

## ***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.***

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

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 “surface-bulk accommodation coefficient” which considers both the potentially non-unity probability of adsorption (sticking) and dissolution into the particle surface-bulk layer.

Answers to specific comments:

“P773, L21 – P774, L2: The recent study of Shiraiwa & Seinfeld, GRL, 2012 showed that equilibration timescale of SOA partitioning becomes indeed long if particle adopt a semi-solid state. Reference to this paper would be appropriate here.”

We will add this reference together with the reference to (Pöschl, 2011).

“P777, L25: The internal time step of ADCHAM is 1-10ms. However, some processes, for example, desorption proceeds in much shorter timescale of nanoseconds with  $\tau_d = 1e-9$  s (Table 1). I am wondering whether 1-10 ms is a good choice for reliable calculations.”

Yes, the operator splitting time step is 1-10 ms but the kinetic-multilayer model for uptake, reactions and diffusion of O<sub>3</sub> and organic compounds solves the coupled ordinary differential equations using the ordinary differential equation solver ode15s in MatLab which uses an adaptive time step which is much smaller than 1-10 ms. The text as it is written now is confusing and I will change from:

“After this ADCHAM handles the condensation and evaporation of all organic and inorganic compounds (Sect. 2.2.1) and the uptake, diffusion and reactions of O<sub>3</sub> in the different particle layers (Sect. 2.4.2). For these processes ADCHAM uses a much shorter internal time step (in this work 1–10 ms).”

to:

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“After this ADCHAM handles the condensation and evaporation of all organic and inorganic compounds (Sect. 2.2.1) and the reversible adsorption, diffusion and reactions of Zox in the different particle layers (Sect. 2.4.2). In-between these processes ADCHAM uses operator splitting with a much shorter time step (in this work 1–10 ms). For the reversible adsorption, diffusion and reactions of the different oxidation agents in the particle-phase, a kinetic-multilayer model (Sect. 2.4.2) is used. This model consists of a coupled ordinary differential equation system which is solved using the MatLab ode15s solver with adaptive and error tolerance controlled internal time steps.”

Zox represent any oxidation agent in the particle phase (e.g. O<sub>3</sub>, OH, NO<sub>3</sub> or NO<sub>2</sub>).

“P783, L8: Please justify thin layer thickness of 1 mm. I guess this value might be critical. Have you done sensitivity studies?”

Yes, we have done sensitivity tests. If you consider that the kg,w loss rate is scaled accordingly (see answer to next comment) this value is not critical for the results. We will add the results from a sensitivity test of the gas-Teflon wall uptake with a thin layer thickness of 1 or 10 mm, in the supplementary material . “P784: Regarding first-order vapor loss rate to chamber. kg,w may depend on chamber size and mixing of chamber. Matsunaga and Ziemann determined its value using a relatively small chamber. For example, at Caltech chamber the smaller loss rate (kw of on the order of 1e-6 – 1e-4 s-1) was observed (see Loza et al., ES&T, 2010 and supplement in Shiraiwa et al., PNAS, 2013). What are the exact orders/values used in ADCHAM simulation? At P784, L10, 50% of compound was estimated to deposit on chamber wall. How this value will change if smaller loss rate is used? Please compare and discuss.”

Since we calculate the vapour loss rate to the chamber walls from the (by default 1 mm) thin layer next to the chamber walls (V<sub>wall</sub>) and not for the total chamber volume (V<sub>chamber</sub>) we use a much larger value for the first-order vapour loss rate (kg,w) than reported by either Matsunaga and Ziemann or Loza et al., ES&T, 2010. In ADCHAM kg,w is increased with a factor on the order of the ratio between the total chamber

