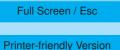**Atmospheric
Chemistry
and Physics
Discussions**

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.

G. McFiggans et al.

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Firstly we'd like to thank the referee for encouraging our clarification of the methodology in the manuscript. We apologise for any lack of clarity in the methodology and aim to shed some light on what we have done. We agree that any paper should describe the methodology sufficiently well that a reader could repeat the investigation should they so wish. To this end we attempt to describe the methodology below, replacing that

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described in section 2.3 of the original manuscript. We'd be most grateful if the referee could let us know whether this is a sufficient description of the recipe or whether there is still further clarification required before the referee can make an assessment of the value of our work. We will endeavour to address the other points in the review (most especially to make it less tedious to read) once we know that the paper can be understood.

To replace Section 2.3:

In order to investigate the sensitivity of the model predictions to available estimation methods across as broad a composition space as possible, a methodology for the generation of the test initialisations of organic molecules of varying functionality has been constructed.
A fully-randomised initialisation of the simulations has not been used. Instead, restrictions have been imposed during the construction of compound functionality and abundance to provide a large but finite number of simulations and a statistically significant distribution of results within a range of conditions representative of, or similar to, atmospheric conditions. This is to ensure that the sensitivity to the estimation methods is assessed on mixtures comprising components functionalised to a similar degree to those expected in the atmosphere.
In the current study only straight-chain aliphatic compounds from methane to C_{12} compounds are considered in the current study and therefore the organic compound carbon number solely determines the chain-length; an evaluation of the sensitivity to the predictive techniques for aromatic and cyclic compounds is ongoing but is considerably more complex. To generate any single compound and prescribe its abundance, the following procedure was used:

1) The carbon chain length was selected using a random number generator con-

strained between 2 and 12. The twister algorithm within the Matlab software package is used. The sequence of numbers produced by this function, which has a period of $(2^{19937} - 1)/2$ is determined by the internal state of the generator which is set based on the CPU clock.

2) Functionality was then assigned to the carbon backbone. 34 functional groups represented within the UNIFAC activity coefficient model were used, including the 9 hydrocarbon subgroups (Hansen et al 1991).

3) Each functional group has a probability of occurrence on a carbon backbone, defined by a set of probability density functions randomly generated for each initialisation. For example, for a chain length of 5, the functional groups COOH, OH, CH2CO might have been assigned a probability of occurrence of 0.134, 0.245, 0.001. For a chain length of 3, the same groups may be assigned a different probability of occurrence of 0.346, 0.102, 0.091. Weighted preference was given to oxygenated functional groups by multiplying the probability of occurrence of each oxygenated group by 100. This was used to increase the likelihood that such groups would populate a given carbon chain, whilst still allowing other functional groups to occur. Figure 1 illustrates a representative distribution for only 6 functional groups for clarity. For a given initialisation for simulations of mixtures comprising 2, 10, 100, 1000 and 10000 compounds, each compound is generated using the same set of probability density functions.

4) The starting point for the total abundance of the generated compound is constrained such that the molar mixing ratio (r) of a compound decreases linearly in logarithmic space with increasing carbon number. The gradient is defined by using a methane mixing ratio of 1776 nmol mol^{-1} (ppb) and a prescribed mixing ratio for all C$_{12}$ compounds of around 1 pmol mol^{-1} (ppt) such that a mixing ratio in nmol mol^{-1} of a compound of carbon number n is given by: $r = 1776\text{-}161.454440909 \times (n\text{-}1)$

This is repeated 2, 10, 100, 1000 and 10000 times for each initialisation.

5) The total "target" condensed organic mass loading is fixed at 10 µgm^{-3} for all partitioning calculations, at all ambient conditions and for all levels of mixture simplicity using the base choice of ideality with the N-N vapour pressure prediction. In order to achieve this, the total abundance of components in each mixture must be varied for each initialisation. The total abundance of the generated compounds described in step 4) above is adjusted iteratively to achieve this condensed mass whilst maintaining the gradient of the molar mixing ratio distribution line (i.e. such that there are fewer larger molecules in each simulation as would be expected in the atmosphere).

To recap, in each base case partitioning simulation, be it for 2, 10, 100, 1000 or 10000 compounds, the base case (N-N, ideality) predicted condensed mass is always 10 µgm^{-3}. For any given initialisation, these molecular abundances are held constant such that, as the vapour pressure method, or assumption of ideality is changed within the partitioning simulation, the total condensed mass changes. This forms the basis of sensitivity comparisons discussed in later sections.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 15379, 2010.