**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol" *by* M. H. Barley and G. McFiggans

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The authors would like to thank the reviewer for their careful consideration of the manuscript and their kind and supportive comments about the work being reported. The authors would like to take this opportunity to make several suggested improvements to the paper in response to these comments.

- *The issue of overfitting, Introduction: introduced at page 18380-lines 5-10, and discussed briefly lines 22-26. I think the paper would benefit from a more thorough discussion of the underlying reasons why overfitting might be an issue for the creation of group methods for vapour pressure datasets of multifunctional*

compounds...

We can provide some discussion about the dangers of overfitting as the reviewer suggests (see below).

I can think of a few possibilities: a) vapour pressure and/or boiling point measurement errors may be large for any individual compound, hence group methods based on these measurements will be in error; b) group-group interactions may sometimes have a large effect on the vapour pressures. The first of these would argue for an approach other than that taken by the authors in terms of the number of compounds used to create a group method. The authors argue for a smaller number to avoid overfitting... Not correct. *...but with a smaller number of samples, the potential for the errors associated with any one sample becomes large. Thus if only two samples are used to describe the contribution of a specific group, and a large measurement error occurs for one sample, the resulting vapour pressure estimates for that group may be large...*

We think there is a misunderstanding about our position on this topic. To create a group contribution method we believe one should use all available relevant data (after an appropriate screen for quality) unless a subset is retained for testing purposes. We do not argue for the use of a smaller number of compounds to create a group contribution estimation method. Our concern is that with increasing complexity of a group contribution method there is a danger of overfitting. It is the number of adjustable parameters in the models that we believe may contribute to overfitting- not the number of compounds used in the fitting. Thus we would agree with the reviewer that if only two compounds are providing inputs to a specific group contribution the potential for errors are large and in such cases we would urge experimentalists to make more measurements on appropriate compounds to improve the models. We agree with the reviewer that the issue of group interactions is potentially very important for multifunctional compounds. This has been recognised in the methods published by Rarey and coworkers (Nannoolal

et al. 2004, 2008, Moller et al. 2008). However there is a lack of data for many of the group interactions specified in these methods and also there is good evidence of specific interactions for certain ortho substituents on an aromatic ring (eg. nitrophenols, salicylic esters etc. (Nannoolal et al. 2004) which are not presently accounted for. Hence there is scope for increasing the number of parameters in these models so the issue of overfitting will become even more relevant.

...Possibility b) implies that methods that do not account for the interactions will be inaccurate... We would agree with the reviewer that methods that do not include group interactions may have reduced accuracy. However in the amended paper we will provide some evidence that inclusion of group interactions don't always result in improved predictions.. *...and/or compounds with interacting groups would not be best for use in constructing the method...* As compounds of atmospheric importance are likely to include two or more functional groups the issue of group interactions is potentially important and if group interactions are significant then it will be important to use such compounds in any model.

The paper would be improved with the addition of a paragraph or two after line 4 on page 18379 with a more detailed discussion of the "overfitting problem", with some examples... We agree with the reviewer that the paper would benefit from a broader discussion about overfitting (please see below). *The authors should attempt to describe the problem in a general mathematic sense as well; how does using all the available information lead to poor predictions?* (It doesn't) *The concept is counter intuitive and needs to be better explained...* We agree with the reviewer that we need to explain more clearly what overfitting is and why it could be a serious issue for group contribution methods. The potential problem with overfitting is around the form of the model (specifically how many adjustable parameters are required to fit the data) rather than the amount of data used in the fitting. Hence we would disagree with the statement implied by the reviewers question:- "how does using all the available information lead to poor

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predictions?" For a specific model the minimum number of datapoints required can be calculated using the theory of experimental design (Montgomery, 1997), but the addition of extra datapoints can only lead to similar or improved predictions (depending upon the distribution of the extra data over the multidimensional variable space). We would not expect that using a subset of the full dataset in the fitting process would give better predictions than using the full dataset.

