

***Interactive comment on* “The sensitivity of secondary organic aerosol (SOA) component partitioning to the predictions of component properties – Part 3: Investigation of condensed compounds generated by a near-explicit model of VOC oxidation” by M. H. Barley et al.**

**M. H. Barley et al.**

mark.barley@manchester.ac.uk

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Response to anonymous reviewer #1 on "The sensitivity of secondary organic aerosol component partitioning to the predictions of component properties – Part 3: investigation of condensed compounds generated by a near-explicit model of VOC oxidation" by Barley et al.

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Comment

3 November 2011

The authors would like to thank the reviewer for their interest in the paper and their constructive comments to which we respond in detail below. New text to be inserted into the paper is shown in bold.

p. 21058, line 27. *It would be informative to have a list of the most important AVOCs and BVOCs used in the emission scenarios. The VOCs are taken from the MCM, but are there major VOCs, relevant for UK that are not yet included in the MCM, and hence not in this study?.*

The following text has been inserted into p. 21059, line 2 immediately after "The snapshots were taken at 18:00 h on the 13th day after the beginning of the simulation":-

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The detailed anthropogenic emissions used in the box model was based on the NAEI emissions inventory which identifies 650 individual species (Goodwin et al., 2001). In order to allow coupling with the MCM scheme, the speciation was represented by 124 species (made up of alkanes, alkenes/dienes, alkynes, carbonyls, alcohols/glycols, ethers/glycol ethers, acids, esters, aromatics and chlorocarbons- see <http://mcm.leeds.ac.uk/MCM/> for a complete list) which accounted for 70% of NAEI emissions by mass. The outstanding ( 500) species, each of which makes a small contribution to the remaining 30% were emitted as surrogates assigned on the basis of chemical class and reactivity. For example, all longer chain n-alkanes greater or equal to C8 were generally used to represent alkane isomers of same carbon number. Cyclohexane was used to represent all cycloalkanes and duodecane was used to represent all alkanes greater than or equal to C10. This latter lumping assumption means that intermediate volatility organic compounds (iVOCs) emitted in the particulate phase prior to evaporation on dilution, which have been postulated to make a significant contribution to SOA by recondensation after gas phase oxidation (Robinson et al. 2007 and subsequent studies), along with all gaseous components >C12 are missing from the mechanism. While this omission may not be a problem for ozone production, it is acknowledged that it may have a substantial impact upon SOA formation and may be a source of error in the current study. Similarly biogenic emissions are represented by isoprene, and alpha and beta pinene. It is recognised that this does not take into account the emissions of other more reactive monoterpenes such as limonene or sesquiterpenes such as  $\beta$ -caryophyllene along with other BVOCs that may be important in UK emissions.

p. 21064, section 3. *General: This is of course not the first study investigating the VOC/NO<sub>x</sub> influence on SOA formation. Yet in this section not a single reference to the literature is made. E.g. the recent review of Hoyle et al. (2011) can be a source of useful references. Also, while there is a description of the results, there is too little*

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*discussion on the reasons why the results have this specific form.*

This section has now been extensively rewritten to address this comment and two additional figures added to the Supplementary material. To avoid the confusion in terminology noted below, we have redefined AVOC and BVOC to be the primary emissions as measured in tons per year and introduce the AVOC or BVOC scaling factor (AVOC-SF or BVOC-SF) to describe the factor by which the average UK emissions (AVOC or BVOC) are multiplied by for a specific scenario.

line 16-17 *"a minimal dependence on the AVOC:BVOC ratio." While there are certainly common features in Figs. 1, S1, S3, there are also important differences, so in my opinion 'minimal dependence' is too strong. The authors should discuss the major differences. In Fig. S2, the N:C limitation at high NO<sub>x</sub>/low VOC seems to be virtually nonexistent, and both N:C and O:C maxima are much weaker than compared to Fig. 1.*

We will clarify the text to emphasise that it is the similarity in the plots for the SOA mass formed that led us to suggest "a minimal dependence on the AVOC:BVOC ratio" (now changed to..a minimal dependence on AVOC-SF:BVOC-SF ratio). A section describing the similarities and differences between the plots in Figs. 1, S1 and S2 has been added to Section 3 of the paper (see below)

line 19. *"has a more complex NO<sub>x</sub>-dependence." One could be more specific: the most important trend is a decrease of SOA mass with NO<sub>x</sub> increase. The region of SOA mass increase with NO<sub>x</sub> increase covers a relatively small region in the plot. Literature references are certainly needed here. Hoyle et al. (2011) shows, from material from several references, that a maximum in SOA yield exists at a certain VOC/NO<sub>x</sub> ratio. For example, Pandis et al. (1991) find a maximal SOA yield at HC/NO<sub>x</sub> = 10-20 ppbC/ppb NO<sub>x</sub> for  $\beta$ -pinene. Limitation of SOA formation at high NO<sub>x</sub> could be due to the formation of relatively higher volatility compounds (e.g. nitrates). Also*

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*the change of reaction mechanism with NO<sub>x</sub> concentration will have an important influence, as NO<sub>x</sub> reacts with peroxy radicals...*

All text from "a unit of AVOC is as likely to..." on line 17 to the end of this section has been deleted and replaced with an improved description of the NO<sub>x</sub> dependence of SOA formation and several references from the literature (see below).