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volume and the volume of the thin air layer adjacent to the chamber walls (V<sub>chamber</sub>/V<sub>wall</sub>). It is only in the simulations in Sect. 3.4 which we have considered gas-wall partitioning (we will clarify this in the text). In this section we test either to use kg,w=1/6 s-1 with a laminar layer width ( $\Delta x$ ) of 10 mm next to the chamber walls or kg,w=1/20 s-1 with a laminar layer width ( $\Delta x$ ) of 1 mm next to the chamber walls. For the 6 m<sup>3</sup> Teflon chamber which is used for these experiments, the 1 mm thick layer in direct contact with the chamber walls contains only  $\sim 1/300$  of the total initial chamber volume. If we instead assume that this layer is 10 mm, it contains  $\sim 1/30$  of the total initial chamber volume and the kg,w values should be decreased approximately with 10 times to get the same effective gas-wall uptake (see attached figure which will be included in the supplementary material). With a laminar layer of 1 mm adjacent to the chamber walls ( $\Delta x=1$  mm), kg,w=1/10 s-1 and V<sub>wall</sub>/V<sub>chamber</sub>=1/300 the gas-phase wall losses are almost identical with a model which calculate the losses from the total chamber volume concentration and an effective kg,w equal to  $1/(10*300)=1/3000$  s-1. However, if the laminar layer adjacent to the chamber walls are larger (e.g.  $\Delta x=10$  mm), the near wall gas-phase concentration is substantially smaller than in the well-mixed chamber volume. Hence, the losses to the walls becomes smaller and the kw,g value which we use cannot be directly derived by scaling the total-volume first-order loss rates with V<sub>chamber</sub>/V<sub>wall</sub> (see attached figure). We include a thin layer next to the Teflon-wall mainly because we want to study the potential effect which the lower gas-phase concentration next to the chamber walls have on the gas-particle partitioning to the particles deposited on the wall. We will include the attached figure in the supplementary material and refer to these tests in the paper. We will change the text on page 784 L3-5 from:

“kg,w and Cw/(Mw $\gamma_{w,i}$ ) in Eq. (4) was experimentally determined by Matsunaga and Ziemann (2010) for n-alkanes, 1-alkenes, 2-alcohols and 2-ketones to 9, 20, 50 and 120  $\mu$ mol m-3, respectively.”

to:

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“ $kg,w$  and  $Cw/(Mww,i)$  in Eq. (4) was experimentally determined by Matsunaga and Ziemann (2010) for a 5.9 m<sup>3</sup> Teflon chamber. For n-alkanes, 1-alkenes, 2-alcohols and 2-ketones  $Cw/(Mww,i)$  was 9, 20, 50 and 120  $\mu\text{mol m}^{-3}$ , respectively.  $kg,w$  varied between 1/3600 s<sup>-1</sup> and 1/480 s<sup>-1</sup> depending the type of compound.”

and in the end of Sect. 2.2.3 we will add:

“Because ADCHAM calculates the gas-wall uptake from the thin layer (volume) adjacent to the Teflon walls and not from the total chamber volume, the  $kg,w$  values used in the model need to be substantially larger than the (experimentally quantifiable) effective total chamber volume  $kg,w$  (e.g. from Matsunaga and Ziemann, 2010). If the mass transport across the laminar layer adjacent to the chamber walls do not pose a strong limitation on the gas-wall uptake ( $\Delta x \approx 1$  mm), the  $kg,w$  value used in ADCHAM can be derived from the experimentally determined effective  $kg,w$ , by scaling this value with the ratio between the total chamber volume and the air volume adjacent to the chamber walls ( $V_{\text{chamber}}/V_{\text{wall}}$ ). However, if  $\Delta x$  is relatively large (e.g. 10 mm),  $kg,w$  in ADCHAM need to be even larger in order to match the experimentally derived gas-wall losses. In the supplementary material we illustrate this with a few examples. Here we also illustrate that the modelled gas-wall uptake is not sensitive to the absolute width of the thin air layer adjacent to the chamber walls, as long as  $kg,w$  is scaled with  $V_{\text{chamber}}/V_{\text{wall}}$  (see Fig S1). In Sect. 3.4 we test the capability of ADCHAM to simulate the losses of organic compounds from the gas-phase to the Teflon walls and wall deposited particles.”

Since we calculate the gas-uptake from the thin air layer volume adjacent to the chamber walls, the  $kg,w$  value used in ADCHAM should not depend strongly on the size of the chamber. In the model this is instead accounted for by the changed chamber geometry. A larger chamber has a relatively smaller volume fraction of air adjacent to the chamber walls and the effective (measurable) losses therefore become smaller.

