

***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.

Received and published: 26 February 2009

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 Abstract

We recognise that the effect of relative humidity on organic PM levels is well established. In this work we explore the prediction of organic PM levels on the formulation of the partitioning model over a range of relative humidities in order to demonstrate the differences between the models. We agree that more needs to be said about the

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models we have considered and have modified the abstract as follows:

'the prediction of the distribution of semi-volatile organic components between the gaseous and condensed phase as a function of ambient relative humidity and the specific form of the partitioning model used has been investigated. A modified and simple mole fraction based model using no molar mass in the calculation was found to give identical results to the conventional mass-based partitioning model which uses a molar mass averaged according to the number of moles in the condensed phase.. A recently reported third version of the partitioning model using individual component molar masses was shown to give significantly different results to the other two models. Further sensitivities to the assumed etc.'

The authors discussion on page 20314 lines 7-10 omits consideration of two recent papers that investigate the effects of varying RH on organic PM levels, namely Chang and Pankow (2008) and Pankow and Chang (2008):

Appropriate references to both works are now included in the amended manuscript:

Starting p20314, line 6: 'Whereas other studies have extensively examined details of the non-ideality in the participation of water in absorptive partitioning (eg. Chang and Pankow, 2008; Pankow and Chang, 2008); even to the extent that phase separation into polar and non-polar phases has been considered (Erdakos and Pankow, 2004; Erdakos et al 2006; Chang and Pankow, 2008); this study largely explores etc.'

Discussion of Molar Mass.

Our interpretation of the vagueness of the phrase *number averaged molecular weight of the absorbing om phase* originates from our familiarity with properties averaged across particle populations - for example, we have extensive experience of HTDMA and CCN measurement derived properties which intrinsically depend on the number

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of aerosol particles, rather than particle mass. Thus, mass and number averaged properties carry different meanings in certain branches of aerosol science. We have therefore extended the definition throughout the current manuscript to state that M_{om} is the molar mass averaged according to the number of moles in the condensed phase. We have modified the text as follows:

'on the non-ideality (deviations from Raoult's Law) of the condensed components M_{om} is the molar mass averaged according to the number of moles in the condensed material (SOA and water) given by Eq 5 below in which all concentrations (C_{OA} and C_i) are in molar units (specifically μmolm^{-3}).

We would further like to clarify the use of molar masses in the paper as follows:

P20318, lines 18-19: We would like to thank the reviewer for pointing out the error in the original Eq. 5. We should have made it clearer that C_i values used in Eq. 5 were defined in terms of molar units (ie. μmolm^{-3}). All calculations with the Mass_4 model (Eq. 4) use the correct (averaged according to number of moles) form of the molar mass and are valid. It should be emphasised that only the Mass_4 model considered here uses any form of averaged molar mass in the partitioning calculation. The reviewer is quite correct that the redefinition of C_i^* values from mass based to mole based (as described in page 20318, lines 18-19) produces a modified form of the partitioning equation which however gives identical results to the original model (Mass_4). In this form of the partitioning model equations 1, 2 and 8 are solved together with no reference to molar mass whatsoever, partitioning the components to a condensed number of moles which is tracked throughout the calculation. Once the partitioning calculation has been completed then the quantities of condensed material (in μmolm^{-3}) can be converted to mass quantities, if required, by multiplying by the appropriate molar mass for that compound. Hence in this formulation of the partitioning model Eq(5) is not used. In response to the reviewers comment *Indeed,*

this redefinition (of Eq 5) must be the reason why all the authors results for the Mass_4 method are the same as for the Mol method it is contended that, as Eq. (5) is not used in the Mol method, any such redefinition is not responsible for the fact that the Mol model gives the same results as the Mass_4 model. In response to the comment *Also, since the Mol method is the same as the Mass_4 method*; we would disagree, for the reason stated above. The two methods do give the same results but the Mol method uses no component molar masses in the partitioning calculation so the two models are not the same. We are hence keen to show that calculations done with the Mol model (after conversion of molar condensed quantities to their mass equivalents) give identical results to those of Mass_4 (in contrast to the Mass_3 model) as we recognise that the Mass_4 model (as the original model) is the benchmark against which other models need to be tested. For this reason we wish to retain the comparisons between all three models in our figures. We also realise that in the text where we are describing the Mol model (equations 8-11) we did not make it clear that all abundances and concentrations are in molar units. The text has now been modified:

