change the formulation “particle surface layer” to “particle surface-bulk layer” when we refer to the

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monolayer thick particle layer at the surfaces where the condensing molecules dissolves. And if we consider reversible adsorption we will always call this layer “sorption layer” and nothing else. When we model the condensation and dissolution of organic compounds into the particle surface-bulk layer we will change the formulation “surface mass accommodation coefficient” to “ $\alpha$ ommodation coefficient” which considers both the potentially non-unity probability of adsorption (sticking) and dissolution into the particle surface-bulk layer.

General comment:

Some parts of the paper were not easy to follow, although the research itself looks very good. I strongly suggest the authors to read the manuscript carefully, and ask a third person for an opinion to improve the presentation quality of the manuscript if necessary.

We will redo some of the model simulations, rewrite the paper according to the comments we have received from all referees and then ask a third person for an opinion on how to improve the presentation quality.

Specific comments.

Comments P775L21 In the future, we intend to use this knowledge, to develop the ADCHEM model (Roldin et al., 2011a). ADCHEM is a 2-D-Lagrangian model for Aerosol Dynamics, gas phase chemistry and radiative transfer which has been used for urban plume studies (Roldin et al., 2011b). One of the main purposes with ADCHEM is to improve the sub-grid scale aerosol particle representation in large-scale chemistry transport models (e.g. Bergstrom et al., 2012). In the first version of ADCHEM aging of the organic compounds in the atmosphere was simulated with a non-equilibrium 2-DVBS approach. The 2-D-VBS method treats the oxidation of organic compounds in a simplified way by generalized OH reactions rates, functionalization and fragmentation patterns (Jimenez et al., 2009; Roldin et al., 2011a and Donahue et al., 2011). Future perspective of the study is the main focus of the paragraph; however, this paragraph is

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located at introduction. Please consider to move this paragraph to the last part of the manuscript.

Yes, we will move this text to the conclusions

P777L2 "homogeneous nucleation". Please clarify how homogeneous nucleation rates for organic compounds were parameterized in the model.

In this work we do not treat the initial activation and growth of the formed molecular clusters explicitly.

On P798, L13-L20 we explain how the homogeneous nucleation is treated in this work.

"We start with one particle size and add new particle size bins during the early stage of particle formation. The new particles are assumed to be composed of non-volatile SOA material and are introduced into the model at an initial diameter of 5 nm. Hence, in this work we do not treat the initial activation and growth of the formed molecular clusters. The new particle formation rate ( $J_{5\text{nm}}$ ) is assumed to be constant during the experiments. A new size bin is added for the time step when the smallest particle size grows larger than 10 nm in diameter. For the experiments which we simulate in this work the SOA mass (condensation sink) increases rapidly during the early stage of SOA formation. This effectively prevents the newly formed particles from growing and thus generally keeps the number of model particle size bins down to less than 20 (see Fig. S1 in the Supplement)"

P779 equation 1 Please cite an appropriate reference for the equations. In addition, please clarify unit of all the parameters.

We will put a proper reference to Eq. 1 and write out the units of those parameters which have any.

P780L10 'In this article we either treat all SOA (monomers + oligomers + organic salts) as one phase or as two completely separated phases.' It was not clear how phase separation was treated in the model. Please clarify it.

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Yes, this sentence and the one after that ("Hence, if the model treats the oligomers and organic salts as a separate phase, then this material has no influence on the saturation vapour pressures of the monomers (Eq. 2).") may be a bit confusing. We will change these sentences and instead write:

"In this article we either treat all SOA (monomers+dimers+organic salts) as one phase or as two completely separate phases, with monomers as one phase, and the dimers and organic salts as a second phase. In this work the phase separation is not modelled explicitly (as in Zuend and Seinfeld, 2012). Instead we simply assume that either the phase separation does occur or it does not. In future model application, we intend to implement a simplified approach to calculate liquid-liquid phase separation (e.g. Topping et al., 2012). If the described phase separation occurs, then the monomers will not dissolve in the phase made up of dimers and/or organic salts. Thus, their saturation vapour pressures are not lowered by dimerization or organic salt formation, which result in less SOA mass in the model (Topping et al., 2012)."

P781-784 Section 2.2.3 introduces many parameters to describe wall losses of both particles and gas phase species. The authors have conducted a sensitivity study on those values in section 3.4. I was unable to understand how the values of those parameters in section 2.2.3 were determined until reading section 3.4. I suggest to rearrange the manuscript so that readers will be able to follow the story smoothly.

