**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model – Part I: Treatment of inorganic electrolytes and organic compounds in the condensed phase" *by* S. L. Clegg et al.

S. L. Clegg et al.

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We are glad that both referees have positive opinions of the ms. The comments of the two referees are addressed below. The second referee made many very helpful individual points, and we have included each one in the text below followed by our response.

Anonymous Referee #1

We have added the missing reference (Clegg, 2004) noted by the referee. We have

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also listed the missing UNIFAC interaction parameters in the Appendix, as suggested by the referee. It is not really possible to quantify the effects of these unknowns, without significant further study. We have also noted in the Appendix that an alternative 'Dortmund' UNIFAC parameter set exists which is optimised for liquid/liquid equilibrium calculations and might yield better results for this aspect of the model than the standard parameter set.

The referee comments on the length of the ms, and the fact that we dealt with size segregation of the aerosols (across 15 bins) in the UCD-CACM model. It was necessary to deal with this because each bin equilibrates individually with the surrounding gas phase, and the approach to equilibrium is different for each size bin. AIM is a purely equilibrium model, and to have ignored the disequilibrium in the UCD-CACM model, or to have lumped together the results of different bins, would have meant that we were not comparing like with like. The referee comments that there is little size effect, but this isn't true of NH3 partitioning (Figures 10 and 13) or of the equilibrium partial pressures of a number of the organic compounds (Figure 17).

Anonymous Referee #2

This is a good paper. But I have a number of suggestions that I think will make the paper more easily comprehended.

Paragraph 1, Introduction: you state that inorganic models are well established. However, this gives the impression that differences among such models are small, while you show here that they are not. I would add a sentence towards the end of the paragraph which points this out. (See also recent comparison of results from different treatments of Feng and Penner, 2007, J.G.R.).

Response: 'well established' means that the models have been developed and in use over a long period - about 30 years. We also state that the activity coefficient models are of varying degrees of complexity and accuracy, so we don't neglect the differences even in the Introduction. There *are* large differences between the models but, as

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shown in the ms (and as the referee understands) these differences do not necessarily make a large impact in atmospheric calculations, in terms of aerosol mass for example.

Page 3, 1st para. 1: you state that you focus on key elements of the activity coefficient treatment in this paper. But you actually calculate uncertainties due to activity coefficients, water content of aerosols associated with the choice of compounds treated, dissociation treatment, and vapour pressure uncertainties. And you partially evaluate uncertainties due to surrogate treatment of the aerosol compounds. You should state where you are going with this paper. Is the idea to evaluate all of these uncertainties and their effects in the model? Or are you going to state which uncertainties are important to reduce? And evaluate the relative importance of each?

Response: We have clarified our intent, and altered the text to read:

This work focuses on the impact on calculated gas/aerosol partitioning of uncertainties in some of the key elements of the thermodynamic treatment of both inorganic and organic aerosol compounds, including: activity coefficients, aerosol water content, solids formation, dissociation equilibria, and the treatment of groups of organic compounds using a reduced number of surrogate species. A current state-of-the-science air quality model (Kleeman et al., 1997; Kleeman and Cass, 1998; Kleeman et al., 1999) is used in the analysis in order to understand the practical effects of errors and uncertainties in atmospheric simulations.

Page 3, para. 2: State explicitly that the UCD-CACM model follows the scheme in Fig 1, with a few simplifications, explained below.

Response: we have amended the text in 2 paragraphs of the introduction to do this.

Page 4, 1st line para. 3: State that the 2D version is (time, height) or whatever the 2D refers to.

Response: The model is 3D Lagrangian, and we have corrected the text on this point.

6th line: Are the gas/aerosol partitioning and total amounts of each species at each

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time Given as input to AIM?

Response: yes, total amounts at each time interval. We have amended the text.

Line 12: here you admit that the inorganic components of the models are very different. Need to clarify statement referred to above, so reader understands.

Response: we have revised this paragraph as requested (new text below):

...In this work we refer to this extended model simply as AIM. This model was developed as a benchmark code of high accuracy, and is therefore suitable as a reference against which the simplified (but much faster) thermodynamic schemes used in atmospheric models such as the UCD-CACM code can be compared. We examine the results of the two models in some detail, for both inorganic and organic components, in order to fully understand the differences between them and their effects in air quality simulations. We note that gas/aerosol partitioning in the UCD-CACM model is calculated dynamically, whereas AIM determines the equilibrium state of an aerosol system. The UCD-CACM model and AIM results are therefore compared for situations where the UCD-CACM result is close to equilibrium, or with equilibrium properties such as activity coefficients and partial pressures calculated directly using the UCD-CACM model. This ensures consistency....

Page 5, 1st full para: Do you mean that particles from different sources are not internally mixed, when you state that they are tracked separately?

