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Discussions

Interactive comment on "Sensitivities of the absorptive partitioning model of secondary organic aerosol formation to the inclusion of water" *by* M. Barley et al.

M. Barley et al.

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Response to Referee 1

The authors would like to thank the reviewer for their careful consideration of the manuscript and identification of several mistakes and omissions and wish to use the opportunity to make several suggested improvements to the paper in response to these comments. The reviewer makes a number of *Major comments* which we address below.

On page 20314, in the absorptive partitioning model formulations section, the authors give a detailed description and discussion of the reformulation of the mass-based absorptive partitioning model into the molar-based model. By using real compounds with

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known concentrations, the authors investigate the effect of water on the SOA formation and discuss the benefits of the molar-based absorptive partitioning model. The advantages of the molar-based absorptive partitioning model using real compounds may be limited by the incomplete understanding of the reaction mechanisms and the composition of the SOA in chamber experiments and in atmosphere.

This comment is rather difficult to understand. Since the component or average molar masses are required for the mass-based approaches and the number of moles (= total mass / molar mass) is required for the molar approach, there is no greater limitation to the use of the molar approach than to the mass-based approach. It is true that all partitioning approaches would be limited by poor knowledge of the partitioning compounds, but this affects all approaches equally. The molar approach is slightly simpler to apply than either mass-based approach when provided with molecular abundance predictions since this model does not require calculation of the mass and average molar mass of condensed material.

After describing the framework of the model, the authors do not show clearly how the results are generated. For example, on page 20318, line 22, the basis set of C_i^* *is redefined. The basis set of* C_i^* *values are separated by factors of 10 in molar units instead of mass units. For Figures 1 and 2, how many bins are used in the calculation? Is the* C_i^* *of each compound (or each bin) separated by an order-of-magnitude? The authors should describe how the results are generated.*

We agree with the reviewer that the bin formalism (following that of Donahue) is defined in equation 9 (p20318) but its use in Figures 1 and 2 is not adequately explained. In the amended text it is clarified that, for a limited number of compounds (such as considered in Figures 1 and 2), it is appropriate to use a specific C_i^* value for each compound (equivalent to having one bin per compound) and to conduct the partitioning calculation on this basis. However, if used with a large number of compounds (in excess of a few thousand) then the binning formulism suggested by Donahue can be used with abundance averaged C_i^* and molecular weight values for each bin as given by equations 10 and 11 on p20319. It is this method that is used for the MCM compounds presented in Figure 10.

The amended version of the paper starting at p20318, line 14 'speciation.
In the current work the following changes have been made: i) inserted intact from original text, ii) insert the original text from section iii), iii) For those cases where large numbers of compounds are considered it may be appropriate to use the convenient volatility-binning formalism of Donahue in which a basis set of C_i^* values separated by factors of 10 in molar units, then continues with the rest of the text from section ii), iv) inserted intact from the original text up to end of paragraph (p20320, line 4)'

On page 20321, line 11, "It is apparent (from Fig. 1) that the Mass 4 method and the Mol partitioning method were in agreement while the Mass 3 method predicts that a greater amount of the more volatile material condenses and (for the condensation of a similar amount of each compound) the discrepancy increases the more volatile the compound. The authors should explain why the discrepancy increases with the volatility of the compound using Mass 3 method?

The discrepancy between the Mass_3 method and the other two methods increases with increasing volatility because (as we are using real compounds) increasing volatility is associated with reduced molar masses. This was demonstrated by repeating the calculations with the same molar mass for acetone and dimethyl ether whereupon the ratio of the mass predicted by Mass_3 to the mass predicted by Mass_4 was the same for the two substances. The text has been modified (starting p20321, line 15): 'the discrepancy increases the more volatile the compound; this is caused by the difference in molar mass between the compounds rather than directly by their increasing volatility'

In the flash calculation, the definition of Ki is not given. What are the Ki values for the compounds?

K_i is not a specific property of a compound but rather the ratio of the mole fraction of the component in the vapour to its mole fraction in the liquid, $K_i = y_i/x_i$ (rearrangement

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of Eq. 12). This ratio (K_i) is then used in eq. 16. We have modified Eq. 12 to make this more obvious (p20322, l6):

$K_i = y_i / x_i$ (12)

What is the molecular weight of each bin used in the calculation for Figure 3?

The caption has been amended to explain that all the bins have the same molar mass (=250 $gmol^{-1}$) in both a) and b). The amended caption now reads: ‘The effect of ambient RH on the partitioning prediction using Mass_3 model and assumed ideality with the same total organic loading in both panels (all organic components have been assigned a molar mass of 250 $gmol^{-1}$): a) dry air’

How are the molecular weights of these bins determined? How sensitive is predicted SOA mass and total condensed mass sensitive to the molecular weight of the bins?

