

Interactive comment on “The role of low volatile organics on secondary organic aerosol formation” by H. Kokkola et al.

H. Kokkola et al.

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We thank the referee for a detailed review of our manuscript. The referee comments were very insightful and we believe that addressing the issues raised by the referee will considerably improve the manuscript.

Here are the referee comments followed by our replies:

The authors present some experimental observations of wall-losses of gas-phase volatile organic compounds (VOCs) in Teflon chambers. They find, as others have previously, that the chamber walls can act as a sink for gas-phase compounds and that the fraction of a given VOC that ends up on the chamber walls vs. in the gas-phase in-

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creases as the volatility of the compound decreases. None of this is new, although the authors have considered a different suite of compounds than previous studies. They aim to expand on previous studies of wall losses by using the results from their individual VOC experiments to understand and model particle formation and growth in alpha-pinene + ozone SOA experiments, with a key final result being the determination/estimation of the amount of very low volatility VOCs that must be produced during the ozonolysis. They conclude that the concentrations of such species are grossly underestimated in terms of their contribution to SOA. They conducted one experiment where they observed nucleation of new particles that occurred concurrent with condensational growth of ammonium sulfate seed particles. Their analysis focuses primarily on simulation and comparison of size distributions; composition measurements were made using an Aerodyne HR-ToF-AMS, although the results from this instrument were used minimally.

It is in the modeling of their observations that I find myself getting lost. They provide very, very few details about the actual mechanics of their model, referring the reader to look to previous work that describes the “SALSA” model for particle growth. However, I find that there are discrepancies between the model description provided by Kokkola et al., (2008) and how the model seems to be used here. Further, I find there is ambiguity in terms of how the nucleation mode has been simulated here. Two specific issues arise, elaborated on in the comments that follow below: (1) in SALSA condensation is apparently dealt with using species where the “saturation vapor pressure [is] set to zero”, which seems wholly inconsistent with the aims of the current work, and (2) the authors state that “nucleation was not explicitly modeled but the number concentrations measured in the two smallest size channels of SMPS were read into the model throughout a simulation,” and thus I don’t understand how they can perform a minimization “between the observed and modeled number concentrations in sizes below 40 nm in diameter” to deduce anything about the properties of the lowest volatility material. Basically, I am finding it very difficult to review this manuscript in terms of

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the scientific conclusions because I don't find that enough information is provided in terms of the methods used. If the authors can provide further detail prior to the close date of this manuscript, then perhaps I will be able to update my assessment. As it stands, I would have to suggest rejection for lack of sufficient detail. Certainly, I think at minimum a full second round of review will be necessary, although I look forward to seeing whether the other reviewers found this as difficult to assess as I did. Separate from these issues, I also believe that the authors' conclusions regarding the volatility of the lowest volatility species are not justifiable (for reasons elaborated upon below).

- We agree with the reviewer that the model description in the manuscript is not detailed enough and we will include a section describing the model details. We will also describe the details of how the modeling was done especially with respect to minimization where the model parameters were optimized in the model to reproduce the growth of nucleated particles.

The following modifications were made to SALSA model:

1) Semi-volatile organic compounds with seven different volatilities were included as chemical compounds. Partitioning between the gas and the particle phase was calculated according to Analytical Predictor of Condensation method (Jacobson, 2007) for the individual organic compounds. The method solves the condensation equation

$$\frac{dC_{org,i}}{dt} = k_i(C_{org,i,surf} - C_{org,gas}) \quad (1)$$

for size sections i . In Equation (1), k_i is the mass transfer coefficient, $C_{org,i,surf}$ is the equilibrium concentration of a condensing compound at the particle surface, and $C_{org,gas}$ is the gas phase concentration of the condensing compound. The saturation concentration at the droplet surface is calculated using the equation

$$C_{org,i,surf} = S'_i C_{org,i,surf} = S'_i x_{org,i} C_{org,sat} \quad (2)$$

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where S'_i is the Kelvin effect, x_i is the mole fraction (assumption of ideality), and $C_{org,sat}$ is the saturation concentration.

2) the number of size classes was increased to 25

3) Nucleation was not calculated explicitly since the nucleation mechanism is not known. The number concentrations for the two smallest size classes were read from the measurements to ensure correct representation of new particle formation. The main point of this study was to use the model to estimate how the competition between the gas-particle and gas-wall transformation affect the particle growth. Since the number concentrations of the smallest sizes were used an input for the model, these smallest bins were not included in the minimization procedure.