• In the modified paper we will start a new paragraph at p18378-line 26:-

For some of the models, particularly the more complex group contribution methods, there may be significant danger of overfitting... (Delete next sentence- ...This would result in a model...) This is a problem that is well understood by the chomometrics and cheminformatics community (e.g. Faber and Rajko, 2007); and occurs when a model starts to describe the noise in the data rather than the underlying trend in the data. An overfitted model will give very good results for the data used to fix the adjustable parameters but much worse results for new data outside the training set. The potential for overfitting depends upon the amount of training data, the number of adjustable parameters in the model, and how well the mathematical form of the model relates to the true trend of the data. As group contributions models for vapour pressures (and other physical properties) become more complex then the ratio of independent data points to adjustable parameters is reduced. This results in a significant number of the parameters being fitted to small subsets of the data because the relevant structural feature is poorly represented in the overall data set. In these circumstances there is a danger that a statistically significant non-zero parameter value may be incorrectly obtained. To take a hypothetical example: a specific group contribution may be obtained by the fitting of vapour pressure data, for say 3 or 4 structurally related compounds (eg C4, C5, C6 dicarboxylic acids) all measured by the same researcher, using the same equipment over a period of one year. As experimentalists often report results for structurally related compounds together in a paper this scenario is

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quite possible but it does raise the question as to the definition of "independent" data. The fitted parameter may reflect biases in the work that would disappear if the data could be combined with that for a more structurally diverse range of di-carboxylic acids produced by a variety of researchers using different techniques. Hence the best way to avoid the danger of overfitting in group contribution models is to ensure that as many independent data points as possible are contributing to the fit for all the adjustable parameters.

Continue the text at the next paragraph:- Furthermore few, if any, of the methods...

- *C6171-line 21 ...On a similar vein: the authors create a simplified version of Nan-noolal et al's group method without really discussing their reasons for the simpli-fication or why they expect it to perform better than the original. This reasoning would greatly improve the paper.*

We will also clarify in the paper that we created the simplified version of the Nannoolal method not because we thought it would give better results than the full model but because we were interested in seeing how it compared to the full model and the other vapour pressure methods. The question we were seeking to answer is:- do the group interactions, secondary group contributions and specific hydrocarbon groups of the full method have a big effect on the accuracy of the predictions for this set of 45 multifunctional compounds? The answer, made clear in the amended paper, is no.

- In the modified paper - starting p18380 line 5 and replacing line 5 to end of paragraph:- In contrast the Nannoolal et al. (2008) method provides 130+ group contributions plus group interactions (all derived from experimental data) to pre-dict the slope of the vapour pressure curve with temperature. To test whether this large number of fitted parameters number (133 required for our test set of multifunctional compounds) clearly improved the vapour pressure predictions, a simplified form of the Nannoolal et al. (2008) equation in which all group interac-

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tions were dropped, and the number of structural groups required to describe the test set was reduced to 15, was created and tested against the other methods. This simplified equation was expected to produce inferior results to the full model although it does retain the functional form with temperature of the full method.

- *Methodology comments: Page 18381, lines 15-20. The authors dismiss a group of methods without adequate justification at this point in the discussion... If not, how can the authors be sure of this statement not having checked out these methods against observations.*

The reviewer is correct in saying that we dismiss a class of methods without presenting direct evidence that the methods would give poor results for these compounds. This was, perhaps, a bit too hasty. The argument we advance in the discussion paper is that, while methods based upon corresponding states may give good results for volatile fluids for which experimental critical points are available, it seems unlikely that they will give similar results for relatively involatile multifunctional compounds. This is based upon the fact that the critical properties will have to be estimated, probably using methods requiring T_b (also estimated for most compounds) and then the vapour pressure curve (defined by the critical pa-rameters and T_b) is extrapolated over a massive temperature range to compare with experimental vapour pressures below 100 Pa. Further more the database for experimental critical properties is much smaller than that for boiling points, and will contain even fewer multifunctional compounds. This suggests that any critical property estimation method will provide rapidly poorer estimates of critical values as the molecular functionality increases and the volatility decreases. However we note that Camredon and Aumont (2006) obtained very acceptable results using a corresponding states method (the Lee-Kesler equation) with critical properties estimated by the method of Ambrose (Reid et al. 1987); although it is noticeable that the scatter of their data increases markedly at lower volatilities in agreement with the above argument. We decided to test the Lee-Kesler method with critical

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properties estimated by the Ambrose method against our test set of 45 multifunctional compounds to see how our results compare with those of Camredon and Aumont . We restricted this test to the best T$_b$ estimation method so that a direct comparison can be made against the best vapour pressure equations. An extra column will be added to Table 4 showing the results and a plot of P$_{est}$ vs. P$_{exp}$ will be included in the figures.

