**Atmospheric
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Discussions**

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Comment

Interactive comment on "Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model – Part II: Predictions of the vapour pressures of organic compounds" *by* S. L. Clegg et al.

S. L. Clegg et al.

Response to Anonymous Referee #1

The referee makes a number of valuable points regarding the methods used to calculate activity coefficients. We agree with all the points made, and have incorporated them into the manuscript where appropriate:

We accept that the UNIFAC "Dortmund" model for activity coefficients is probably to be preferred over the standard model, and would make most difference for those SOA compounds that are soluble in the aqueous phase. However, it is also true that the

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"salting out" effect mentioned by the referee isn't incorporated into the model, mainly because of a lack of data. It seems likely that the inclusion of salting out, together with more accurate vapour pressures and a revision of the assignment of surrogate compounds are higher priorities. These comments are most relevant to Part I of our work, and will be addressed by a statement there regarding the differences between the standard and Dortmund UNIFAC activity coefficient models.

Figure 1 shown by the referee - the poor prediction of infinite dilution activity coeffiicents of alkanes and alkenes in water is striking, and is consistent with what one of us (SLC) found using another very different model (COSMO) which the referee is also familiar with. However, this does not affect the UCD-CACM model because these compounds have extremely low solubility in water and are therefore assumed to occur only in the hydrophobic liquid phase within the aerosol particles.

The points made regarding the limitations of the Joback and Reid boiling point prediction method, and the fact that the effects of polar functional groups on properties such as boiling points are not purely additive, are important. The statements we have added to the ms in response also to Referee #2's comments to directly address/incorporate these points. See below.

Response to Anonymous Referee #2

General points:

1. We agree with the referee about the need to identify the compositions of eighteen surrogate compounds in this work (rather than referring only to previous papers). The structures of all the compounds are now shown in a figure in the Appendix of the revised ms.

2. Clearly, making recommendations as to the best vapour pressure prediction method to use would be very helpful to readers, as the referee states. In our opinion it is not possible to do this authoritatively without also carrying out a comparison of the methods

for multifunctional compounds for with boiling points and vapour pressures are known. This is a subject for a separate study. However, some guidance can be given - the comments of Reviewer #1 were particularly helpful in this respect - and we have added the following statements to the ms:

To section 3.1: Some general comments regarding the boiling point methods can be made: first, the linear relationship employed by Joback and Reid (1987) between the sum of group contributions and boiling point is only valid over a limited range of molecular size - e.g., for molecules with up to about 8 -CH2- groups in the case of linear alkanes, and up to 15 -CH2- groups for n-alkanols (Cordes and Rarey, 2002). Second, the effect of polar functional groups such as -OH and -COOH on boiling point and is not simply additive, as is often assumed in group contribution methods. Of those methods considered here, those of Joback and Reid (1987), Stein and Brown (1994), and Wen and Qiang (2002a,b) are essentially additive, whereas that of Constantinou and Gani (1994) is logarithmic, and the method of Marrero-Morejon and Pardillo-Fontdevila (1999) has a dependency on molecular mass. In the equations of Cordes and Rarey (2002) and Nannoolal et al. (2004) the sum of group contributions is divided by a term in the number of atoms in the molecule. The ACD method appears to differ from the others in that predictions use a combination of internal database of boiling points and a structure/fragmentation algorithm.

Also to section 3.1, regarding the very high boiling points predicted by the Joback and Reid method: For many of the molecules this is due to the method's known limitations with respect to molecular size, noted above.

The second paragraph of the summary has been modified to: The boiling point methods that yield predictions that agree most closely are those of Nannoolal et al. (2004) which is a refinement of the approach of Cordes and Rarey (2002), the ACD method, and that of Stein and Brown (1994). Cordes and Rarey (2002) have shown that their method, also used by Nannoolal et al. (2004), is significantly more accurate than those of Stein and Brown (1994) and Constantinou and Gani (1994) for a test set of 1863

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components. The ACD approach tends to yield higher values of Tb for the oxygenated SOA- forming surrogate compounds than the other methods, but not for the primary surrogate compounds P1-8. Of the methods examined in this study those of Nannoolal et al. (2004) and ACD are likely to be most accurate. However, Cordes and Rarey (2002) caution that results obtained with all group contribution methods for molecules with large numbers of functional groups should be used only with great care, as they are subject to a large uncertainty.