Specific comments:

P14616/L21: The authors should also include a reference to the work by Loza et al. (2010, ES&T, 44, 5074). The authors only consider relatively high vapor pressure products that are ketones or aldehydes. They do not consider alcohols or carboxylic acids, which are very important for SOA. They also rely on extrapolation to lower vapor pressures, which, while necessary and reasonable, leaves open questions as to the exact behavior and the dependence on functional groups. The authors do note this limitation, but it is unfortunate. Matsunaga and Ziemann demonstrate that functional groups matter to the wall partitioning, and this should be mentioned.

- We are aware of the limitations of describing wall partitioning only as a function of volatility. However, this is the first order approximation and without data available for wall partitioning properties of all alpha-pinene oxidation products it is currently the best guess. To our knowledge methods for modeling particle formation and growth in an oxidation chamber with multiple condensing compounds haven't been presented in the literature. Our method could be

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useful in modeling experiments where complex mixtures of SOA precursors (e.g. from plants) are used. We will include discussion on the limitations of our method in the revised manuscript.

We will also include the reference to Loza et al., in the revised manuscript.

P14618/L18: Since the authors show in Fig. 2 saturation concentrations ($\mu\text{g}/\text{m}^3$), I suggest that here they give the vapor pressures as saturation concentrations instead of in Pa. Or both.

- We will change the saturation vapor pressures to saturation concentrations.

P14620: The authors should report the seed particle surface area concentration, not just number concentration, since it is surface area that is most pertinent to this study. Including the total seed particle surface area would also be useful, as this number can be compared directly to the bag surface area.

- We will include the value for the seed particle surface area concentration of $416 \mu\text{m}^2/\text{cm}^3$.

P14620: For the non HR-ToF-AMS user, what is meant more specifically by “in HR analysis panel in Igor pro.”

- We rephrased the words to ‘Sulphate, organics, ammonium and nitrate mass loadings were determined in the high resolution AMS datasets and O/C ratios by elemental analysis as described in Aiken et al., (2008).’

Aiken, A. C.; Decarlo, P. F.; Kroll, J. H.; Worsnop, D. R.; Huffman, J. A.; Docherty, K. S.; Ulbrich, I. M.; Mohr, C.; Kimmel, J. R.; Sueper, D.; Sun, Y.; Zhang, Q.;

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Trimborn, A.; Northway, M.; Ziemann, P. J.; Canagaratna, M.; Onasch, T. B.; Alfarra, M. R.; Prevot, A. S. H.; Dommen, J.; Duplissy, J.; Metzger, A.; Baltensperger, U.; Jimenez, J. L. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* 2008, 42, 4478–4485.

P14620: More information is needed regarding “the VBS approach.”

- We will include a more detailed description of the model and the treatment of condensing organics of seven different volatilities.

P14621: The authors need to elaborate on the statement “nucleation was not explicitly modeled but the number concentrations measured in the two smallest size channels of SMPS were read into the model throughout a simulation.” Doesn’t this basically mean that the nucleation mode concentration is not really simulated at all? That is at least my reading of this sentence. I will return to this below.

- It is correct that the nucleation mode concentration is not simulated as explained above. We will make this clear in the revised manuscript

P14622: The authors use their observations to estimate rate coefficients associated with transfer of the gas-phase VOCs to the walls. It is somewhat difficult for the reader to get a sense for the fidelity of these estimates (which the authors admit are quite uncertain) without the authors actually showing an example graphically. I suggest that the authors show a model fit to the data explicitly in a figure.

- We will include an example figure of time dependent evolution of gas phase concentration from injection to leveling of the concentration. In addition, we will show the theoretical curve describing the same evolution.

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P14622: The authors' note that the behavior of pinenediol is anomalous compared to the two other VOCs, with the concentration slowly increasing after injection rather than peaking and decreasing to a steady state. They state that "within the scope of this study, we were not able to identify the mechanisms causing this behavior." However, I believe that this is fully within the scope of the study, and actually I would contend somewhat critical to the study. Why the different behavior? What does this potentially imply for the SOA experiments?

- To say that this is not within the scope of this study is poor wording. We can not explain the missing peak. We can only speculate if there are some wall deposition or undetected particle formation after which evaporation takes place and equilibrium concentration is reached. However, the implications of this is that also for pinanediol, the equilibrium is reached quickly and we can justify using the equilibration rate determined for nopinone in our modeling.

It would have been very useful had the authors carried out an experiment where, after addition of the individual VOCs, they added clean air and watched the decay of the VOC concentration in the chamber to test the reversibility of the process.

- We agree that this would have been a useful test.