Starting p20319, line 1: 'by explicitly incorporating individual compounds less accurately than using a total abundance averaged C_{bin}^* for all components in a single bin (Eq.10) Equation 10 (where all concentrations are in μmolm^{-3}). This is identical to a condensed abundance averaged value'

And starting p20319, line 19: 'iv) calculation of an abundance averaged molar mass for each bin (C_i in μmolm^{-3}):' Equation 11 We have deleted the sentence beginning (starting p20320, 8) 'This form of the partitioning model can only provide useful results' as this is not true.

On non-ideality The reviewer is quite correct that we assume liquid phase ideality in this work (other than the indication of the direction of the effect of non-ideality on predicted mass loadings in section 3.3.3). While this is clearly a simplification

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we do not fully agree that it reduces the calculations to mathematical exercises and remain convinced that it does not negate our conclusions in any way. Notwithstanding the many valiant recent attempts to describe impacts of non-ideality on semi-volatile organic partitioning, at the present time the chemical composition of condensed material in the troposphere is invariably constrained too poorly to predict deviations from ideality. The aim of this paper is simply to demonstrate the ability of the molar formulation of the model to account for partitioning of compounds of widely varying molar masses whilst remaining consistent with Raoult's Law - not to explore atmospheric aerosol non-ideality. None of the recent studies concerned with assessing the sensitivity of the means by which assumption of liquid phase ideality affects the predicted aerosol composition quantify the uncertainties associated with non-ideality of real atmospheric aerosol component mixtures in comparison to other potential errors in the partitioning model (such as errors in the estimation of vapour pressures). It is certainly true that, for some calculations the assumption of liquid phase ideality will be a gross simplification. However, it is also very likely that errors in calculating SOA composition in the moist atmosphere caused by assuming liquid phase ideality may be considerably less significant than the errors associated with the uncertainties in component vapour pressures. Even if we were to attempt inclusion of non-ideality in our calculations assuming it has a large effect, numerous assessments of state-of-the-art activity coefficient models suggest that we can only replicate 'real' observed non-ideal behaviour of a very small subset of the organic functionality relevant to the atmosphere (Clegg and Seinfeld, 2006; Raatikainen and Laaksonen, 2005; Tong et al 2008 and references therein) thus limiting the scope of any conclusions drawn. Indeed, in systems containing only organic components (Topping et al., 2005b) or both organic and inorganic components (Clegg Brimblecombe, 2003), it has been shown that an assumption of ideality reproduces more accurately the component activity than often-assumed description of non-ideality based on dissimilar component interactions. In any case, in section 3.3.3, we have already included the following discussion: 'in no case is condensed organic mass independent of RH. The

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shape of the dependence will obviously vary with the form of the activity coefficient expression, but organic component non-ideality will not generally lead to a small dependence on RH. It should be noted that the same degree of non-ideality in the different volatility components leads to a different mass loading and dependence of mass loading on RH. If the deviation from non-ideality is negative, the dependence on RH is greater if the more volatile component is non-ideal than if the less volatile component is non-ideal. Conversely, if the deviation from non-ideality is positive, the dependence on RH is greater if the less volatile component is non-ideal than if the more volatile component is non-ideal. Such a crude exploration of the effects of non-ideality obviously does not account for effects such as phase separation or mixed solvent systems and assumes that the resultant condensed phase is miscible across its entire composition range. The molar-based model has been explicitly coupled to a multicomponent thermodynamic model and this is the subject of a more detailed study of these phenomena'. We are fully aware of the impacts of non-ideality, but a full exploration of these impacts is outside the scope of the manuscript, which concerns itself with partitioning sensitivities other than component non-ideality. We contend that the cautionary statements included in section 3.3.3 are quite clear and the area of non-ideality is the subject of a comprehensive and systematic ongoing study.

