**Atmospheric
Chemistry
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Discussions**

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.**

Anonymous Referee #2

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This paper compares several different theoretical approaches for predicting vapor pressures of organic species that are used as surrogate species in the UCD-CACM model. Surrogates include polar/multifunctional species and more hydrocarbon primary emissions. The paper shows that the predicted vapor pressure can vary by an order of magnitude or more depending on which approach is used. The paper illustrates how this uncertainty affects model predictions of gas-particle partitioning.

This is an important topic and the paper is worthy of publication. The strength of the paper is that it compares predictions of multiple different approaches for predicting va-

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por pressures. Since these techniques have been developed in other fields, this paper helps educate the atmospheric chemistry community on these techniques. There are a few areas where the paper could be improved:

1. The paper was hard to follow, mainly because of the heavy reliance on the UCD-CACM naming scheme A1, P1, etc. Essentially to make sense of the paper one needs to look up the Griffin et al. 2003 reference. The paper would be greatly improved by including a table and/or figure which actually defines each of the surrogate species. A few of the species are named at various places in the text, but doing this for all the species in one central location would help understand the implications of the results in a context that is broader than the UCD-CACM model.

2. The paper has a review-like quality to it, comparing predictions of different, previously published techniques; therefore, it would benefit from more concrete recommendations for which of these approaches seems best and for future research. For example, the paper could be improved if it tried to be more specific about which types of compounds the models predictions diverge.

3. Model measurement comparisons. The paper compared the model predictions to vapor pressure data for a few compounds. The limited model measurement comparison is to be expected, given the limited availability of data. These comparisons are helpful. However, ultimately these vapor pressures are used to predict gas particle partitioning. Therefore, comparisons with actual partitioning data (e.g. chamber SOA yield curves) would be insightful. The challenge of course is that the aerosol is made up of 1000s of compounds most of which we cannot even identify, never mind calculate vapor pressures for. (Note that the bit of text on page 8. "The use of surrogate compounds allows gas-aerosol partitioning..."; I found misleading. The surrogate compounds may be based on a small number of identified compounds (the paragraph says 38) but, in reality, the aerosol contains a much larger number of semivolatile compounds.) My understanding is that UCD-CACM uses the small number of surrogate compounds to predict the overall gas-particle partitioning of this entire mixture (1000s

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of compounds). Instead of comparing the vapor pressure of the surrogate to a small number of compounds, a much more informative comparison would be if the calculated vapor pressures of the surrogate compounds combined with the yields can accurately reproduce the SOA partitioning measured in smog chambers. Comparisons with actual partitioning seem like the critical test, since that ultimately is the whole reason for this exercise. This gets into how the surrogate compounds are used by the model; ie what they represent. At a minimum I think that this should be spelled out more clearly.

An interesting counterpoint to this approach is the empirical approach of Odum et al of fitting chamber data that forms the basis for many air quality models (of course developed by some of the authors here). The paper mentions in the past (Griffin 2005?, page 9) vapor pressures of the surrogate compounds have been modified to get better agreement with chamber data. This is tending towards the Odum approach. It might be worth clarifying these two approaches more.

Some other more specific comments

Page 6 "In the UCD-CACM model P8 represents a range of mostly involatile ...." I thought that the model assumes that all of the primary emissions are nonvolatile? Or at least historically this has been the case (as stated in the intro). I see in paper 1 you have investigating partitioning of primary emissions so you have not begun to investigate that assumption. This should be clarified.

Page 8. p(highest)/p(lowest) the paper uses the word "factor"; to describe what is in the bracket. The word "ratio" might be clearer here? Also in Table 8. I found this bit pretty confusing and had to read the text several times to figure out what the numbers in the bracket were versus the number not in the bracket.

Page 8 "The ranges are largest for the primary hydrocarobons" I found this a little surprising since I thought the big challenge was multifuncational compounds. Therefore, I thought there would be more disagreement for the SOA species. For example, on page 6 the paper says "the uncertainties associated with the ACD predictive method

are significantly greater for these compounds than for the primary surrogates." Page 11 also had a statement that seemed to imply more uncertainty for SOA species "these uncertainties seem likely to remain even as SOA composition becomes known ..."

Comparisons in Table 8 do not seem to make much sense. The fact that the model compounds used to develop surrogates span a wide range does not seem a big issue because in the end each surrogate is supposed to represent the aggregate behavior of some substantial component of the aerosol. Comparisons with actual chamber SOA data would get at how well the surrogates represent the aggregate partitioning behavior (of course divergences could be due to yields or something else beyond vapor pressures).

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11049, 2007.

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