It is clarified in the text that Figure 3 shows the effect of the inclusion of water in the Mass_3 calculation for organic material of a range of volatilities but with all the same molecular weight. The text starting p20323, line 19 now reads: ‘8 decades of the $log_{10}(C^*)$ basis set from -2 to +5 is 2.5, 1.8, 4.0, 4.0, 6.0, 5.2, 6.2 and 8.0 μgm^{-3} organic mass respectively (all components have the same molar mass of 250 $gmol^{-1}$), as shown in Fig. 3. The inclusion of water’.

Figure 4 explores the effect of the amount of water present on the amount of SOA formed using all three models for the same volatility distribution as seen in Figure 3 but with a range of molecular weights. The effects of this has been clarified by amending the text so it now reads, starting p20324, line 2): ‘If, however, a realistic range of molecular weights is assigned to these bins (for example the least volatile bin (-2) was assigned a molar mass of 300 $gmol^{-1}$, the next bin (-1) 250 and so-on in steps of 50 up to bin +1 at 150 and then continuing in steps of 25 so that the most volatile bin (+5) is assigned a molar mass of 50 $gmol^{-1}$; see caption to Figure 4); then the results differ. The Mass_4 and Mol models predict identical amounts of condensed organic and total mass, while the Mass_3 model predicts slightly higher organic mass and a much greater increase in condensed water with increasing RH (Fig. 4). The discrepancy between the predictions for SOA made by the Mass_3 and either of the Mass_4 or Mol models in this example is small and it is sensitive to the molar mass distribution assigned to the bins. For example if all organic components have the same molar mass then this discrepancy disappears; if the molar mass of each bin is doubled (so that the distribution across the range of bins varies from 600 to 100) then the discrepancy between the models remains the same (0.76 μgm^{-3}); however if the molar mass distribution above is used but with each value increased by 50 then the discrepancy is reduced (to 0.746 μgm^{-3}); while if each molar mass value is decreased by 30 from the above distribution then the discrepancy increases (to 1.127 μgm^{-3}). These calculations demonstrate that it is the ratio of the molar mass of the organic components that determine the difference in predicted SOA between the models' (finish p20324, line 7).

On page 20324, line 8, "It should be re-emphasized that this change in predicted total material solely results from changes in the partitioning coefficient resulting from the reducing average molecular mass of condensing species with increasing RH, but not changes resulting from variation in component activity coefficient with changing condensed water content, i.e. the first, but not the second, term in Eq. (25) in Seinfeld and Pankow (2003).". The presence of water in the particle phase lowers the average molecular mass of the condensing species and changes the partitioning coefficient. Does the condensed water considered as an absorbing phase like other condensed organic compounds? If yes, the condensed water increases the total amount of absorbing phase. The change in the predicted total materias is also attributed to the presence of condensed water, which increases the amount of absorbing phase (organic compounds + water).

The first term in Eq 25 of Seinfeld Pankow (2003) explains the change in K_p with RH resulting solely from the change in molar mass. The reviewer is correct that the change in total material also results from the presence of additional absorptive mass; however, as we correctly stated in the paper, the change in K_p solely results from the reduced averaged molecular weight. The text has been amended to clarify that the importance of water is that it is considered as an absorbing phase like the organics and hence causes an increase in the total amount of absorbing phase leading to more SOA. Noting that the references to Seinfeld Pankow have now been replaced with an earlier reference including the original statement of equation 6 (pointed out by reviewer 2), the text following on from p20324, line 12 now reads; ‘but not the second term in Eq. 17 in Seinfeld et al. (2001). The condensed water is treated as an absorbing phase in the same way as the condensed organic components and this is reflected in an increase in the total condensed mass. The second term in Eq. 17 of Seinfeld et al. (2001) may lead to a’.

On page 20326, line 6, ‘From Fig. 6b it can be seen that’. Figure 6b is not shown in the paper.

We would like to apologise for the reference to Figure 6b which should have been to Figure 7. This has been amended, Starting p20326, l6: ‘From Fig. 7 it can be seen that’

On page 20326, line 9, ‘(i.e. the high atmospheric molar abundance compared with the Ci value of water expressed in molar terms compared with the lower molar abundance of the higher MW organic components relative to their Ci* values.)’. This sentence is not clear. Please clarify*.

We agree with the reviewer that this sentence is not clear. The entire discussion of figures 6 and 7 has been amended and simplified.

Starting at line 12 on p20325, the modified text now reads: ‘Assuming an activity coefficient of unity for all components and the same molecular mass (250 $gmol^{-1}$), the predicted condensed mass of the least volatile compounds ($B+C$) is almost two orders of magnitude greater at 0.95 saturation ratio of A than when A is absent at low $B+C$

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total loading, less than a factor of three greater at intermediate $B+C$ loading and less than 20% greater at high $B+C$ loading. The additional condensed mass of A with the increasing saturation ratio of A is similar at all total concentrations of $B+C$'. Equation 18 has been deleted. Starting p20326, line 8, the modified text now reads: 'Figure 7 shows the change in RH dependence for three different values of the total abundances of the two organic components ($B+C$). As in the previous case, the dependence on the saturation ratio (in this case RH) of the most volatile component with concentration of the condensed organic mass of components $B+C$ is large. The great decrease in RH sensitivity with increased total loading of $B+C$ can be seen. It can be seen from Figure 7 that there is a lower additional mass of condensed water at 95% RH compared with dry conditions than the additional mass of component A in Figure 6. This is because of the lower molar mass of water compared with component A. The additional number of moles of component A in Figure 6 and of water in Figure 7 is the same with changing saturation ratio (or RH).' Equations 19 and 20 have been deleted.

