**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "The sensitivity of secondary organic aerosol component partitioning to the predictions of component properties – Part 1: A systematic evaluation of some available estimation techniques" *by* G. McFiggans et al.

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We'd like to thank the referee for their useful comments and fully understand the hesitancy to recommend publication given the content of the review. We believe that the recommendations for major changes is entirely based on misunderstanding of the intentions of the paper and the methodology employed. It appears obvious that our explanation of both is inadequate and this has been fully revised in the updated manuscript.

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Here we attempt to clarify both intent and methodology such that an evaluation of suitability for publication can be assessed.

The first thing to note is that we are absolutely **not** claiming that the components in the mixtures we are studying will be found in the atmosphere. The sole intent of the publication is to explore a number of property estimation techniques that have been used in atmospheric applications in the context of absorptive partitioning of semi-volatile secondary organic aerosol components. In order to make such the evaluation more useful in an atmospheric context, the methodology we employ aims to a systematically explore the sensitivity under conditions that may be broadly expected in the atmosphere and for components that have broadly the functionality and property spectrum that might be found in the atmosphere. This is because most, if not all, of the property estimation techniques have been developed for, and extensively applied to, conditions of the chemical process industries and it is not clear that technique evaluation under such very different conditions would be valid. We merely aim to provide more relevant sensitivity analyses than have hitherto been conducted.

The second thing to note is that this is part 1 of a three part investigation. The second part relates to sensitivity of the properties (hygroscopicity, density etc.) of the predicted condensed mixtures to the estimation techniques, the third part presenting the sensitivity of the predicted aerosol when the technique is applied to components from a near-explicit atmospheric VOC-degradation model. In part 1, we have chosen to evaluate the estimation techniques using a semi-random generation of mixture components so as not to be vulnerable to the accusation that we are reliant on compounds that may result from a systematic bias in the selected compounds. This could result from i) specific VOC emission profiles, ii) incomplete or inadequate mechanistic knowledge or any number of other potential sources of variability in the chosen specific model. We feel that the semi-random approach presents a more

generally applicable and convincing sensitivity study of the estimation techniques. The third part of the investigation which evaluates sensitivity using the near-explicit mechanism bears out the general findings from this part 1 paper. It extends the findings beyond those in this paper to consider the sensitivity of contributions of classes of compounds from the near-explicit mechanism to SOA and to sensitivity across a range of emission scenarios. There are a number of technical considerations in the mechanism evaluation, related to parsing of molecular structures for use of the estimation techniques, that required substantial description and justifies the separation of the two studies.

Again, it must be stressed that the focus of the current, part 1, paper is not to investigate the partitioning of compounds that are found in the atmosphere. It is to assess the sensitivity of diagnostics used to describe atmospheric aerosol to estimation techniques that have been used in atmospheric modelling under generic conditions closer to those found in the atmosphere than the conditions used to derive and develop (and previously used to evaluate) the techniques. This is clearly stated on page 15389 of (and throughout) the original manuscript "It is important to note that it is not the intention to present a sensitivity of absorptive partitioning calculations of the exact mixtures of compounds found in the atmosphere; only to examine the behaviour of the model under similar conditions to those observed in the atmosphere".

Here we will address the detailed comments that the referee has made:

Major comments:

1. *Section 2.2. Please split the description of the vapour pressure models into further paragraphs so that the boiling point estimation methods are described in the ïňĄrst,*

and the saturation vapour pressure models in the second. Also, please summarize the applied combinations in a separate table or in the end of the section.

Section 2.2 has been rewritten, separating the description of the vapour pressure models into three paragraphs. The first describes the boiling point predictive techniques, the second describes the vapour pressure predictive techniques and the third describes the combination of techniques used in the paper. A referenced table of the techniques has been included.

2. *Section 2.3, second paragraph. Please justify the two applied restrictions. In particular, why the total concentration of the compounds decreases linearly with the carbon number? Secondly, the requirement that the total condensed mass is ïňĄxed under the base case assumptions is somewhat counterintuitive – to me, keeping the total mass in the system (gas & particle phases) fixed would be more intuitive. Also in many applications, the people would be interested in knowing how large errors to the SOA mass (rather than to the total concentration) are caused by the choice of the saturation vapour pressure estimation methods.*

Section 2.3 has been completely rewritten.

