

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

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“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. 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.”

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We agree that Table 1 was confusing. Table 1 has been redone and now provides a complete list of the properties of the SOA surrogates as used in the model. We agree that a list of caveats should be included. The following paragraph has been added in the conclusions: To develop this model several assumptions have been made. Readers should be aware of these assumptions and that several uncertainties remain. Which molecular structure for BiDER should be chosen? Can the products formed in experimental chambers be formed under all conditions in the atmosphere? For example, if BiDER is formed by reaction in an organic phase, it is possible that it is not formed when the compounds tends to condense on water. To what extent does the oligomerization occur in the atmosphere for BiMGA and BiNGA. Are the estimated Henry’s law constants and saturation vapor pressures reliable enough for extrapolation to atmospheric conditions? Barley and Figgans (2010) showed that results of model to SOA formation are very sensitive to saturation vapor pressures.

“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?”

BiDER is a product with an unknown structure. We used the structure of tetrols by default (even if it is probably not its real structure) to have an estimation of the activity coefficients. Impacts of the choice of the structure on vapor pressure values has been investigated by using a structure different from tetrols (now sections 3.3).

“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?”

C10561

Saturation vapor pressures were calculated to provide order of magnitude estimates. Some were actually derived by fitting the model to data (BiPER, BiDER). Some were used as estimated (BiMGA, BiNGA), but an effective partitioning constant taking into account oligomerization (and not the actual saturation vapor pressure) was used in the model. Explanation on saturation vapor pressure fitting have been added to section 2 – Model development, to better explain to the reader how the model parameters were estimated.

“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? ”

These values are representative of SOA formed by isoprene oxidation under low and high NO_x conditions. They are used to calculate the effect of temperature on partitioning with the equation of Clausius-Clapeyron. The effective enthalpies of vaporization represent indeed SOA populated by several species with different volatilities. Since the concept of surrogate species is to lump several chemical species with similar properties into one surrogate species, it seems appropriate to then use these effective enthalpies of vaporization. Clarifications were added to better explain this point.

“Page 20566. Again, how do the authors know the estimation of vapour pressure for the SIMPOI 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

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Nanolal vapour pressure method (see Barley et al 1009)? 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.“

As explained above, saturation vapor pressures were calculated to provide order of magnitude estimates and to ensure that the model parameters derived from the experimental are commensurate with theoretical estimates. The goal of this work is not to assess which QSAR method is the best. Moreover as saturation vapor pressures have been selected to reproduce experiments, they are not a degree of freedom of the model. Conducting a sensitivity study on saturation vapor pressures is then not appropriate because the values are not chosen by the users of the model.

“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).“

We added the following text as an introduction to the section regarding humid conditions: Several methods have been used to account for the influence of water on SOA formation. On one hand, one can treat the atmospheric particles as internal mixtures (all particles of a same size have the same chemical composition) and solve he thermodynamics with possible phase separation (e.g., mostly organic and aqueous phases) as performed by Pun (2008) and Zuend et al. (2010). On the other hand, one can treat the atmospheric particles as external mixtures with aqueous (mostly inorganic) particles being distinct from hydrophobic (mostly organic) particles as performed bu Pun et al. (2002, 2006). The latter approach is used here.

“Page 20573: Is there any particular reason for adopting a modified Henrys law framework to describe the equilibrium condition? The use of Raoults law would be valid would it not? This would also mitigate the need for use of infinite dilution activities.

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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.“

Raoult's law would indeed be valid and would in fact give the same results. A modified Henry's law was used for several reasons. First, models usually calculate absorption in an aqueous phase according to Henry's law (like AEC for organic species or ISORROPIA for inorganic species), thus it is useful to provide estimated Henry's law constants. Second, the thermodynamic model UNIFAC could introduce errors. In the aqueous phase, species should be closer to the infinite dilution state (because they are diluted) than to the ideal state. It is then important to represent well the infinite dilution state. With Henry's law, the uncertainties around infinite dilution are grouped within a single parameter: the Henry's law constant.

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