- In the modified paper the first paragraph of Section 2 Methodology(p18381-lines 13-20) will be replaced with:-

Vapour pressure estimation methods based upon the principle of corresponding states seem unlikely to be able to give good predictions for complex multifunctional compounds of atmospheric importance. This is because these models require values for the compound's critical temperature(T$_c$) and pressure(P$_c$). These methods can give good results for volatile fluids, particularly if experimental T$_c$ and P$_c$ are available (Poling et al. 2001). However for the compounds of interest in this work critical values would have to be estimated, and the estimation methods (e.g. methods by Joback and Ambrose - Reid et al. 1987) typically use a T$_b$ value; which will also be estimated. Hence there is considerable scope for an accumulation of errors. Also the database for experimental critical properties is much smaller than that for boiling points, and will contain even fewer multifunctional compounds. This suggests that any critical property estimation method will provide rapidly poorer estimates of T$_c$ and P$_c$ as the molecular functionality increases and the volatility decreases. Despite the logic of these arguments it is important to note that Camredon and Aumont (2006) obtained very acceptable results using the Lee-Kesler equation with T$_c$ and P$_c$ estimated by the method of Ambrose (Reid et al. 1987); although it is noticeable that the scatter of their data increases markedly at lower volatilities in agreement with the above argument. Despite our reservations about corresponding states methods we decided to test the same method against our test set of 45 multifunctional compounds to see

how our results compared to those of Camredon and Aumont.

Also the second paragraph on p18385(lines 14-21) will be deleted (see responses to Reviewer 1) and the first paragraph on this page (lines 3-13) will be moved to after item G) on p18386-line 4. The sentence "This work will also consider some variants on the Nannoolal method, a corresponding states method (Lee-Kesler), and two methods that don't require a boiling point. " will be inserted at p18386-line5. The text will continue "...The accuracy of these methods will be compared to the accuracy of the best combined methods once these have been found using Test Set 2". This will then be followed by the description of a simplified version of the Nannoolal vapour pressure equation (presently p18385-lines 3-13), then a description of the method of Moller et al.(see responses to Reviewer 1) followed by a description of the Lee-Kesler and then the text presently at p18386 line7 (starting "The Simpol.1 method of Pankow and Asher") through to p18387- line 3. The new text describing the method of Lee-Kesler will be:-

The Lee-Kesler method (or LKA method) (Reid et al. (1987) -section 7.2) requires the critical temperature(T$_c$) and critical pressure(P$_c$) for each compound, and these properties were calculated by the estimation method of Ambrose (Reid et al. (1987) section 2.2) using the best available estimated T$_b$ values (provided by the N-Tb method- see below). The vapour pressure equation is:-

$$\ln P_{VPr} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \tag{1}$$

where P$_{VPr}$ is the reduced vapour pressure (= P/P$_c$ with P and P$_c$ both in atmospheres) and T$_r$ is the reduced temperature (= T/T$_c$ with T and T$_c$ both in K). ω is Pitzer's acentric factor, while f$^{(0)}$ and f$^{(1)}$ are polynomials in T$_r$:-

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \tag{2}$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6 \tag{3}$$

and ω is estimated from the T_b and critical properties using the following three equations (Reid et al. (1987)-section 2.3):-

$$\omega = \frac{\alpha}{\beta} \tag{4}$$

$$\alpha = -\ln P_c - 5.92714 + \frac{6.09648}{\theta} + 1.28862 \ln \theta - 0.169347 \theta^6 \tag{5}$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{\theta} - 13.4721 \ln \theta + 0.43577 \theta^6 \tag{6}$$

where $\theta = T_b/T_c$.