We still want to have a clear separation between the model description and the model applications and evaluation. Thus, we want to keep Sect. 2.2.3 and 3.4 as separate sections. However, early in Sect. 2.2.3 we will refer to Sect. 3.4 for the sensitivity tests of different parameters. We will also refer to Sect. 3.4 and the figures in Sect. 2.2.3 when we describe the specific parameters (i.e.  $\Delta x$ ,  $V_{\text{wall}}$ ,  $E$  and  $kg, w$ ). We will add a sensitivity test in the supplementary material where we test how the modelled gas-wall partitioning is influenced by the assumed width of the layer next to Teflon walls (chamber volume next to the Teflon walls ( $V_{\text{wall}}$ )), and the laminar layer width ( $\Delta x$ ) next to the chamber walls. This test we will also refer to in Sect. 2.2.3.

P789 R1a-R6 Please clarify how the reaction constants were determined.

In Sect. 3.3 and 3.4 where different dimerization processes are considered, we will compare the reaction constants which we use with the range of values given by (Ziemann and Atkinson, Chem. Soc. Rev., 41, 6582-6605, 2012). We will also include a new Table in Sect. 3 which describe which processes that were considered, and the parameter values that were used for each model application.

P794 equation 18 Please clarify how the value for mass accommodation coefficient was determined.

In the revised version (based on the comments from M. Shiraiwa) we intend to only used unity mass accommodation coefficients (surface-bulk accommodation coefficients) for all simulations. This is at least to some extent motivated by our model results in Sect. 3.1.

P801L26 'In this work we model the organic salt formation between ammonium and carboxylic acids as a process occurring in the particle surface layer and particle bulk and not in the gas phase.' It was not clear why the authors have made this assumption, after telling 'part of the ammonia uptake could be attributed to reactive uptake of NH<sub>3</sub> and organic acids from the gas phase (Kuwata and Martin, 2012).'

In Na et al., 2007 the authors propose a mechanism where the organic salts between carboxylic acids and NH<sub>3</sub> seem to form in the gas-phase and then the organic salts condenses (Fig. 5 in Na et al., 2007). However, we think that the organic salt formation could occur both in the particle surfaces-bulk layers (by reactive uptake) and in the particle bulk-phase (at least if the SOA particles are exposed to NH<sub>3</sub> after they are formed). Thus, we treat the organic salt formation in similar way as for common inorganic salts formation (e.g. NH<sub>4</sub>NO<sub>3</sub>). We wanted to make it completely clear how we treated the organic salt formation. By reactive uptake, we mean that NH<sub>3</sub> and the carboxylic acids condenses and dissolved in the particle surface-bulk layer and then react and form organic salts. We don't think it is possible to tell if the organic salt for-

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mation occur in the gas-phase too or only in the particle surface-bulk layer and particle bulk, based on the measurements by Na et al., 2007 and Kuwata and Martin, 2012. However, based on the knowledge about inorganic salt formation (e.g.  $\text{NH}_4\text{NO}_3$ ) it seems unlikely that the organic salts between ammonium and carboxylic acids would form in substantial amount in the gas-phase, especially since the carboxylic acids are relatively weak acids.

We will change the above mentioned sentence to:

"In this work we model the organic salt formation between ammonium and carboxylic acids as a process occurring in the particle surface-bulk layer and particle bulk, analogous to inorganic salt formation (e.g.  $\text{NH}_4\text{NO}_3$ )."

P810L21 'Experimental evidence suggests that there are no substantial differences in chemical composition of  $\alpha$ -pinene SOA particles upon evaporation in thermodenuders' I am not sure if it is true. For instance, Kuwata et al. (2011) has demonstrated that chemical composition of  $\alpha$ -pinene SOA particles after evaporation is different from original particles.

Yes, you are correct. We will add a reference to Kuwata et al. (2011) and discuss the different results in this study compared to the one by Cappa and Wilson, 2011. We will also mention that both these studies were conducted with thermodenuders where the increased temperature may affect the phase-state of the SOA particles, and hence there evaporation behaviour. There are also substantial differences between these studies concerning how the SOA particles were produced (e.g. RH, OH-scavenger,  $\alpha$ -pinene and O<sub>3</sub> concentrations).

Figure S1 Change the ordinate to logarithmic scale, since the figure is mapped by  $\text{dN}/\text{dlogDp}$ .

Yes we will do that.

Figures S4, and S6 Add units for ordinates.

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Thank you, we will do that.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C1451/2014/acpd-14-C1451-2014-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 769, 2014.

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