Yes, according to Eq. 4  $kw,g,i=kg,w$  if  $p_0 = 2.5 \times 10^{-2}$  Pa and  $Cw/(Mww,i) = 10 \mu\text{mol}$

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m<sup>-3</sup>. Hence, if no SOA is formed 50 % of the compounds will be found at the chamber walls and 50 % in the gas-phase at equilibrium. The equilibrium concentration fraction found on the chamber walls will not change if we use Eq. 4 and a smaller loss rate ( $kg,w$ ) since the  $kw,g$  will also decrease with the same amount. However, in practice it will influence the model results because it will take longer time before the equilibrium is reached and other processes (e.g. SOA formation) will have time to distort the concentrations away from the equilibrium values.

“P784, L24: Is this the same for all substances? Shouldn't it be scaled with the mean free path of the molecule? What values did you get after fitting?”

Yes, we have used the same laminar layer width for all substances. You are probably correct that in principle it should be scaled with the mean free path of each molecule. However, the difference in mean free path of the different SOA monomer molecule is relatively small ( $5 \times 10^{-8}$  –  $6 \times 10^{-8}$  m), and these values are several orders of magnitude smaller than the smallest value of the laminar layer width which we use (1-10 mm).

In Section 3.4 we test to run the model with a laminar layer width of 1 or 10 mm.

On P784, L24 we will change from:

“The width of the laminar layer was used as a model fitting parameter.”

To:

“In Sect. 3.4 we study how different values of the laminar layer width influence model results.”

“P785: When full-moving method is used, how do you treat coagulation? Do you have a new diameter grid for coagulated particles or do you merge into the existing diameter grid? In the latter case, how do you deal with difference of chemical composition between coagulated and pre-existing particles?”

Yes, we merge into the existing diameters (full-stationary method). We will clarify this in

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the text on P785 and on Page 780-781 Sect. 2.2.2 where we describe how the model treats coagulation and how the different particle layers are merged together.

Because, we use the full-stationary method we cannot differentiate between the chemical composition of the coagulated and pre-existing particles. With this method, coagulation just affects the average chemical composition, number and mass concentrations in each size bin.

To Sect. 2.2.2 we will add the sentence:

“The particle mass and number concentrations of the formed particles are split between the existing particle size bins using the full-stationary method.”

On P785, L13-L18 we will change the text from:

“For all simulations performed in this article, we have used the full-moving method where the diameter grid moves with the particles. Hence, this method has no numerical diffusion problems when particles grow by condensation or evaporate. Homogeneous nucleation is considered by adding new particle size bins when new particles are formed (Sects. 3.2 and 3.3).”

to:

“For all simulations performed in this article, we have used the full-moving method for condensation and evaporation. With this method the diameter grid moves with the particles. Hence, this method has no numerical diffusion problems when particles grow by condensation or evaporate. Homogeneous nucleation is considered by adding new particle size bins when new particles are formed (Sects. 3.2 and 3.3). For coagulation we use the full-stationary method where the formed particles mass and number concentrations are split between the existing diameter bins (Sect. 2.2.2)”

“P786, L1: It is mentioned that no interaction coefficients of AIOMFAC are available for PANs, organonitrates and peroxides. This is not entirely true; Zuend & Seinfeld, ACP, 2012 (Appendix A and Table A2 of that paper) introduced peroxide-ion interaction

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coefficients in AIOMFAC, based on a polarity series and analogy approach.”

Thank you for clarifying this. We will change the text from:

“For other important functional groups i.e. nitrates, nitros, PANs and peroxides no inorganic functional group interaction parameterizations are available. Hence, for these functional groups we only consider organic-organic functional group interactions. In total the model considers 52 different UNIFAC functional subgroups, with interaction parameters from Hansen et al. (1991), except for alcohols (Marcolli and Peter, 2005) and nitrates, PANs and peroxides for which we use the parameterization from Compernelle et al. (2009).”

to:

“For other important functional groups i.e. nitrates, nitros, PANs and peroxides we only consider organic-organic functional group interactions. In total the model considers 52 different UNIFAC functional subgroups, with interaction parameters from Hansen et al. (1991), except for alcohols (Marcolli and Peter, 2005) and nitrates, PANs and peroxides for which we use the parameterization from Compernelle et al. (2009).”

“P789, L6: Is R6 correct? I wonder such 3-body reaction is very slow even in the condensed phase. You need references to justify this reaction and reaction rate coefficient.”

Yes, you are correct. R6 should only be  $\text{carbonyls(p)} + \text{O}_3(\text{p}) \leftrightarrow \text{secondary ozonides(p)}$ . We will change this in the manuscript and add a reference to Maksymiuk et al., 2009.