P14623: I am not certain I understand the reasoning behind the use of a constant OC effective wall concentration "for all oxidation products of alpha-pinene." Shouldn't this depend explicitly on the amount of material formed, which will vary experiment to experiment?

- The effective wall concentration is a compound dependent property (Matsunaga & Ziemann 2010). It is not depending on the amount of material formed. Thus, it

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would have to be determined for all oxidation products of alpha-pinene in order to calculate the partitioning on the wall more accurately. To use the same effective wall concentration for all compounds is a first order approximation and our experiment with α -pinene, pinanediol and nopinone indicates that it is a fairly good assumption.

P14623: The units for cis-pinonic acid are incorrect, and Jimenez et al. (2009) is not an appropriate reference. Regarding the new particle formation from cis-pinonic acid, I do not understand why it was not possible to simply introduce less material, well below the saturation concentration. This should prohibit particle formation to any great extent. Was this because of instrumental limitations?

- Yes, decreasing concentration would have been a problem because of instrumental limitations. Even for pinanediol, the low gas phase concentration caused large variance in the measurements. In the revised manuscript, we will use saturation concentration of the order of $1 \times 10^2 \sim \mu\text{g}/\text{m}^3$ with corrected units.

The authors should state the concentration of alpha-pinene used during the experiments in relevant units (i.e. $\mu\text{g}/\text{m}^3$). A simple calculation based on the injected amount (2 microliters) and the bag volume (4 liters), assuming a density of 0.9 g/ml, suggests the alpha-pinene concentration was 450 micrograms/ m^3 .

- We will change the concentration units to $\mu\text{g}/\text{m}^3$

Fig. 3: With the color scale as chosen, I find it very difficult to visually assess the differences in the size-distribution image plots. I suggest that it would be beneficial if the authors were to select 5 or so periods where they present the size distributions as 2D representations for each of the different cases (i.e. $dN/d\log D_p$ vs. D_p). Or, perhaps

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alternatively, they might add a second column of panels that take the difference or ratio between the calculated and observed distributions. This would help the reader to better distinguish visually the differences.

- We will include a second panel of 2D representation of size distributions to make it easier to compare measured and modeled distributions.

P14624/L20: I find the statement here to be unclear as to whether the authors are considering specifically the particles in the nucleation mode or all particles when they refer to their 0.3 organic mass fraction number.

Presumably they are referring to the condensation mode, since the nucleation mode particles are too small to be detected by the AMS given the transmission function of the aerodynamic lens. This should be made clearer.

- It is correct that we are referring to the organic mass fraction of all particles and will make this clearer in the revised manuscript.

Also, the observation that the organic mass fraction increases does not, in my opinion, “support the conclusion that the new particles were grown by LVOC’s”. It actually only supports a conclusion that the new particles are grown by condensation of organics. The label “LVOC” has not been justified at this point by the observations.

- This is correct and we will rephrase this to say that the new particles are grown by condensation of organics.

In the discussion of the O:C ratio (P14624), the authors are making a common mistake, namely the assumption that O:C directly correlates with volatility. Yes, it is

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true that O:C can correlate with volatility, but the size of the molecules involved must also be taken into account. Consider a simple example: if one begins with a sesquiterpene vs. a monoterpene, the O:C of the resulting SOA will be lower for the sesquiterpene. But this is not because the SOA is (necessarily) of higher volatility. It is because the sesquiterpene is a C15 compound whereas monoterpenes are only C10 compounds. Thus, fewer oxygen containing functional groups need to be added to the sesquiterpene to make the products sufficiently low volatility to condense.

The authors need to account for such issues in their discussion. Further, they seem to be taking from Jimenez et al. (2009) what they want, and missing that there are some lines on Jimenez Fig. 4 that could give a $\log C^ = 10^3 - 10^4$ for O:C = 0.4; this would hardly be considered “low” volatility in the way the authors mean.*

Also, during the discussion of the O:C ratio (P14624) the authors almost seem to be (mis)-leading the reader to think that the reported O:C ratios are for the nucleation mode aerosol. They are not. They are reporting the bulk O:C of the condensation mode aerosol since the nucleation mode is not observed by the AMS. I suggest rephrasing is needed to remove any potential confusion.

- The O:C ratio was considered only to give indication that the volatility could be low. We do not consider it as a proof for low volatile compounds and will make it clearer in the revised manuscript by only stating the values of the O:C ratio and that this value is for the total aerosol mass.

