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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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Review of Kokkola et al.

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 increases 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 discrepencies 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 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

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the lowest volatility species are not justifiable (for reasons elaborated upon below).

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.

P14618/L18: Since the authors show in Fig. 2 saturation concentrations (ug/mˆ3), I suggest that here they give the vapor pressures as saturation concentrations instead of in Pa. Or both.

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.

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

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

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.

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.

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?

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.

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?

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?

The authors should state the concentration of alpha-pinene used during the experi-

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ments in relevant units (i.e. ug/mˆ3). 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/mˆ3.

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. dNdlogDp vs. Dp). Or, perhaps 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.

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. 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.

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 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* = 10ˆ3-10ˆ4 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.

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 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.

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

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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 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.

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* = 2.5x10ˆ-5 ug/mˆ3 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

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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 x 10ˆ7 ug/mˆ3, to a species with a C* = 2.5x10ˆ-5 ug/mˆ3, would require (approximately) the addition of 12/2 = 6 alcohol groups. This would translate to an O:C of $\sim$ 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 ug/mˆ3. 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* = 2.5x10ˆ-5 ug/mˆ3 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.

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.

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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?”

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 ug/mˆ3) were increased from 0.001 to 0.14. Here’s an example: if 25 ug/mˆ3 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 ug/mˆ3. Now, if the yield of the C* = 0.01 ug/mˆ3 species is increased to 0.14 the predicted SOA concentration increases to 5.5 ug/mˆ3. And the lower the overall concentrations, the larger the difference. For example, if only 10 ug/mˆ3 of alpha-pinene reacts, the base-case parameters would predict 0.14 ug/mˆ3 of SOA, but the updated parameter would give 1.92 ug/mˆ3, 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.

Minor comments:

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

The manuscript could use some rewriting for grammatical clarity.

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.

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Please use metric units throughout (not inches).

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