“P790, L12: What do you mean treat as reactive uptake? Do you use uptake coefficients? Please specify equations to calculate reactive uptake process. I am wondering why you do not treat R2b same as R2a: let aldehyde partition into particle surface, then react at surface. Do you have any evidence that such reaction occurs upon collision of gas molecule to surface (e.g., Eley-Rideal mechanism)? Eley-Rideal mechanism may

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apply for uptake of very reactive gases such as OH and NO<sub>3</sub> (Pöschl et al., ACP, 2007; Shiraiwa et al., ACP, 2009), but I doubt it also applies for aldehydes.”

Yes, we agree that this is confusing. We will remove R1b and R2b on P789 and the sentence “The dimer formation rate in the particle surface layer formed between compound j found in the gas phase and compound i found at the particle surface is treated as a reactive uptake.” on P790, L10-L12.

By reactive uptake we mean adsorption onto the particle surface followed by rapid reactions with other molecules found at the particle surface. But, yes we agree that it is better to split these processes into partitioning to the particle surface followed by reactions in the particle phase.

No we do not have any evidence that such reaction occur upon collision of gas molecules to surfaces. We will redo all model runs where this mechanism was included (Fig 10 and 11) and replace it with a mechanism where short-lived dimers forms in the particle phase and then rapidly are degraded back to monomers again (within minutes). Possibly, this could explain the observed relatively slow and size independent first evaporation stage.

“P790, L6: What is the difference between reactions R1-R6 and R7+R8? Why do you need implicit dimer formation when you have explicit dimer formation?”

We will remove R1-R4 and represent these reactions with R7 and R8, because in this section we mainly want to focus on the general treatment of oligomerization (dimerization) in the model. Instead of R1-R4 we will briefly describe the different types of particle phase dimerization mechanism with references.

We will keep R5 and R6 because they cannot be modelled with R7 and R8.

“P792, L12: The latest update of KM-GAP also includes thermodynamics (Shiraiwa et al., PCCP, 2013) and simplified gas- and particle-phase chemistry (Shiraiwa et al., PNAS, 2013).”

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We will change from:

“Recently, Shiraiwa et al. extended the kinetic multilayer model to also include condensation, evaporation and heat transfer (KM-GAP) (Shiraiwa et al., 2012).”

to:

“Recently, Shiraiwa et al. extended the kinetic multilayer model to also include condensation, evaporation and heat transfer (KM-GAP) (Shiraiwa et al., 2012), thermodynamics (Shiraiwa et al., 2013a) and simplified gas- and particle-phase chemistry (Shiraiwa et al., 2013b).”

“P 792, L15: How is adsorption/desorption treated? How does competition for adsorption sites work if there is no sorption layer? Does the first bulk layer have other properties than all others?”

For the uptake of O<sub>3</sub>, NO<sub>2</sub> and other oxidation agents we include a sorption layer where the molecules compete for the adsorption sites. However, for the partitioning of other compounds we use Eq. 1 and assume that the compounds dissolve in the surface-bulk layer using Raoult’s law corrected with activity coefficients from AIOMFAC.

In the manuscript we will change from:

“In ADCHAM we do not separate the quasi-static surface layer and near-bulk surface layer into two separate layers, but instead use a one monolayer thick surface layer. The uptake of all organic and inorganic compounds except O<sub>3</sub> into the surface layer from the gas phase is modelled as a condensation/evaporation process where we take into account the possibility of non-unity sticking probability (surface mass accommodation) (Sect. 2.2.1).”

to:

“For the oxidation agents we model the uptake to the sorption layer as a reversible adsorption processes, followed by diffusion to and from the particle surface-bulk and

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bulk-layers. In this work the partitioning of organic and inorganic compounds to and from the monolayer thick particle surface-bulk layer is instead modelled as a condensation/evaporation process (Eq. 1), taking into account the possibility of non-unity surface-bulk accommodation (Sect. 2.2.1). However, in principle ADCHAM could also model the gas-particle partitioning of organic and inorganic compounds as a reversible adsorption process.”

“P 792, L22-27: It would be nice to have an explanation why this is split.”