*On the equivalence of $K_{p,i}$ and the reciprocal of C_i^** We do not agree with universal equivalence. This is wrapped up in the difference in usage of molar mass in the different model versions. The manuscript presents a comparison between $K_{p,i}$ defined by the Mass_4 model with $1/C_i^*$ defined for the Mass_3 model. We apologise for not making this clear and we have now clarified this in the revised text. The reason why the Mass_3 model gives different results from the Mass_4 model is because the $K_{p,i}$ defined in Eq. 4 is not the same as the $1/C_i^*$ defined in Eq. 3 because of the different definition of the molecular weight terms (M_i vs. M_{om}). We agree that there should be no 'so long as', however the definitions in the literature are inconsistent. Our contention is that Eq. 3 is incorrect. The Mass_3 model (Donahue et al., 2006)

implicitly assumes that all condensing components have the same molecular weight as this is the only condition under which M_i and M_{om} can have the same value. The only condition under which the Mass_3 and Mass_4 models can predict the same aerosol mass is when all condensing components have the same molar mass (as this is the only condition under which M_i and M_{om} can have the same value). Alternatively, the only way for $C_i^* = 1/K_{p,i}$ using the respective definitions in equations 3 and 4 is to modify the activity coefficient in Eq. 3 as explained in the supplementary material to Donahue et al (2006). We have modified the text as follows:

Starting p20316, line 6 'of $K_{p,i}$ will have units of μgm^{-3} . In comparing these formulations it is important to note that C_i^* (Eq.3) is not the reciprocal of $K_{p,i}$ (Eq.4) as M_i is not the same as M_{om} (see below). Calculation of the partitioning in both models etc.' Also starting p20317, line15 'condensing species (M_i in Eqs. 3 and 5). One way that the equilibrium coefficient ($K_{p,i}$), as defined in Eqn 4, can be made to equal the reciprocal of the mass concentration of the saturated vapour (C_i^*), as defined in Eqn. 3, is through use of a modified activity coefficient

On model reformulation

We agree with the reviewer that the sentence 'The provision of the identity of a large number of potential species contributing to the SOA mass allows reformulation of the partitioning model in terms of the molar abundance of components' is rather clumsy. The point being made is that, so far as a model expressed in molar terms is concerned, model input in terms of molecular abundance predicted by explicit degradation schemes is a more accessible data source than a mass concentration of a product of volatility fitted to chamber data. The provision of data from such a degradation scheme thus can lend itself to either a molar or mass-based partitioning formulation, whereas data derived from chamber measurements only lend themselves to mass-based calculations, and only then with an assumed molar mass. Of course, direct compound identification and concentration determination in chamber experiments will allow either model to be used equally well.

Starting p20318, line 6 'atmospheric VOCs. These explicit models provide calculated molecular concentrations of a large number of species potentially contributing to the SOA. This allows the reformulation'

3. Clarifications Needed.

On model simplicity

The Mol method is intrinsically simpler. Using the Mass_4 model, equations 1, 2 and 4 must be solved simultaneously and iteratively. As M_{om} in equation 4 is a function of the composition of the condensed phase, the iteration modifies two variables (C_{OA} and M_{om}). The Mol model requires simultaneous iterative solution of equations 1, 2 and 8, containing no molar mass and modifying only C_{OA} . Once the composition of the condensed phase (in molar units) has been obtained it can be converted to mass concentrations using the molecular weight of each condensed component. Also, although all the examples used in this paper require conversion to mass concentrations for comparison purposes it should not be assumed that all possible calculations using these models will have this requirement; thus we disagree with the *a priori* statement that 'Since the final quantity of interest is the mass concentration of organic PM'. An example would be predicting the molar composition of SOA from atmospheric concentrations in molar units, or calculating molar abundances (or molar ratios) of functional groups for comparison with appropriate analytical techniques. The latter output is the target for $^1\text{H-NMR}$ spectra from ambient samples using our ongoing efforts.