On page 20327, line 6, 'Figure shows the predicted dependence of the condensed mass on the availability of a fully-miscible but involatile core, behaving ideally.'. The number of Figure is missing. The authors may refer to Figure 8. For the pre-existing core study, do the authors investigate the effect of loading of preexisting particles on the SOA formation?

We thank the reviewer for pointing out the omission. The text reads: 'Figure 8 shows the predicted dependence of the condensed mass' Starting p20327, line 7 the text has been clarified to emphasise the fact that we explore the impact of core loadings on SOA formation: 'It can be seen that at constant RH the condensed semi-volatile organic mass increases with core mass as would be expected from the above discussion. However as the total absorptive mass still increases with RH due to the increased liquid water content; so the amount of condensed semi-volatile organic also increases with RH'

p20329, line 11: '?' This was a formatting problem and is now resolved

On page 20329, line 26, ‘Bin 1 (-1 in the Mol method) contains a higher abundance of species than the bins on either side.’. For the Bin 1, which method is referred to?

We have amended the text to make it clear that we are comparing bin 1 in the Mass_3 method with (roughly) bin -1 in the Mol method. The text now reads: ‘46.9 ngm^{-3}, Mol 43.0 ngm^{-3}. Bin 1 in the Mass_3 method (roughly corresponds to bin -1 in the Mol method) contains a higher’ The x-axis caption of Fig. 10 has also been changed to make it clear that the bin numbers in the figure refer to those using the Mass_3 model.

On page 20330, line 3, ‘The distribution of SOA over the seven lowest volatility bins as predicted by these two models at 80RH is shown in Fig. 8.’. The authors refer to the wrong figure. Figure 8 describes the core mass dependence of condensed organic mass determined using the molar partitioning model.

The amended text now reads: ‘lowest volatility bins as predicted by these two models at 80% RH is shown in Fig. 10.’

On page 20330, line 9, ‘A much more significant difference occurs for bin 1 where the Mass 3 model predicts 39.06 ngm^{-3} compared to 4.81 ngm^{-3} for the Mol method. This is related to the very high levels of condensed water predicted by the Mass 3 model at 80RH. By reducing the RH in the Mass 3 model to 24.27, the amount of condensed water was the same as predicted by the Mol model at 80RH. The predicted SOA in bin 1 was reduced to 5.58 ngm^{-3}, in closer agreement with the Mol model.’ Is there any reason why the authors lower the RH in order to match the predicted amount of condensed water using Mass 3 model and Mol model?

The text has been amended to make it clearer that the lowering of the RH was done to show that the amount of material in bin 1 was closely related to the amount of condensed water. Once we reduced the amount of condensed water predicted by the Mass_3 model to the same level as predicted by the Mol model we got much closer agreement between the two models about the amount of bin 1 SOA formed. This implies that the Mass_3 model is getting the wrong answer because it overpredicts the

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amount of condensed water which then acts as an absorbing medium for increased SOA formation. The modified text now reads: ‘This is related to the very high levels of condensed water predicted by the Mass_3 model at 80%RH. When the results were recalculated using the Mass_3 model but with the RH reduced to 24.27% (so that the Mass_3 model predicted the same amount of condensed water as the MoI model at 80%RH), the predicted SOA by the Mass_3 model for bin 1 was reduced to 5.58ngm^{-3}, in much closer agreement with the MoI model (4.81 ngm^{-3}) and demonstrating that the major factor in the high SOA content predicted by the Mass_3 model for bin 1 was the very high condensed water mass.’

MINOR COMMENTS p20327, line 1:‘*Furthermore, as has been previously reported, the contribution of the more volatile organic component to the organic aerosol is predicted to be significantly greater at high concentrations (and higher RH)*’

This is a straightforward consequence of the partitioning model and is a general result implicitly found in every study implementing the partitioning model. It directly follows from Raoults Law and we merely report the finding.

p20329, line 25: The text has been corrected with a closed parenthesis: ‘In the absence of water the two methods give similar amounts of SOA (Mass_3 46.9 ngm^{-3}, MoI 43.0 ngm^{-3}).’

p20330, line 26: To clarify the text it has been amended to read : ‘The Mass_3 model contravenes Raoult8217;s Law with the result that lower molecular weight components partition preferentially to the condensed phase in comparison with the Mass_4 and MoI models.’

Figures. The figures have been modified according to the reviewer recommendation where appropriate (other than Figure 6 x-axis label is retained as ‘saturation ratio’ to contrast it to the ‘RH’ used in Figure 7 since component A in Figure 6 is not water). The y-axis limits on figure 5 are different to scale the figures appropriately; they are not inconsistent.

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