Response: yes, we have made this clear in the text.

Page 6, 1st para: when you say a "single bulk aerosol phase" is assumed do you mean that all sizes are lumped together and an internal mixture assumed?

Response: yes, we have made this clear in the text.

2nd para: "Models may not predict the same amounts of inorganic solids" This differs

from your introduction where you state the inorganic treatments are well-established (and hence well known).

Response: 'well established' doesn't mean they all agree. We believe this is adequately clear and have not altered the ms.

Page 7, last para: Do the differences in calculation of Gibbs free energy differ significantly? You should state whether this is an issue to be explored or not.

Response: Gibbs energy minimisation is only a mathematical technique for calculating the equilibrium state of a system. The calculation could be done using equilibrium constants to achieve an identical result. We haven't made any changes.

Page 8: 1st full para: the UCD CACM model exchanges water dynamically. What about HNO3 and NH4? Are these treated dynamically? How about any of the other species? Also clarify here again, that the differences in equilibrium vs dynamic behavior are not analyzed, because the focus is on a detailed comparison of a time period which is in equilibrium in the UCD CACM model.

Response: the UCD-CACM model treats all species dynamically. We have made this clear in the ms.

2nd full para. Near end: what "additional terms" are needed? What do you mean by the "extra" liquid phase? The sub-cooled phase associated with hydrophobic components?

Response: the paper gives the equation for a system containing a single liquid (aqueous) phase. The 'extra terms' are for the hydrophobic phase which has been added to the expanded model. We have clarified this.

Page 8 last paragraph: Later on I was confused because in several places you state that the activity coefficients in both codes are calculated using the UNIFAC method. You should go through the paper, and when you state this, also state that the UDC-CACM model bases its calculations on the properties of single electrolytes, not aqueous ions.

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Response: UNIFAC is used only of the organic components of the aerosol. We have made this clear in section 2.2 in each reference to UNIFAC.

End of page 9: at this point in my reading, I decided that the paper would benefit from a table describing each component calculation for each model, so it was clear what was different in each model. There are so many different components and different procedures, that it is hard to know what is important to retain.

Response: we have added a table, as the referee requests, to Appendix B.

Page 10: middle of page: here you mention that UNIFAC is used in both models for activity coefficients. Should also state that UCD CACM does not calculate these for ions.

Response: the text has been amended to clarify this.

Page 11, 3rd paragraph: does the AIM model somehow use UNIFAC to calculate activity coefficients independent of the ions and undissociated organics?

Response: yes, this is a consequence of the overall scheme used to combine the results of the ion activity calculations, and the organic activity calculations, in a self consistent way. It is a necessary simplifying assumption.

Page 12: 1st para in Section 2.4: Does paper II arrive at a "best" method for calculating vapour pressures?

Response: we were able to make some recommendations, but the uncertainties - even using the best methods - remain very large. We have not altered this paragraph.

Page 13: 1st para: "ignore interactions . . . between the TWO inorganic and organic (uncharged) species" which two are you talking about here??

Response: the word 'two' should have been deleted.

1st para, section 3.1: It seems to me that the addition of NH3 starts at 13:00, not 18:00.

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There is a minimum at 18:00, and a max at 17:00 and 19:00. End of para: How big is P8 compared to other compounds?

Response: the NH3 addition peaks at 18:00, but begins earlier. We have clarified this.

Page 14: 1st line: what sizes are bins 6 – 15? Maybe include table?

Response: 0.1 to 10 um. We have clarified this.

3rd para: RH is above 60% at times other than midnight to 8 or 9 am. i.e, at 9 am and at 10am. Also, you state that AIM predicts less water between about 11 and 1 pm, do you mean at 12p here? (the RH is 60% at 1:00p).

Response: we mean 9 am to 1 pm (now corrected). Our other statements of the time are correct.

last para: which model is displayed in Fig 9?

Response: UCD-CACM model as given in the caption.

Page 15, 1st line: is Fig 9 the same for the other model? 2nd para: Is Figure 10 at 8am?

Response: yes, we have clarified this.

Page 16, last line, 1st full para: delete sentence. 1st sentence next para: I would start: 'in contrast to the simulations for AIM shown in Figs 7, 8 (and 9??), in these AIM calculations . . . '

Response: we have not made this change.

Last para: here you say that the 2 activity coefficient models result in different predictions of pHNO3 and pNH3 – state again that this is because UCD CACM does not allow dissociation in its calculations.

Response: done.

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Page 17, 1st full para: The amounts are the same after 9am in the normal AIM model.

Response: corrected.