One reason is that we treat the uptake onto the particle surface in different ways (see previous comment). A second reason is that these processes occur on different timescales. The diffusion and reaction of ozone and other oxidation agents with the organic compounds are generally substantially faster than the mixing of the organic compounds. A third reason is that we do not always consider heterogeneous oxidation.

To the manuscript we will add:

“The main reason why these processes are treated by two separate modules is that the uptake, diffusion and reaction of O<sub>3</sub> and other oxidation agents generally occur on substantially shorter timescales than the diffusion of the organic compounds..”

“P 793, L6-8: This is not always true for KM-SUB. It does not always use identical width for bulk layers. Moreover, for KM-GAP, the layers shrink and grow.”

OK, thank you for clarifying this to us. Then we will remove the sentences: “Shiraiwa et al. (2010, 2012) use identical layer width for all bulklayers. Hence, in their expression for the bulk to bulk transport velocity the average travel distance of molecular diffusion between two layers is simply given by the layer width and not the more general  $(\delta k+1+\delta k)/2$ .” from the manuscript.

“P793, L15: Just a comment: In KM-GAP, the factor of  $4/\pi$  is omitted, based on direct derivation by Fick’s law.”

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“P793, Eq16: This equation holds in absence of chemical reactions. Please state this.”

Yes, we will add the sentence:

“Equation 16 contains no terms for the chemical formation and degradation of  $X_i$  because this is considered by separate modules for oligomerization (Sect. 2.3.4), heterogeneous oxidation (Sect. 2.4.2) and organic salt formation (Sect. 2.3.3).” “P793, L11-12: How is surface concentration treated, in  $\text{cm}^{-2}$  or  $\text{cm}^{-3}$ ? If treated as  $\text{cm}^{-2}$ , how is it converted into a bulk concentration for this calculation?”

The surface concentration is treated in  $\text{cm}^{-3}$

“P793, L22-24: This is a big assumption. Particularly small oxidants or water molecules can easily diffuse into solids. For example, bulk diffusivity of H<sub>2</sub> into glass/SiO<sub>2</sub> is  $\sim 1\text{e-}8 \text{ cm}^2 \text{ s}^{-1}$  (Bird et al., 2007) and that of ozone in amorphous solid protein is  $\sim 1\text{e-}10 \text{ cm}^2 \text{ s}^{-1}$  (Shiraiwa et al., PNAS, 2011). If you assume no bulk diffusion for solids in ADCHAM, no water would be taken up by glassy particles (in contrast to Zobrist et al., PCCP, 2011). Also there are no dissolution effects.”

Yes, we understand your point and agree. We will remove this correction factor and allow the particle layers to change width (volume) during the simulations. We will change Eq. 16 to instead solve for the absolute volume concentration of each compound ( $\text{m}^3$ ) in each layer and not for the volume fractions in each layer. This we do by removing the particle layer volume ( $V_k$ ) in Eq. 16. Because of this we will redo all simulations in the manuscript where we use the correction factor in the kinetic-multilayer model.

“P794, L9: When the number of layers increased, then do you also increase number of differential equations?”

Yes, one differential equation for each layer, each particle size and each compound.

“P794, L16-18: Do you arbitrarily assume bulk diffusivity of organics as  $D_y=0$ ? Such treatment may affect which molecules contribute to  $\theta_s$  arbitrary. Is there any legitimation to do this?”

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No maybe you are right that this is unphysical. It could possibly be realistic if some of the organic compounds are very surface active (surfactants) and are not happily mixed in the organic bulk-phase. But for pure  $\alpha$ -pinene SOA this are probably not the case.

We will remove the text on P794, L15-L24 and Eq. 18, and redo all simulations which are affected by these assumptions using a fixed value surface mass accommodation coefficient (probably unity).

“P796: Is it only ozone that is considered to undergo reversible adsorption? It is not clear whether organic molecules are also treated as same way as ozone, or are they directly transported into the first bulk layer using eq(1)? I wonder why ozone and other organics are not treated in the same way (either with condensation or reversible adsorption).”

Yes, it is only ozone and other oxidation agents (e.g. NO<sub>2</sub> and OH) which are considered to undergo reversible adsorption. The uptake of all molecules which are considered to contribute to the particle mass is treated as a condensation process using Eq. 1. The main reasons for this is that: (i) ADCHAM build on the atmospheric chemistry transport model ADCHEM, which use Eq. 1 to consider condensation and dissolution into the particle phase, and (ii) reversible adsorption require knowledge about the desorption lifetime of the organic molecules, which to our knowledge generally is not well known. However, in principle we could consider that organic molecules are taken up by reversible adsorption, in a similar way as we do with the oxidation agents.

