

Interactive comment on “Modeling secondary organic aerosol formation from isoprene oxidation under dry and humid conditions” by F. Couvidat and C. Seigneur

Anonymous Referee #2

Received and published: 25 October 2010

The authors present a framework for modeling the evolution of aerosol formed from isoprene oxidation based on an a-priori knowledge of experimental yields and molecular composition.

Mechanistic modeling of SOA formation is complex and challenging. However, it is also an essential area in our ability to elucidate and resolve key issues remaining with organic aerosol. The authors use their framework to suggest that the hydrophilic properties of SOA formed from isoprene oxidation suggest current parameterizations could be underestimated in current models. The work presented is interesting and worthwhile for publication in ACP. An assessment on the use of surrogate molecular species

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is interesting as it allows propagation of model complexity into large scale frameworks.

I do however have some concerns with regards key aspects of the modeling framework which the authors should address before publication.

I fear that some important sensitivities to model parameters are not explored or not explained with sufficient clarity. Also, there tends to be not enough discussion regarding choice of approach in combining key model parameters. Specifically, we know that the uncertainties in parameters such as pure component vapour pressures can hugely influence modeled SOA. A reference to those sensitivities should be at least included in the current manuscript, as should a list of appropriate caveats of the authors approach. Without assessing sensitivity of the model framework to ALL parameters, particularly when there is capability to do so, leaves some of the conclusions drawn from the work a little uncertain.

Specific concerns

Table 1 presents calculated and selected saturation vapour pressures for the surrogate species. Its is difficult linking this to the text in a coherent manner. On page 20566 line 16, the authors state that the saturation vapour pressure of BiDER was chosen to be different from tetrol vapour pressures, but the molecular mass and structure the same. How is this consistent? On page 20568 line 12 the authors state some saturation vapour pressures were selected to minimize the error between modeled and measured SOA mass. Does this mean that actually the SIMPOL method is not accurate or does this mean that the use of surrogate species requires ‘nudging’ of model parameters to explain observed mass? There should be a clear and concise introduction to the method used to derive these parameters in section 2 – Model development. For example, does your methodology centre on a nudging on component vapour pressures to arrive at known SOA mass concentrations..thus allowing the model to be extended to other conditions?

Page 20563: Again, the authors state the method chosen for estimation of activity

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coefficients but not for pure component vapour pressure. Relevant references as to the caveats associated with choice of predictive technique should be given:

Page 20564. The authors reference effective enthalpies of vaporization for SOA in both low and high NO_x conditions. Are these values representative of isoprene degradation products or simply a generic SOA? Also, are two values really adequate given we know products of SOA formation to populate a broad volatility distribution? Also, how are the values used in this study? Is there an equation these refer to?

Regards to the effect of water on soa formation, one should reference other relevant conclusions in other studies:

Page 20566. Again, how do the authors know the estimation of vapour pressure for the SIMPOL technique is correct? It is not appropriate to simply use a method based on frequency and ease of use. Validation of any vapour pressure estimation technique requires correlation with experimental data, an area which is proceeding successfully with interesting results (e.g. Booth et al 2009, Barley et al 2009). Of course, it is currently not possible to prescribe a generic choice of vapour pressure method beyond these types of comparison with 100% assurance. However I do feel sensitivity studies could be explored, particularly since section 3 is entitled 'Influence of parameters'.

Wouldn't it be just as easy to test estimations from other techniques such as the Nannoolal vapour pressure method (see Barley et al 2009)? The sensitivities to choice of vapour pressure method could then be explored. If the choice of vapour pressure method under-predicts component volatility, this could lead to 'lucky' replications of SOA mass and impact on chemical pathways deemed important.

Page 20573. Extension to humid conditions. There isn't adequate reference to other sensitivity studies in this area. (e.g. Barely et al 2010). It would also be useful to provide some brief references to the continuing arguments for/against mixed phase aerosol in such conditions at this stage (e.g. Zuend et al 2010).

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Page 20573: Is there any particular reason for adopting a modified Henry's law framework to describe the equilibrium condition? The use of Raoult's law would be valid would it not? This would also mitigate the need for use of infinite dilution activities. Again, the requirement to reference activity coefficients to the infinite dilution reference state could introduce large errors. If there are papers showing the ability of UNIFAC to replicate these variables, at these concentrations, for atmospherically relevant compounds, they should be given.

References:

1. Sensitivities of the absorptive partitioning model of secondary organic aerosol formation to the inclusion of water. M. Barley, D. O. Topping, M. E. Jenkin, and G. McFiggans *Atmos. Chem. Phys.*, 9, 2919-2932, 2009
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3. Solid state and sub-cooled liquid vapour pressures of substituted dicarboxylic acids using Knudsen Effusion Mass Spectrometry (KEMS) and Differential Scanning Calorimetry. A. M. Booth, M. H. Barley, D. O. Topping, G. McFiggans, A. Garforth, and C. J. Percival *Atmos. Chem. Phys.*, 10, 4879-4892, 2010
4. The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol M. H. Barley and G. McFiggans *Atmos. Chem. Phys.*, 10, 749-767, 2010

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