Page 18, 1stfull para: “at low RH most of A1-5 would be in the gas phase” But Fig 14b shows that $> 80\%$ of A5 and $> 95\%$ of A1-4 are aqueous!? So certainly not “most” Last sentence: need to state again: UCD CACM does not explicitly include calculation of the organic anion activity coefficient.

Response: this discussion is about the aqueous phase / hydrophobic phase partitioning of the total particulate amounts of the compounds, not partitioning between the gas and aerosol phases. We have modified the text in several places to make this clear.

Page 20, 1st para: here you say that the treatment of organic dissociation does not matter – but it was earlier said to be the major effect (page 18, bottom).

Response: the treatment of dissociation of the organic species has very little influence on the total gas/aerosol partitioning. This is not true of the inorganic species though. The ms discussion of this is clear.

1st para, section 3.2.1: why use the model of Nannoolal? Was this determined to be “best “ in paper II? Or later in para. you state that for P2 the fraction in aerosol phase is not reasonable. Is this because Nannoolal method is poor?

Response: yes, it's one of the better models. P2 (succinic acid) represents a range of organic diacids, of varying carbon number, but itself has only 4 C atoms making it fairly volatile. Thus it does not seem to be a good representative of the whole group. The discussion is clear on these points.

Page 21: Since the model result for P2 is not reasonable, are you stating here that the Robinson et al. work is not reasonable?

Response: no, we agree with Robinson. We have modified the text to read:

These results - that the primary organic compounds will partition between the gas and

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aerosol phases - are at least qualitatively consistent with the work of Robinson et al. (2007), who argue that most primary organic particulate emissions are semi-volatile.

Page 22: last para: "based upon estimates such as those tabulated here. Here or paper II?

Response: Paper II. We have corrected the text.

Page 23: "SOA concentrations roughly double" I can't see this in the figure, which uses different scales on the plots. You also need to give the totals for the domain. 'species UR7 and UR17'. What are these?

Response: we have modified this somewhat, to: 'As shown in Fig. 21b, predicted SOA concentrations come close to doubling in some areas when the lower vapor pressure estimates are used.' We have omitted the reference to UR 7 and UR17 which is unnecessary.

Page 24, last para: The solution identified here only addresses the differences shown in Fig 2. Is this solution really needed? How do you know?

Response: we are only suggesting possible ways forward in this discussion, methods that sould lead to a 'surrogate-based' model yielding results that would more closely approach those of a model in which each compound were treated individually. We have not made any changes.

Page 26: the assigned lower limit for H2O is responsible for large differences, but here you state that this retention is seen in the atmosphere. So is the CACM approach better? "it would be preferable to directly model metastable aqueous aerosols" – you haven't shown this. What is your reasoning?

Our point here is that aerosols, both inorganic and organic, tend to retain water at low RH and to exist in a metastable state (supersaturated wrt the solutes). The UCD-CACM model retains small amounts of aerosol water for computational reasons only and is actually modelling an aerosol in which the equilibrium solids form (ie. *not*

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metastable). It would be better if the model did not have this limitation, but allowed aerosols to dry out completely in cases where the metastable sate was not assumed.

Page 27: ..than from improved predictive techniques for vapour pressure or activity co-efficients.. But you state above that the method used in CACM (Mydal and Yalkowsky) is poor. Should say that paper II shows that "uncertainties in the vapor pressure are a factor of 2, and that this is larger than activity coefficient uncertainties based on calculating ions or undissociated molecules only" – paper 2 makes no assessment of which method for vapor pressure is best?

Response: yes, the vapour pressure predictive technique are not good but it seems to us that they are unlikely to greatly improve in the near future, due to the difficulties of modelling the behaviour of polar molecules. It seems to us that uncertainties in the predicted vapour pressures are often a factor of 5 or greater, and that uncertainties in the activity coefficients could approach this value. The influence of these uncertainties depends on whether the vapour pressure of the compound is such that it would be expected to partition fairly evenly between gas and aerosol phases, or whether it would be expected to reside entirely in one phase or the other. Paper II does make some recommendations about predictive methods, but even the better ones, like all such models, do not yield good results for polar molecules.

We have not changed the Discussion.

Page 29: table 4: What does the # column in Table 4 refer to?

Response: # is the number of occurrences of the group in each molecule. Corrected.

Table 1 caption: state that these are in the aqueous and hydrophobic phases and at 8:00am.

Response: corrected.

Figure 4 caption: add that this is level 1 of UCD results.

Response: done.

Fig. 5 caption: add that this is UCD CACM model level 1 results.

Response: done.

Figure 9: which model is this?

Response: the UCD-CACM model, as stated in the caption.

Fig 10: Explain that AIM and UCD-CACM differ if not = 1. Is this at 8:00am?

Response: yes, we have added this to the caption.

Fig 21: The scales in the 2 figures need to be the same.

Response: corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10971, 2007.

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