It is also true that the UNIFAC-based vapour pressure method yields enthalpies of vaporisation that are larger in magnitude, and more negative, than the Myrdal and Yalkowsky method predicts. However, these enthalpies are not consistent with experimentally based values for other hydrocarbons of similar molar mass, which suggests they are not accurate and that the predicted vapour pressures at 25 oC are too low. We have added a sentence to the Summary to make this clear.

3. Model/measurement comparisons. The referee is right to say that comparisons with chamber SOA data would be insightful, as the ultimate aim is to accurately predict SOA partitioning.

In the present model, as the referee notes, some optimisation of the surrogate vapour pressures has been carried out to improve agreement with chamber SOA data. A detailed comparison of model predictions with chamber data would certainly be valuable but is, in our opinion, a subject for another study. A key question in such a comparison would be the degree to which the explicit chemical mechanism represents the reactions leading to SOA formation. In this study we focus only on the prediction of vapour pressures.

The Odum/Pankow empirical method of representing SOA yields, and the explicit chemistry used in the UCD-CACM model, are two very different approaches to understanding and predicting aerosol yields. Over time, as our knowledge improves, it is likely that the two methods will converge. Our results in Part I suggest that a combina-

tion of the two approaches, and comparison of their behaviour, may be relatively simple for the gas/aerosol equilibrium elements of the problem. The details of the chemical reactions leading to SOA formation, and the identification of the SOA compounds, seems to us the more difficult problem and is outside the scope of both parts I and II of our work.

Specific points:

Page 6 "In the UCD-CACM model P8 represents a range of mostly involatile.."

Response: the manuscript was not clear, as the referee has commented. We have modified it to: "...P8 represents a range of involatile hydrocarbon material found in aerosols, the composition of which is not well understood."

Page 8 "po (highest)/po(lowest) the paper uses the word factor..."

Response: we agree with the referee that "ratio" is a better term for this, and have used it in both the text and Table 8 of our revised ms as the referee suggests. We have not altered the use of () and [] for the different types of ratio.

Page 8 "The ranges are largest for the primary hydrocarbons"...

Response: we have looked at this again. It is certainly true that the uncertainties associated with the ACD prediction method are lower for the P surrogates than the SOA (A and B) surrogates, because P1-8 are largely hydrocarbon in nature. (We say "largely" here, because two of them are diacids.) However, if the UNIFAC-based predictions are excluded, on the grounds that the method yields predictions generally very much lower than the others, and because it can only be applied to one of B1-5, then the ranges are broadly comparable across the classes of compounds. We have amended the manuscript to reflect this.

Although this isn't what would be generally expected - properties of hydrocarbons are easier to predict than those of multifunctional compounds - the sample here is small, and it should be remembered that two of P1-8 are diacids and not pure hydrocarbons.

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Table 8: this shows that the ranges of individual organic compounds that the surrogates A1-5 and B1-5 represent are very large (orders of magnitude), and that in a few cases the vapour pressure of the surrogate is outside this range. The reviewer suggests that this is not important because "...in the end each surrogate is supposed to represent the aggregate behaviour of some substantial component of the aerosol." The author also states that comparisons of chamber SOA data are what is needed to determine how well the surrogates represent aggregate partitioning into the aerosol.

Response: we agree that comparisons with chamber SOA data are good tests of aggregate predicted partitioning. However, this is not the point we intend to make here. In any model based upon an explicit chemical mechanism the aggregate partitioning of semi-volatile compounds is simply the sum of that of the individual compounds. Surrogates are used to represent groups of individual compounds and, if they are to do so without error in gas/aerosol partitioning calculations, should have essentially the same physical properties. Table 8 shows that this is not true, and that the properties of the individual compounds grouped together (to be represented by each surrogate) also diverge widely. This makes it possible that an air quality simulation with gas/aerosol partitioning of all model compounds calculated directly - which is what the surrogate approach is intended to emulate - could yield very different results from the same model using surrogates.

The comparisons that we show in Table 8 emphasise that surrogate compounds, which are used in order to limit the use of computational resources in the air quality models, must be employed very carefully if they are not to introduce errors and biases of their own.

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