The first of the two applied restrictions (that the total abundance of the compounds in each simulation is constrained such that the molar mixing ratio (r) of a compound decreases with a linear reduction in base 10 logarithmic space with carbon number) was unfortunately expressed incorrectly in the paper by equation 4. The sentence stating the equation should read "...such that the mixing ratio r in $\mathrm{nmol/mol}$ of a compound of carbon number n is given by: $r = \frac{1776}{(1776/0.001)^{\frac{n-1}{11}}}$. This has been corrected in the revised version. Nevertheless, the stated text is correct in that the total concentrations

of compounds was calculated by assuming a logarithmic concentration reduction for each randomly selected individual component according to its carbon number. This is constrained at the low carbon number by the methane mixing ratio of 1776 ppbv. The logarithmic reduction is to ensure a falloff in VOC concentration to roughly part per trillion levels for larger carbon number compounds, broadly in line with what is observed in the atmosphere. No exact rigorous relationship was sought. As indicated throughout - the idea was not to exactly replicate the atmospheric composition but to assess method sensitivity in broadly the correct atmospheric regime.

The second restriction (that "the total "target" condensed organic mass loading is fixed for all partitioning calculations using the base choice of ideality with the N-N vapour pressure prediction to 10 μgm^{-3}. The total mixing ratio is therefore adjusted iteratively to achieve this condensed mass whilst maintaining the gradient of the molar mixing ratio distribution line as described in Eq. (4)") has been chosen to ensure that the sensitivities are not influenced by the availability of condensed mass. The condensed mass determines the relative contributions to the mass by components of different volatilities. A higher mass of material would lead to a higher relative contribution from more volatile material and conversely a lower mass of material would lead to a higher relative contribution from less volatile material. It is considerably easier to assess the sensitivity under conditions of constant total concentration as the referee has suggested, but this would change the predicted sensitivity with some attributable to the mass produced in each simulation. The methodology suggested by the referee could easily have been adopted, but it is not as completely intuitive as the referee suggests for the reason outlined above. In the third paper in the investigation, a further sensitivity to the emissions used in the near explicit VOC degradation model has been conducted. This provides the variability in the predicted SOA mass (and the other metrics) that the referee asks for. Since the current paper does not aim to reproduce exact atmospheric conditions, this sensitivity is better provided in the part 3 paper.

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3. *Section 2.3, third paragraph. Please describe explicitly the probability distributions which give the probability that a functional group is attached to a carbon skeleton. Judging from Figure 1, the distributions are Gaussian. This choice should be justified because given the absence of a comprehensive picture on the composition of atmospheric SOA, an intuitive choice would be to use uniform distributions. Also, is it guaranteed that does the method lead to generation of compounds that 1) exist, and 2) if so, are they present in the atmosphere at all? Please discuss.*

The explicit probability distributions used to attribute the functionality are indeed Gaussian. However, these are fresh randomly generated Gaussian distributions for each initialisation. Across the 1000 initialisations, this effectively provides uniform probabilities of occurrence of functional groups across all initialisations. A figure illustrating this has been included in the manuscript as a second panel to Figure 1. The sharper Gaussian distribution is chosen for each initialisation to try to ensure that as broad a range of functionality is explored across all initialisations. In reality, it would probably not be very different if uniform probability distributions as suggested by the referee were used for each initialisation. Again, it is not the intention that atmospherically-present compounds (or, indeed, real compounds) are generated, just that the sensitivity to the estimation techniques is conducted on a "bucket" of functional groups that is generated for each initialisation and apportioned to a distribution of carbon backbones that reduces in concentration with increasing carbon number, as is broadly observed in the atmosphere.

4. (denoted 3. in the review) *Section 2.3., third paragraph. Please describe more in detail the applied method. Also, the last sentence ("To summarise. . .") should be clarified. Finally, the authors could give some examples of the individual compounds that result from the generation procedure to illustrate possible outcomes.*

As stated, section 2.3 has been completely rewritten in line with our response to referee 1. An example initialisation has been selected and the compounds generated in the two and 10 compound representations of the initialisation have been tabulated. In addition, a further figure has been provided showing how the concentration of compounds for this initialisation have been changed in response to the iteration to generate 10 μgm^{-3}.