We will add a sentence which clarify that for the simulations presented in this article we model the uptake of organic compounds from the gas-phase to the particle surface-bulk layer using Eq. 1, but the ADCHAM model could also model this uptake as a reversible adsorption process analogous to KM-GAP.

“P797: Why eq28 and 29 do not have transport terms, but only reactions? You have two equations for Xi, eq16 and 29. Do you decouple and solve mass transport and chemical reactions separately for Xi? Why do you treat ozone and Xi differently?”

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Yes, we solve the mass transport of organic compounds and there chemical reactions separately. We have made this separation because; the mixing or organic compounds are often a relatively slow process compared to the diffusion and reaction of O<sub>3</sub> or other oxidation agents. Additionally, e.g. for  $\alpha$ -pinene ozonolysis, the SOA do not consists of unsaturated organic compounds which can undergo reactions with O<sub>3</sub> in the particle phase. Hence, for these simulations the kinetic multilayer model which describes the reversible adsorption, diffusion and reactions of O<sub>3</sub> in the particle phase is not used.

“P798: ADCHAM includes many processes: gas- and particle-phase chemistry, coagulation, thermodynamics, diffusion in the bulk, wall loss, etc. In the section of model applications, all processes are not always included and some are switched off. I suggest having a table, specifying which processes are included in certain application.”

Yes, this is a very good suggestion we will include a table which specify which processes that are included and which are not.

“P800: I would suggest putting current section 3.3 to section 3.2, directly after modelling DOP evaporation. SOA evaporation is direct follow-up of DOP evaporation from the same publication.”

Yes, we will change the order of section 3.3 and 3.2

“P802: The AIOMFAC model treats organic acids as undissociated (p9158, Zuend et al., ACP, 2011). How did you introduce the dissociation products and their activity coefficients? This cannot be done without modifying AIOMFAC or using the activity coefficients of the undissociated compounds. Please clarify.”

Yes, sorry for not clarifying this in the text. We use the activity coefficients of the undissipated pinonic acid. We will clarify this assumption in the text.

“P803, L22: Recently, Zhou et al., Faraday D., 2013 estimated bulk diffusivity of  $\alpha$ -pinene  $2e-14$  cm<sup>2</sup> s<sup>-1</sup> at dry condition. This study can be used to justify the use of high diffusivity.”

C1471

Thank you, we will include a reference to this paper to motivate the tests we do with higher diffusivity. We will also test to run the model with a bulk diffusivity  $2e-14 \text{ cm}^2 \text{ s}^{-1}$  for the monomers.

“P804, L14-16: I wonder if the diffusion scheme (mass-balance to keep volume layer intact, as described on P794) has an influence on a comparison of modeling results and this estimation formula. It seems that diffusion scheme in ADCHAM tend to be shorter (for example, compared to KM-GAP), as diffusion could only be limited by this mass balance effect.”

We will redo these simulations again without keeping the volume-layer widths intact.

“P804, L17-19: What are fitted parameters and fitted values for these experiments? How is the model fitted? Please clarify.”

The organic salt effective solubility product (Eq 32) is the only parameter which value is not based on tabulated values in the literature. We have included the default model parameter values in Table 2 with references. Most of them are taken from measurements in dilute water solutions. To use these values for the organic phase, with very little water is a big assumption which we try to be honest and explain (see Sect. 2.3.2, P787). We will refer to this section and also consider if part of this text should be moved to Sect. 3.2 instead. We will also test to run the model with lower solubility (Henry's law coefficient) of  $\text{NH}_3$ , because this was pointed out by referee #3.

“P806, L13: Is  $\text{NH}_3$  allowed to adsorb on the sorption layer, or is it directly partitioned into the first bulk layer?”

$\text{NH}_3$  is partitioning directly into the first bulk layer (which we will call the particle surface-bulk layer, since this is what it is in our model representation). The second sentence on P779, Sect. 2.2.1 describes how the  $\text{NH}_3$  partitioning is modelled:

“Dissolution of ammonia into the particle water and/or organic phase surface layer is treated as an equilibrium process, considered after the diffusion limited condensa-

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tion/evaporation of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and organic compounds (Eq. 1) (of which carboxylic acids influence the particle acidity and hence the ammonia dissolution).” Here we will add a reference to Jacobson Aerosol Sci. Technol., 39, 92–103, 2005 which developed this way of treating the  $\text{NH}_3$  uptake after the condensation of acids.