- *page18384/eq 9:-the equations should be modified so that the same variable is used for the same quantity throughout all the equations...* We will change the T_{rb} in the equation to T_p and put a note that $T_p = T_{rb}$ in the original reference.

- *page18385/lines 1-10:- The issue of simplification of more complex methods and the reasoning behind the choices made needs to be more adequately explained. Table 1 summarizes what was done, but the text does not give a description or justification for what was done. Why not just use the original groups?* As mentioned above, we created the simplified version of the Nannoolal et al. (2008) vapour pressure equation because we were interested in seeing how it compared to the full model and the other vapour pressure methods. The full model has primary and second order groups and group interactions, and the suspicion was that while some of these features might be important for obtaining accurate vapour pressures for relatively volatile compounds (particularly the hydrocarbons and monofunctional compounds which will dominate the experimental vapour pressures used in fitting) they might have an insignificant effect upon the estimation of vapour pressures for low volatility multifunctional compounds

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of primary interest to this work. The primary groups are required to describe the molecule and it is important that all heavy atoms (C, O, N, Cl) are accounted for. However the use of 31 groups to describe hydrocarbon structures is probably driven by detailed vapour pressure data for these compounds and we decided to simplify the method by taking an average value (see Table 1). We retained all the main non-hydrocarbon functional groups (with some averaging, e.g. for alcohols) to account for all heavy atoms and because the size of the group contributions for these functional groups were so much larger than those for the hydrocarbon groups (see Table 1). The second order groups are corrections for specific structural features and generally give small group contribution values. Also although the group interactions could potentially be important for our test set and some of the group contributions are quite large it should be noted that their contribution to the slope of the vapour pressure curve is inversely proportional to the number of heavy atoms in the molecule. The simplified Nannoolal model was designed to be a version without second order groups or group interactions and with a minimal number of primary groups to find out if these addition features had a detectable impact upon the vapour pressure predictions for the compounds in our test set 2. If this simplified version gave similar results to the full version of the Nannoolal vapour pressure equation then it would suggest that for our test set of compounds (and by extension for compounds of atmospheric interest) it is the form of the Nannoolal equation (Eq. 9 in the Discussion paper) that contributes to the quality of the vapour pressure predictions rather than the detailed hydrocarbon groups, structural correction factors and group interactions of the full method. We will alter the text in this section to clarify this point.

- In the modified paper the paragraph on page18385/lines 3-13 was replaced with the following:-

The full N-VP model has primary and second order group contributions and group interactions (GI in Eqs. 10 and 11); some 133 parameters are required to de-

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scribe the compounds of Test set 2. To test whether all these parameters are important for the estimation of the vapour pressures of the 45 multifunctional compounds a simplified vapour pressure equation was created with 15 parameters (see Table 1). This simplified Nannoolal model (referred to in this work as the N-Sim method) was designed to be a version without second order group contributions or group interactions and with a minimal number of primary group contributions. The aim was to find out if these addition parameters, which might be very important for determining the vapour pressures of the relatively volatile hydrocarbons and monofunctional compounds which will dominate the experimental data used in the parameter fitting, had a detectable impact upon the predictions for the low volatility multifunctional compounds of primary interest to this work. The primary groups are required to describe the molecule and it is important that all heavy atoms (C, O, N, Cl) are accounted for. However the use of 31 groups to describe hydrocarbon structures is probably driven by detailed vapour pressure data for these compounds and we decided to simplify the method by taking an average value (see Table 1). We retained all the main non-hydrocarbon functional groups (with some averaging, e.g. for alcohols) to account for all heavy atoms and because the size of the group contributions for the functional groups were so much larger than those for the hydrocarbon groups (see Table 1). The second order groups are corrections for specific structural features and generally give small group contribution values. Although the group interactions could potentially be important for our test set and some of the group contributions are quite large it should be noted that their contribution to the slope of the vapour pressure curve is inversely proportional to the number of heavy atoms in the molecule. Hence their impact upon the vapour pressures of the relatively large molecules in Test set 2 may be limited. On this basis the second order group contributions and group interactions were dropped from the N-Sim method.

