**Atmospheric
Chemistry
and Physics
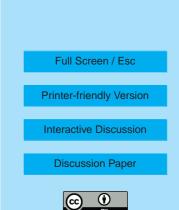Discussions**

Interactive
Comment

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

Anonymous Referee #1

Received and published: 5 January 2009

This paper discusses the prediction of secondary organic aerosol (SOA) formation by considering the condensed water as an absorbing phase using different forms of SOA model. This paper shows how the condensed water changes the distribution of organic components between the gaseous and particle phases at different relative humidity (RH). With a priori known composition of the SOA, the authors suggest to reformulate the mass-based absorptive partitioning model into a molar-based model using actual compounds. Overall, this paper is not very carefully written and should be revised before publication.

Major comments

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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 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.

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.

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?

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

On page 20323, in 3.2 predicted impacts of inclusion of water using the volatility basis set approach section, the authors show how the water affects the SOA mass using the Donahue et al. (2006) gaseous and particle phase concentration profile. The authors discuss how the molecular weight of the bins would affect the SOA mass and total condensed mass. What is the molecular weight of each bin used in the calculation for

Figure 3? On page 20324, line 2, "If, however, a realistic range of molecular weights is assigned to these bins (varying from 300 for the bin for log10Ci* = -2 in Fig. 3, to 50 for the bin for log10Ci* i = 5) then the results differ.". 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?

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).

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

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.

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?

On page 20329, line 10, "versions of the partitioning model, using the distribution of the predicted closed shell components simulated by (?)." Information is missing.

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?

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.

On page 20330, line 9, "A much more significant difference occurs for bin 1 where the Mass 3 model predicts 39.06 ng/m3 compared to 4.81 ng/m3 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 ng/m3, 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?

Minor comments

On page 20327, line 1, "Furthermore, as has previously been reported, the contribution of the more volatile organic component to the organic aerosol mass is predicted to be significantly greater at high concentrations (and higher RH).". Any references?

On page 20329, line 25, "In the absence of water the two methods give similar amounts of SOA (Mass 3 46.9 ng/m3, Mol 43.0 ng/m3.". Closed parenthesis is missing.

On page 20330, line 26, "The Mass 3 model contravenes Raoult's Law with the result that lower molecular weight components partition preferentially in comparison with the Mass 4 and Mol models.". Which phase (gas or particle) that lower molecular weight

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

components partition preferentially?

Different terms have been used for labeling relative humidity on the x-axis in Figures 5-9 (RH, relative humidity, saturation ratio).

Figures 5a and 5b: y-axis label is not consistent.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20311, 2008.