P14625: I do not understand how the authors have determined that “the stoichiometric coefficients typically used for VBS do not produce enough low-volatility gases to reproduce the growth of the nucleation mode particles.” As they stated, nucleation is not actually simulated, but instead “the number concentrations measured in the two smallest size channels of SMPS were read into the model throughout a

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simulation." Related, how can this be reconciled with the optimization of "total number concentrations in sizes below 40 nm in diameter." Isn't the number concentration of nucleation mode particles in the model constrained by the observations, making this a non-unique parameter for comparison? I am having an extremely difficult time connecting the modeling to the observations because not enough information is given regarding the model formulation.

- As explained above, the input number concentrations were not involved in the minimization routine.

On a related note, after reading the SALSA model description paper (Kokkola et al., 2008), I am further confused as to how exactly vapor pressure-dependent condensation and growth were simulated in the current study since the SALSA model apparently treats condensation "using the Analytical Predictor of Condensation scheme with a saturation vapor pressure set to zero using the expression for the collision rate by Lehtinen et al. (2004)" (Kokkola et al., 2008). Presumably the model was updated to use non-zero saturation vapor pressures? Otherwise I don't see how it was actually used in this study. This should be addressed explicitly. Further, in looking at the paper by Lehtinen et al. (2004), I do not actually see any "expressions" (which I take to mean equations).

Thus, it is unclear to me how exactly condensation is simulated. It appears to me that Lehtinen actually deduce concentrations of condensable species from observed particle growth. But this seems backwards to what is being done in the current study, namely that concentrations of species with particular vapor pressures are determined in the gas-phase from the reaction of alpha-pinene with ozone and then these vapors are allowed to condense.

Certainly I believe that substantially greater detail regarding the exact implementation

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of the model (nucleation and condensation) is required. Without further details I am finding it very, very difficult to assess the scientific results from this study.

These points will be clarified in the revised manuscript with a detailed description of the model.

If the SALSA model does use species with "saturation vapor pressure[s] set to zero" (Kokkola et al, 2004), then how are particles evaporating in the current study? Evaporation: the authors, in their interpretation, completely neglect the fact that condensed phase reactions can (and likely do) occur that modify the effective volatility of the SOA. They mention this only in passing towards the end of the manuscript, but really this neglect strongly influences the interpretation of the model/measurement comparison and must be dealt with up front. There are numerous studies that have now demonstrated this. Thus, the volatility of the VBS species are not necessarily directly relatable to the volatility of the SOA later in time. The lack of evaporation may indicate a high concentration of a very low volatility species that is formed from the gas-phase, as the authors postulate, but it could just as easily (and I would argue, more likely) indicate the occurrence of condensed phase reactions that effectively decrease the volatility of the SOA, making it appear much less volatile than one would think based on consideration of the VBS parameters alone. Thus, I do not find the argument that there must be some species with $C^* = 2.5 \times 10^{-5} \mu\text{g}/\text{m}^3$ formed in high yield directly in the gas-phase convincing. If the authors truly believe this to be the case, they must provide a plausible chemical pathway to obtain species with such low volatility directly from gas-phase reactions. I think they will find this next to impossible, especially if they aim to reconcile any mechanism with the observed O:C, which is only 0.4. To decrease the volatility of a compound, one can add functional groups. Very approximately, alcohols provide the greatest decrease per functional group added, approximately two orders of magnitude. (A carboxylic acid is just the sum of a ketone and an alcohol.) So, to get from alpha-pinene, which has a $C^* \sim 2 \times 10^7 \mu\text{g}/\text{m}^3$,

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to a species with a $C^* = 2.5 \times 10^{-5} \mu\text{g}/\text{m}^3$, would require (approximately) the addition of $12/2 = 6$ alcohol groups. This would translate to an O:C of ~ 0.6 , much larger than the 0.4 that was observed. An O:C = 0.4 is more consistent with the addition of only 4 alcohols, which would give a C^* of $\sim 0.2 \mu\text{g}/\text{m}^3$. And since it is likely that other functional groups (e.g. ketones, peroxides) will be added, which provide smaller decreases in volatility per added oxygen, this likely provides a lower bound. Thus, I do not believe that a $C^* = 2.5 \times 10^{-5} \mu\text{g}/\text{m}^3$ is justifiable from gas-phase, non-oligomerization reactions alone. And I certainly do not think that the results here provide conclusive evidence of the formation of such a species from gas-phase processes, especially since this conclusion seems to come, in large part, from consideration of the evaporation behavior, not the formation behavior. Conclusion #2 should be removed and statements regarding the volatility of the OVOC species should be removed from the abstract.