- *page18387/lines 17-26:-I appreciate the authors approach to ensuring that the*

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data are of adequate accuracy for comparison to the different methods. They should include a discussion of which species/species classes/species groups are excluded from their test dataset by their approach.

- Add some text (page18388/line 8):- These criteria inevitably excluded a wide range of compounds from this test set. In addition to the exclusion of most multifunctional compounds the selected molecules tend to have a low molecular weight and the criteria that they need to be stable at the experimental boiling points may exclude some functional groups (eg. nitrate, some nitro compounds and some aldehydes) which encourage decomposition at elevated temperatures. The requirement of liquid phase vapour pressure data below 40Pa means that very regular molecules are excluded because they will have relatively high melting points (an extreme example is camphor). In the case of aromatics, alkyl substituents disrupt the crystal packing and lower the melting point so several of these appear in the list but more regular aromatics (eg. benzoic acid) are excluded because of this requirement.

- *page18388/top paragraph:-The selection of no more than two samples from a functional group in generating the test set strikes me as being a problem: if one or both of these measurements has significant errors, will this not result in large apparent biases of the predictions?...* In selecting the two compounds for each functional groups we did some basic checks to ensure that the vapour pressure data didn't have significant error. In particular, for these compounds, there were usually other datasets from other authors, perhaps at higher temperatures, which could be compared to the selected dataset as a check for consistency. The number of compounds was kept to two so as to avoid having a test dataset completely dominated by a functional group (eg. -OH), as the errors shown by each estimation method would be closely correlated for a range of alcohols and this would significantly distort the results. This is a well established principle in cheminformatics where sophisticated methods have been derived to ensure that test sets

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have a good distribution. An example is the sphere exclusion method (Golbraikh and Tropsha 2002) in which once a compound has been selected for the test set a (multidimensional) "sphere" is drawn around it and all compounds within this sphere are now excluded from the test set because they are too similar to the compound already selected. We haven't been able to use such a method in this work but we have tried to keep to the principle that compounds in the test sets should be significantly different to each other... *This is a counter argument to concerns over overfitting that the authors should address* We would disagree with the reviewer that this relates to the overfitting problem. If we were fitting parameters to a model we would use all the appropriate available compounds (unless we kept some back for use in a test set) and certainly would not restrict ourselves to two compounds for each functional group.

- *page18388/line 16, condition number 1. This is a potentially serious omission. Both alkenes and aromatics have significant yields of secondary organic aerosol from the oxidation of these precursors...* We would agree with the reviewer that compounds (particularly multifunctional compounds) derived from alkenes and aromatics can make a significant contribution to SOA. *The oxidation products may include unbroken ring groups and double bonds...* we agree... *Their exclusion here implies that large classes of compounds known to be significant organic aerosol precursors have been eliminated from the test set...* We think there is a serious misunderstanding here. We have included alkene and aromatic groups in the vapour pressure calculations and as you can see from Table 3 aromatic compounds in particular are very well represented. The point of condition 1 was just to say that all compounds selected should have two or more functional groups other than alkenes and aromatic rings. This was done to provide a more rigorous test of the vapour pressure estimation methods as it is the non-hydrocarbon groups that have the most impact upon the calculation of both T_b and the slope of the vapour pressure curve. Also while we would agree with the reviewer that alkenes