On the choice of partitioning compounds We accept that the range of compounds used in Figure 1 are not particularly relevant to atmospheric studies. This was not the point. For Figure 1 we needed a series of compounds covering a wide range of volatilities to most clearly demonstrate the difference between Mass_3 and the other

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models. For the lowest volatility compound we selected a dicarboxylic acid (maleic acid) which may be significant for SOA formation from anthropogenic sources (and this is the subject of ongoing work and a manuscript in preparation; Barley et al., 2009). The other compounds had to be more volatile and were selected, in part, for their reliable vapour pressure data. We avoided including more atmospherically relevant compounds of lower volatility than maleic acid because: a) they would partition to the condensed phase at close to 100% so there would be no detectable difference between the predictions of the Mass_3 model and the other two models, and b) the difficulty in obtaining reliable vapour pressure data for such compounds. The text has been modified to make this clearer:

Starting p20320, l19 'The component physical properties used in the test cases are summarised in Table 1. They were chosen to provide a wide range of vapour pressures rather than for their atmospheric relevance. However maleic acid may be a significant contributor to SOA under some conditions and the other compounds were selected because they had very different volatilities to maleic acid; and good quality vapour pressure data were available. A wide range of volatilities was needed to highlight the differences between the models. All calculations were etc.'

Minor Comments:

On the volatility and solubility of partitioning components . If there is no bright line between water soluble and water insoluble compounds then surely there is no bright line between volatile and involatile compounds? Both properties show a continuum of values and it is quite arbitrary where a line is drawn between soluble / insoluble and volatile / involatile. The authors agree that there is inconsistency in the common usage of the terminology and for precision have now modified p20313, line 21 to read: 'producing a range of VOC oxidation products of widely varying volatilities' and have modified p20313, line 23-24 to read: 'The organic aerosol fraction contains a mixture of compounds with a wide range of solubilities in water and it has been estimated etc.'

However, it should be noted that OVOCs is still correct if imprecise usage: the VOCs have been oxidised and so are now oxidised VOCs (i.e. the scratched car was red, but is no longer necessarily so). It is not claimed that the OVOCs are volatile oxidised OCs (VOOCs).

On the requirement for a single phase We agree with the reviewer that absorptive partitioning theory does not require a single phase. However p20314, line 1-4 does not deny this. The sentence starting 'However, instead of dissolution of components in a single dominant solvent,' quoted by the reviewer refers back to the previous sentence .. 'a widely used approach has been to consider the partitioning of semi-volatile organic components in a manner analogous to that described for semi-volatile inorganic components above.' There is no indication that absorptive partitioning theory would only work for a single phase system just that the 'widely used approach' has used 'an organic medium sufficiently similar in nature for the system to act as a single phase organic solution.' However, we have generalised the sentence to: 'However, instead of dissolution of components in a single dominant solvent, the absorptive partitioning model for organic material has most frequently been used to consider absorption of semi-volatile organic components into an organic medium sufficiently similar in nature for the system to act as a single phase organic solution. This is not a requirement for the absorptive partitioning model and separate phases have been considered in a number of studies (e.g. Chang Pankow, 2008).'

Ambiguous nomenclature and mis-attribution of equation 6 We have kept the equation in the same form as in the 2001 paper. However the reviewer is quite right that MW_{om} and M_{om} are the same number averaged molecular weight. We have amended the equation accordingly. Also we thank the reviewer for clarifying the origin of Eq. 6; we have updated the references accordingly. The text has been amended: Starting p20317, line 1: Deleted Seinfeld and Pankow (2003) Inserted Seinfeld et al. (2001) Starting p20317, line 4: 'expression was derived as their Eq.(17)' Starting

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p20317, line 6: 'where MW_{om} is a number averaged molar mass identical to M_{om} in Eq. (4). The first term denotes the RH-dependence etc.'

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

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