“P810, L8-10 & P813, L27-28: I would not agree with this assumption. Why organic molecules cannot adsorb/absorb on non-volatile oligomers? With this assumption, if particle surface is fully covered with oligomers, then no organic molecules are allowed to partition into the particle phase. I wonder why such unphysical assumption is necessary.”

Yes, we agree that this assumption may be unphysical. We will redo all simulations in Sect. 3.3 which are biased by this assumption, using a unity surface mass accommodation coefficient instead.

“P810: Oligomer implies that it consists of multiple monomers. In the model, only dimer (even though dimer is a part of oligomer) is included and I would suggest using the word dimer for clarification when you discuss the modeling results. Otherwise it sounds that further oligomerization (trimer, tetramer, etc.) is treated in the model.”

Yes, thank you for pointing this out to us. We will change from oligomer to dimer when we discuss the model results.

“P810, L21: Please put a reference here.”

Yes, we will add a reference to Cappa and Wilson, 2011 but and also mention (which was pointed out by referee #1) that the experiments by Kuwata et al. (2011) actually show a change in chemical composition upon evaporation of  $\alpha$ -pinene SOA. 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 their evaporation behaviour.

“P813, L10-12: What are weakly and tightly bound surface oligomers? How do they

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differ in the ADCHAM model? What is the chemical identity for surface and bulk oligomers?”

Yes, we agree that the phrasing weakly and tightly bound surface oligomers are confusion. We will change to short-lived and long-lived dimers found in the particle surface-bulk layer.

“P814, L4-7: Do you have any justification for this assumption? I think that it is too simplified. Based on the Langmuir adsorption mechanism which commonly applies for adsorption of gas molecule to the surface, the surface concentration of gas molecule X, [X]<sub>s</sub>, can be described using the gas-phase concentration [X]<sub>g</sub> as follows (eq86 by Poschl et al., ACP, 2007):  $[X]_s = K_{ads} [X]_g / (\sigma \cdot (1 + K_{ads} [X]_g))$  where  $\sigma$  is molecular cross section of X and  $K_{ads}$  is adsorption coefficient. Thus, [X]<sub>s</sub> may not be simply proportional to [X]<sub>g</sub> (cpinal(g)).”

Yes, we agree. It is probably too simplified. For the revised simulations we will not use this assumption. Instead we will always treat the condensational uptake (or reversible adsorption) and the particle-phase oligomerization as to separate processes and not model it with Eq. 33.

“P814, L22: In the section 8 of Ziemann & Atkinson, Chem. Soc. Rev., 2012, reaction rate coefficients of dimerization are reviewed extensively. I suggest comparing your values with them.”

Thank you, yes we will do that.

“P815, L10: It is still not clear for me the difference between short-lived surface oligomer and longer-lived bulk oligomer. Are their chemical identities different? What is their chemical lifetime (short vs. long)?”

Yes their chemical identities and way of forming are different. We assumed that the short-lived surface oligomers were formed by the reactive uptake of pinonaldehyde. The term surface oligomer refer to that they are formed at the particle surface, in con-

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trast to the longer-lived bulk oligomer which is formed in the particle bulk-phase. We will change this terminology and simply refer to short-lived and long-lived oligomers and clearly clarify how they are formed and which degradation rate (lifetime) which we have used for the different simulations. We will include this information in the new table which explain the different assumptions and processes which are used for the different simulations. For all simulations where we include the reactive uptake of pinonaldehyde and formation of short-lived surface oligomers we used a lifetime of 2/3 h for these dimers. For the longer-lived oligomers formed in the particle bulk-phase we used lifetimes of 3.2 h for Fig 10, 22 h for Fig. 11 and 11 h for Fig 12.

“P817, L1: Why “layers” in plural form? Isn't it only one surface layer?”

Yes, it is only one surface-bulk layer. We will change to layer instead.

“P817, L27 and P818, L1: Are these formation rate and decomposition rate fitted? In what range were they varied? Please compare with values reviewed by Ziemann and Atkinson, 2012.”