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and aromatics are very important contributors to atmospheric chemistry, the un-reacted alkenes and aromatics (such as alpha and beta pinene, toluene, methyl benzene etc.) make little contribution to SOA because they are far too volatile to condense under normal atmospheric conditions. It is only after their reaction to form oxygenated species (in some cases with several functional groups- eg. dicarboxylic acids and poly-ols) that they can contribute significantly to SOA due to their reduced vapour pressure. *...Alternatively, the authors may account for these compounds in different ways. For example, by "not considered functional groups" do the authors mean that other subgroups are used to describe these compounds? I assume that this is the case, since they have included limonene and propylbenzene in Table 2 and a number of aromatics in Table 3. E. g. instead of just "alkenes" and "aromatics", do the methods compared have "=C=", "=CH-", and "=CH2" groups...* Exactly- although the subgroups used vary depending upon which estimation method is being used. For example the methods of Nannoolal et al. 2004, 2008, use 5 groups to describe an aromatic ring and a further five groups to describe alkene structures. These groups were used as appropriate to calculate the vapour pressures of the compounds in both test sets. *...Or have they excluded two of the classes of compounds which contribute the largest share of secondary organic aerosol formation from their work...* It depends which class of compounds the reviewer is referring to. We have excluded unchanged hydrocarbons (such as toluene, benzene, alpha and beta pinene) because they are too volatile to contribute significantly to SOA. We would like to have included compounds such as nitrophenols and pinic acid which are obtained by the atmospheric oxidation of the above hydrocarbons but because there is a lack of data we had to use other compounds containing two or more non-hydrocarbon functional groups in addition to alkene and aromatic groups. *...(aromatics being the largest contributor to anthropogenic SOA, and monoterpenes the largest contributor to biogenic SOA)...* If the reviewer means unchanged aromatics and monoterpenes we can't agree with this statement for reasons outlined above. If

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the reviewer would allow us to put "oxidised" or "functionalise" in front of "aromatics" and "monoterpenes" we could agree.

- It is clear that the wording of condition 1) is open to misinterpretation. In the modified paper we will reword condition number 1 to make it clearer:-

Page18388- line 16:- 1) The compounds must contain two or more non-hydrocarbon functional groups

2) The vapour pressure data...

- *page18389/eq. 15:- Given the rigour of the selection process for vapour pressures earlier, the introduction of this equation to allow a larger number of compounds to be compared to "observations" raises some concerns. How accurately are the terms in the equation known, and how does this effect the accuracy of the resulting estimate of sub-cooled liquid vapour pressure)...* The likely errors arising from the use of Eq. 15 can be quantified as they hinge on the accuracy of ΔS_{fus} , ΔC_p and T_m values. The size of the correction is roughly proportional to $T_m - T$ so it is those compounds where this quantity is the largest that will have the highest sensitivity. Assuming an error in experimental ΔS_{fus} of +/- 20%, an error in T_m of +/-2K and in ΔC_p(usually estimated) of +/-40% then the range of the corrected vapour pressure of phloroglucinol will be within a factor of 1.8 of the final value quoted in Table 3. Similarly the results for 2-Hydroxy benzoic acid will be within a factor of 2.3. Phloroglucinol and 2-Hydroxybenzoic acid have $T_m - T$ values of up to 114 and 122K respectively. More typical is 2,6 Dinitrotoluene with $T_m - T$ = 52K and a range of corrected vapour pressures within +/-30%. For those cases where $T_m - T$ is less than 30K, and only the first term in Eq. 15 is used, the effect of assuming an error in ΔS_{fus} of +/- 40% changes the corrected vapour pressures by less than +/-50% for Musk Ambrette and +/-25% for Heliotropin. Hence for most compounds the likely error in the correction will be comparable to the scatter in the original experimental data, e.g. see Booth et al

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2009; but for a few compounds the potential errors will be more significant... *The authors make an attempt earlier to use only direct observations for their experimental data, but here they allow an indirect estimation to be used to generate the data. This needs to be clarified.* The reviewer makes a valid point. We would have much preferred to have used only liquid phase vapour pressures but this would have given us a very small dataset to work with. We have taken steps described in the criteria for selection of compounds for Test set 2 to minimise the error in the correction to sub-cooled liquid vapour pressures (eg. requiring an experimental $\Delta H_{fus}$for the correction if the experimental temperature is more than 30K below the melting point). For most compounds the potential errors in the correction could change the sub-cooled vapour pressures by up to +/-50% and this is generally very small compared to the differences between the estimated and experimental vapour pressures seen for the compounds. However for a couple of compounds (Phloroglucinol and 2-Hydroxybenzoic acid) the potential errors in the sub-cooled vapour pressures are more significant and could influence the results for these compounds.

- In the modified paper some sentences will be added at the end of section 2.2 (p18390/line14).