5. (denoted 4. in the review) *Section 2.4, page 15390, lines 23-30. The authors con-clude that ". . .the selected conditions adequately serve to illustrate the sensitivities". Again, the authors fail to justify that the generated mixtures reflect the composition of the atmosphere. I agree with the authors that it is not possible to address the issue comprehensively, but I'd suggest that the authors generate mixtures (with a smaller degree of randomization) that are based on the available information on the atmospheric, semi-volatile organics and investigate whether the main conclusions of the study still hold.*

The above comments have clarified the intent and scope of the paper sufficiently to rebut this comment. To reiterate, as clearly stated on page 15389 of (and throughout) the original manuscript "It is important to note that it is not the intention to present a sensitivity of absorptive partitioning calculations of the exact mixtures of compounds found in the atmosphere; only to examine the behaviour of the model under similar conditions to those observed in the atmosphere". In addition, part 3 of the investigation presents a systematic and comprehensive investigation of the sensitivities to the estimation techniques to compounds generated from 24 sets of conditions for around 2700 compounds generated under 206 emission scenarios using the Master Chemical Mechanism. These simulations serve to represent mixtures based on the best available atmospheric VOC degradation information generating semi-volatile organics. These investigations clearly demonstrate that the main conclusions of the study still

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hold and the current paper demonstrates the generality of the sensitivities.

Minor comments:

1. *Introduction. Please describe and justify briefly the metrics used in the study.*

A more complete and fully referenced description and justification of the metrics has been provided.

2. *Introduction, sixth paragraph, page 15384. The usage of the terms such as "uptake" and "condensation" do not reflect the fact that the atmospheric gas / particle partitioning is a reversible process. Please change the terminology accordingly.*

We agree with the referee that the terminology is a little sloppy and have amended it accordingly.

3. *Section 2.3, third paragraph. Please list the considered functional groups in a separate table. Are they all found in atmospheric organic compounds?*

A table of the functional groups along with a discussion of their likely atmospheric presence has been presented.

4. *Section 2.5. Please provide references and a brief discussion that motivates the use of the last three metrics.*

This has been provided.

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5. *Section 3.2. Please explain the contents of Figure 6 in more detail. For example, what do the blue and green boxes and symbols signify?*

This has been clarified in the figure caption and section 3.2.

6. *Page 15394, line 25. I do not see how the discussed feature is "...somewhat predictable...", please elucidate.*

The reason for the predictability of the differences in the volatility distributions for the same initialisation but using different means of predicting the vapour pressure (i.e. volatility) is that the same components will be present in each case, but the volatility predicted will differ using each method. Unless any differences between the vapour pressure estimation techniques were completely systematic and independent of functionality, then the distribution of predicted components will be different. This has been explained in the text.

7. *Page 15398, line 9. The meaning of the expression '...atmospherically relevant functionality Tong et al. (2008)." is unclear.*

We apologise. This was a typographical error and the Tong et al. reference should have been parenthesised. This has been corrected.

8. *Figures. Please describe the figures in detail in the captions rather than in the text because with the current form, it is hard to extract key findings from the text.*

Both the text and captions have been clarified in the amended manuscript.

9. *Figure 1. Why the probability distributions are (at least shown as) continuous? Shouldn't they be discreet with respect to the carbon number?*

The pdf for each functional group has been calculated as a real number, with the probability for the integer values extracted for each carbon number. The figure is really a cartoon schematic of the approach, but has now been replaced with discrete probabilities as suggested.

10. *Figure 4. What calculations does the line "Act" represent?*

This has been replaced with "non-ideality" in the legend and clarified in the text and caption.

Technical comments.

1. *Introduction, last paragraph. Please state the publishing status and (preliminary) titles of the companion manuscripts.*

These have been provided.

2. *Figures 3 and 4. Title of the y-axis is missing, please provide.*

These have been inserted.

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3. Figure 5. The scale of the y-axis is missing, please p(rovide).

This has been inserted.

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