Yes, they are fitted in order for the model to agree with the measurements. We have run many simulations with formation rates varying between 10-21 cm<sup>3</sup> s<sup>-1</sup> and 10-25 cm<sup>3</sup> s<sup>-1</sup> and degradation rates of 1 h<sup>-1</sup> to 1/30 h<sup>-1</sup>. We will clarify this in the article. We will compare the reaction rates with those from Ziemann and Atkinson, 2012.

“P818, L 4: The difference of bulk diffusivity between monomer and dimer seems to be too small. This contradicts with the assumption that only dimers block the surface, so that no monomers can evaporate.”

Yes, we agree. We will either model the diffusion coefficients of monomers and dimers with the Stoke-Einstein relationship and without obstruction theory (Eq. 19) or with substantially larger difference in diffusivity between monomers and dimers (at least 2-orders of magnitude) and then use the obstruction theory.

“P823, L19: The range of kO<sub>3</sub> values seems reasonable, but it may be as high as 1e-

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15 cm<sup>3</sup> s<sup>-1</sup>. You could compare with kBR values listed in Table 6 in Berkemeier et al., ACP, 2013, which derived kBR values as 1.7e-17 – 1.7e-15 cm<sup>3</sup> s<sup>-1</sup> by fitting to multiple data sets of oleic acid ozonolysis.”

We will add a reference to Berkemeier et al., ACP, 2013.

“P827, L26 & P831, L2-3: Are these values fitted values? Please justify or compare with literature values. For example, k<sub>f</sub> can be compared with Ziemann & Atkinson, 2013 (k<sub>f</sub> = 1e-4 – 0.06 M<sup>-1</sup> s<sup>-1</sup>). Please note that Shiraiwa et al., PNAS, 2013 found that heterogeneous reaction rate for formation of peroxyhemiacetal was enhanced by two orders of magnitude in the presence of carboxylic acid (k<sub>f</sub> = 12 M<sup>-1</sup> s<sup>-1</sup>, 2e-20 cm<sup>3</sup> s<sup>-1</sup>).”

Yes, these values are fitted for the model to agree reasonably well with the measurements. We will clarify that we did run the model with different values of D<sub>0,O3</sub>, k<sub>O3</sub> and k<sub>f</sub>, and then decided to use the values that gives best agreement between the model and measurements. We will also compare these values with Ziemann and Atkinson, 2013 and Pfrang et al., ACP, 2011 (where you use a D<sub>0,O3</sub>=5.5x10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup>).

“P832: In the present manuscript the results of salt formation are based on modelling a system without sulfuric acid and with rather high gas phase concentration of ammonia. Recent study by Yli-Juuti et al. (2013) modeled nanoparticle growth in the atmospheric conditions with also sulfuric acid present. Their results suggest that only a small fraction of organic acids forms salt in the particle phase, unless ammonia/amine concentration is high, and that mainly sulfate salts are formed. Pointing out clearly the potential effect of high ammonia concentration and lack of sulfuric acid on the conclusion drawn here and reference to Yli-Juuti et al. (2013) paper would be appropriate here.”

Yes, we will refer to this study and clearly write that the NH<sub>3</sub> levels used in this study are orders of magnitude higher than in the atmosphere and that for atmospheric conditions sulphuric acid which is a much stronger acid than the carboxylic acids will primarily

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react with ammonia and amines. Based on the comments from referee #3 we will also run a simulation with substantially lower more atmospherically relevant NH<sub>3</sub> concentrations, and based on these results comment on the atmospheric importance of this type of organic salt formation in the atmosphere.

“P833, L5: I suggest adding several more references in addition to Abramson et al.”

Yes, we will add several more references here, among others the study by Zhou et al., Faraday Discussions, 2013.

“P855, Fig. 3: The surface layer seems to be thicker than monolayer, but I guess it is kept as monolayer? What does the double arrow mean (mass transport?)? Please clarify in the figure caption.”

Yes, it is kept as a monolayer. It is only in the figure (Fig 3) which it looks thicker. We will try to make this layer narrower in Fig 3, to not confuse the reader. Yes, the double arrows represent the mass transport. We will clarify this in the figure caption.

Thank you for the minor comment edition. We will change these mistakes.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C1458/2014/acpd-14-C1458-2014-supplement.pdf>

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

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