A basic error analysis was done for several compounds to estimate the impact of potential errors in the key parameters of Eq. 15. Assuming potential errors of +/-40% for estimated quantities (ΔC_p and some ΔS_{fus} values- see Table 3); +/-20% for experimental ΔS_{fus} and +/-2K for T_m then for most compounds the calculated error in the final sub-cooled vapour pressure values was within +/-50%; although for a couple of compounds (Phloroglucinol and 2-Hydroxbenzoic acid) the potential error was substantially higher (up to a factor of three). For most compounds these potential errors are of the same order as the experimental scatter in low vapour pressure values (e.g. see Booth et al 2009), and are small compared to the differences between the estimated and experimental vapour pressures seen

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in this work; but for Phloroglucinol and 2-Hydroxbenzoic acid the errors may be more significant and could influence the results for these compounds.

- *page18389/line 5:- minor issue: could the authors include CAS codes for the species in Table 3...*

  We can provide CAS codes (where available) for the compounds in Table 3.

- *page18390/eq 17:-not clear if "n" is across different compounds within a class or over all compounds examined in the dataset, from the text.*

  We will clarify the meaning of "n"- it refers to the n datapoints for the specific compound.

- In the modified paper:- page18390-line 21 is changed to:-

  where the summation is over the n experimental points in the dataset for the specific compound being considered.

- *page18390, general comment on section 3.1:-If I've understood correctly, the procedure was to find the T_b value giving the closest P_{est} to P_{exp} (i.e. minimizing eqn. 17), then do stats on the resulting T_b compared to the known T_b? There needs to be a sentence towards the start of this section making this clear.* The reviewer gives a good summary of the method. We will clarify the start of this section as requested.

- In the modified paper:- page18390/line 17-Section 3.1:-

  For each compound in Test set 1 the predicted vapour pressure was calculated for each point in the dataset using the experimental T_b value. The T_b value was then changed to the value giving the closest fit of P_{est} to P_{exp} (as defined by minimising the objective function - Eq. 17). The experimental T_b was then subtracted from the fitted T_b (to give ΔT_b) and the resulting values analysed statistically for each method across all the compounds (see Table 4).

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  Eqn. 17)

  where the summation...

- *page18391/line 16:- The authors treat the relative simplicity of equation 2 as a reason for its use, without giving justification for doing so. It makes sense to select an equation due to it giving smaller standard deviations relative to observations than a more complex equation, but not because it is a simpler equation...*

  We accept that the fact that an equation is simpler is not a good reason to select it and will drop that comment from the text.

- In the modified paper starting at page18391-line15:-

  As the methods using Eq. (2) gave smaller standard deviations than the corresponding methods using Eq. (1), the Baum equation (Eq. 2) was selected for further comparison...

- *page18393/lines 5 through 12:- While the small sample size invalidates comparisons twixt the figures, there is nothing to prevent the authors from regenerating figure 1 using the subset of the species in figure 2, in order to allow that comparison...*

  At the request of Reviewer 1 we have added extra figures to the paper including plots of P_{est} vs. P_{exp} for all the cases shown in Figure 1. The present Figure 2 has been deleted and replaced by two figures of two panels each. In the first new figure the first panel will show a scatter plot of P_{est} vs. P_{exp} for the N-Tb/N-VP, N-Tb/M-VP, and JR/MY along with the SIMPOL.1 method for 36 compounds while the second panel will show the same three combined methods along with Capouet and Muller (CM) results for 9 compounds. These figures can be easily compared to the equivalent figure showing P_{est} vs. P_{exp} for the 12 combined methods of the original Figure 1 for all 45 compounds. The authors hope this will satisfy the requirements of the reviewer.

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- *page18395/eq 20:- Why use this version of the Antoine equation versus a higher order? The authors mention both extrapolation and interpolation? A higher order would be safer for the latter than the former. Given the earlier attempts to use only direct experimental data, the use of extrapolation here needs a bit of justification.*

  In this section we develop a model to illustrate how the vapour pressure values obtained from different estimation methods impact upon the amount of organic aerosol formed under an atmospherically sensible scenario. To do this we needed to define a base case and it was logical to define the base case using experimental vapour pressures. However the experimental vapour pressures were measured at a wide range of temperatures and we need to realistically correct the experimental vapour pressures to a common temperature (in this case 25C or 298.15K) at which we will run the simulations. As more than half of the experimental temperature ranges don't include the required temperature an extrapolation was usually required. The two coefficient Antoine is known to give a reasonable approximation to known vapour pressures over small temperature intervals and is thus better at extrapolating vapour pressures than more complex forms with extra coefficients (Poling et al. 2001). The accuracy of the resulting vapour pressure values at 298.15K is not critical to the calculation as we are comparing the relative effects of vapour pressure values rather than absolute values.