- It is true that we cannot provide a pathway for fast production of compounds of such low volatility. On the other hand, we are not aware of pathways that can convert semi-volatile compounds to low-volatile compounds instantly in the particle phase. The observed nucleation mode growth requires that there are molecules of very low volatility in the chamber. In addition, these molecules have to remain in the particle phase almost immediately when they come in contact with particles of few nanometers and very high Kelvin effect. As our simulation indicates, compounds with equilibrium concentrations of the order of $1 \times 10^{-2} \mu\text{g}/\text{m}^3$ would evaporate from particles of tens of nanometers. In addition, there are studies showing that highly oxidized molecules are formed in the gas phase reactions of α -pinene (e.g. Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lönn, G., Schobesberger, S., Dal Maso, M., Trimborn, A., Kulmala, M., Worsnop, D. R., Wahner, A., Wildt, J., and Mentel, Th. F.: Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, Atmos. Chem. Phys., 12, 5113-5127, doi:10.5194/acp-12-5113-2012, 2012.).

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We will add more discussion on the possibility of particle phase transformation inhibiting the evaporation and tone down conclusions of formation of low-volatiles in the gas phase.

P14626/L16: The authors state: "In addition, according to our model and the AMS data, in a type of an experiment that was presented in this study, the organic fraction dominates the aerosol mass only in sizes smaller than 80nm in diameter." They have, however, not actually really presented the AMS data in a compelling way to allow the reader to understand this statement. For example, I would think that at minimum the authors might present composition-resolved size distributions at different points in the experiment to make this point. I also do not understand why it matters to have the organic fraction "dominate" to "properly measure the low volatile condensed matter." Presumably, and measurement technique worth anything would be able to distinguish between the seed material and the organic material. Thus, whether the organic fraction "dominates" becomes inconsequential. What matters is whether sufficient material can be collected.

- This was also poor wording on our part. The fact that most of the condensing matter in the newly formed mode was organic was used to ensure that the growth is not by e.g. sulphuric acid. We will include a composition resolved size distribution of the AMS data.

P14626/L21: The authors should give some example of what they mean by "measurement devices to detect the low volatility compounds." As written, I find this to be exceptionally vague. What type of "measurement devices?"

- This was again poor wording. The meaning of this sentence was to point out that due to wall losses of low volatile compounds, it becomes difficult to get

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enough mass for analysing different chemical compounds with for example mass spectrometry.

Conclusions/Implications: I believe that the authors need to do a much more thorough job of considering the implications of their results. This could be as simple as estimating how predicted SOA concentrations would change if the yield of the lowest volatility VBS species ($C^ = 0.01 \mu\text{g}/\text{m}^3$) were increased from 0.001 to 0.14. Here's an example: if $25 \mu\text{g}/\text{m}^3$ of some alpha-pinene were allowed to react and the parameters in Table 1 are used, an equilibrium calculation would give an SOA concentration of $1.0 \mu\text{g}/\text{m}^3$.*

Now, if the yield of the $C^ = 0.01 \mu\text{g}/\text{m}^3$ species is increased to 0.14 the predicted SOA concentration increases to $5.5 \mu\text{g}/\text{m}^3$. And the lower the overall concentrations, the larger the difference. For example, if only $10 \mu\text{g}/\text{m}^3$ of alpha-pinene reacts, the base-case parameters would predict $0.14 \mu\text{g}/\text{m}^3$ of SOA, but the updated parameter would give $1.92 \mu\text{g}/\text{m}^3$, a nearly 14 fold increase. This work would suggest that, if one were to comb the literature, that one should find a correlation between chamber size (i.e. surface area-to-volume) and SOA yields for a given system. Have the authors looked into this to support their contentions? How do their observed yields compare with the literature? The yield here is not actually even reported.*

- We are not aware of studies that have examined the dependence of wall losses of gaseous organics on chamber size. Such studies have been concentration of particle wall losses.

Minor comments:

Abstract, Line 5: I find the phrase "contribution to climate" to be vague.

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- Here we mean the radiative effects and changes in cloud properties caused by SOA. This will be clarified in the revised manuscript.

The manuscript could use some rewriting for grammatical clarity.

- We will check the grammar for the revised manuscript.

I suggest the authors use the more common PTR-MS as opposed to PTR-TOF (especially since they define PTR-TOF as proton transfer reaction mass spectrometry, and not proton transfer reaction time of flight). If nothing else, they should use PTR-ToF-MS.

- We use the abbreviation PTR-MS in the revised manuscript.

Please use metric units throughout (not inches).

- We will use only metric units in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 14613, 2013.

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