- In the modified paper the following two sentences will be added in at p18396/line 1:-

  For the majority of compounds an extrapolation to 298.15K was required. The two coefficient Antoine is known to give a reasonable approximation to known vapour pressures over small temperature intervals and is thus better at extrapolating vapour pressures than more complex forms with extra coefficients (Poling et al. 2001). These values at 298.15K will be referred to as...

- *page18396/lines 5-7:- Did all the methods employed give the same compounds*

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in the Donahue bins, and in the same relative distribution?... Answer No. *...One might expect not, from the earlier discussion but if so, it would argue that the condensation might be less sensitive to the method employed than might be expected from the earlier discussion...* We agree:- The quoted distribution of compounds in the Donahue bins is for the base case using the "experimentally derived" vapour pressures. Once we moved onto using the estimated vapour pressures then some of the compounds may change bins. If we allowed all the compounds to change to estimated values then there was sufficient movement between bins that in some cases no OA was formed at all. To provide a better assessment of the sensitivity of OA to changes in vapour pressure values we had to move to only allowing one compound at a time to change to an estimated vapour pressure which means that all other compounds stay in their respective bins while the single compound may change bins if the change in vapour pressure is sufficiently large.

- In the modified paper this point is made clearer a bit later in the document:-

  page18397/line 22:- If the partitioning calculation is redone with the experimentally derived vapour pressures replaced by estimated values then the compounds may move between the Donahue bins (see end of Section 4.2) and the amount of predicted OA varies dramatically (between 0 and 110 μgm^{-3}) depending upon which estimation method is used...

References

Booth, A. M., Markus, T., McFiggans, G., Percival, C. J., Mcgillen, M. R., and Topping, D. O.: Design and construction of a simple Knudsen effusion mass spectrometer (KEMS) system for vapour pressure measurements of low volatility organics, Atmos. Meas. Tech. Discuss., 2, 893-914, 2009.

Camredon, M. and Aumont, B.: Assessment of vapor pressure estimation methods for secondary organic aerosol modeling, Atmos. Environ., 40, 2105-2116, 2006.

C8070

Faber, N. M. and Rajko, R.: How to avoid over-fitting in multivariate calibration - The conventional validation approach and an alternative, Analytica Chimica Acta, 595, 98-106, 2007.

Golbraikh, A. and Tropsha, A.: Predictive QSAR modeling based on diversity sampling of experimental datasets for the training and test set selection, Journal of Computer-Aided Molecular Design, 16, 357-369, 2002.

Moller, B., Rarey, J., and Ramjugernath, D.: Estimation of the vapour pressure of non-electrolyte organic compounds via group contributions and group interactions, J. Mol. Liquids, 143, 52-63, 2008.

Montgomery, D. C.: Design and analysis of experiments, J Wiley Sons, New York, 1997.

Nannoolal, Y., Rarey, J., Ramjugernath, D., and Cordes, W.: Estimation of pure component properties Part 1. Estimation of the normal boiling point of non-electrolyte organic compounds via group contributions and group interactions, Fluid Phase Equilibria, 226, 45-63, 2004.

Nannoolal, Y., Rarey, J., and Ramjugernath, D.: Estimation of pure component properties. Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions, Fluid Phase Equilibria, 269, 117-133, 2008.

Poling, B. E., Prausnitz, J. M., and O'Connell, J. P.: Properties of gases and liquids, Chapter 7, McGraw-Hill, New York, NY, USA, 2001.

Reid, R. C., Prausnitz, J. M., and Poling, B. E.: Properties of gases and liquids, McGraw-Hill, New York, NY, USA, 1987

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