*...In the modelling work of Capouet et al. (2008), for  $\alpha$ -pinene, a decrease in SOA yield with increasing VOC/NO<sub>x</sub> is seen at high VOC concentrations, and this was attributed to an inefficient ozone production from VOC oxidation at low NO<sub>x</sub>, such that not all VOC reacts. Given that the authors use an explicit model where reaction paths and product formation can be followed, can they say if any of these or other factors give rise to the complex NO<sub>x</sub>-dependence?*

In this work we see an interesting contrast between the variation in the amount of SOA formed with increasing VOC/NO<sub>x</sub> ratio between the anthropogenic and biogenic case. For the anthropogenic case a factor of 10 increase in AVOC-SF causes a roughly similar increase in SOA formed. For the biogenic case the amount of SOA formed initially increases much faster (up to 100 times for a 10 fold increase in BVOC-SF) but then tails off, until at the highest levels, changing the BVOC-SF from 100 to 1000 only leads to double the mass of SOA formed. This looks similar to the results of Capouet et al. (2008) but a detailed mechanistic investigation is outside the scope of the current paper, but should form the focus of a more comprehensive study. A section describing this has been added to the manuscript (see below).

line 21-23. *The O:C ratio. No reasons are given for the limitations at high VOC/low NO<sub>x</sub> and low VOC/high NO<sub>x</sub>. At high VOC, I would think that due to the higher SOA, also compounds with higher volatility, hence less functionalities and smaller O:C, can condense. Is this the reason? What would be the cause for the limitation at low VOC/high NO<sub>x</sub>?*

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The reviewer is quite correct in the stated reason for O:C ratio limitation at high VOC/low NO<sub>x</sub>. A sentence explaining this will be added to the text of the paper. The situation at low VOC/high NO<sub>x</sub> is more complex. For the low AVOC case (Fig. S2) the SOA composition in this region provides some explanation for the O:C ratio limitation (see below) but a detailed description of the causes of this limiting behaviour is outside the scope of this work.

line 24 *"showing less NO<sub>x</sub> limitation than VOC limitation." Is it not the other way around? NO<sub>x</sub> limitation means that the considered property (here N:C) is limited by the limited presence of NO<sub>x</sub>. From figure 1, one can see that in the VOC limited region there is less N:C than in the NO<sub>x</sub> limited region.*

We believe the reviewer is mistaken. For the high VOC area, low NO<sub>x</sub> (top left hand quarter- NO<sub>x</sub> limited) we get N:C ratios of less than 0.1 (most of the region is well below 0.05). In the low VOC, high NO<sub>x</sub> region (bottom right quarter-VOC limited) we get N:C ratios in the range 0.1-0.12. We disagree with the reviewers statement "From figure 1, one can see that in the VOC limited region there is less N:C than in the NO<sub>x</sub> limited region." and stand by our original text.

Additional concerns about Section 3 have been raised by Reviewer 2. In response to comments from both reviewers the rewritten Section 3 is reproduced here with the new text in bold

Figures 1, S1 and S2 (see Supplementary Material) show predicted particulate properties across a range of emissions. **S3 and S4 provide information on the distribution of some key functional groups to help in interpretation.** Plots S1 and S2 are analogous to the conventional isopleths used to illustrate the dependence of ozone production on VOC and NO<sub>x</sub>. When plotting ozone isopleths, it is important that the "specific reactivity" of the VOC mixture is constant with increasing VOC. It is

not clear that an analogous “specific particulate forming capacity” of a mixture exists that should be maintained constant in the current plots. Figure 1 shows the variability in the properties when simultaneously increasing the AVOC-SF and BVOC-SF at equal rates. Figure S1 in the Supplement shows variability in the properties for the 36 scenarios with the lowest biogenic scaling factor (0.01); S2 shows them for the 36 scenarios with the lowest anthropogenic input (also 0.01). The properties are logarithm of the condensed mass ( $\mu\text{g m}^{-3}$ ); average O:C ratio; average molar mass and average N:C ratio. All averages were calculated for the same atmospherically relevant standard condition within a scenario  $T = 293.15\text{ K}$ ,  $\% \text{ RH} = 70$  and  $3.0\ \mu\text{g m}^{-3}$  involatile core **using the N-N/VP vapour pressure method and assuming liquid phase ideality**. The standard scenario (1/1/1  $\text{NO}_x$ -SF/AVOC-SF/BVOC-SF), first introduced in section 2.1 is found at (0,0) in Fig.1. This scenario is run with 6219 ppt  $\text{NO}_x$ , 28828 ppt ozone and 31302 ppt VOC, of which 18231 ppt are due to methane. Predicted SOA mass (for the standard condition) is  $0.0547\ \mu\text{gram.m}^{-3}$ ; average O:C ratio is 0.9683, average N:C ratio 0.2112 and average molar mass 219.56.

The three plots for **the amount of SOA mass formed** show similar trends with rising VOC and  $\text{NO}_x$ , suggesting a minimal dependence on the AVOC-SF:BVOC-SF ratio. **Due to the different levels of anthropogenic and biogenic inputs (see section 2.1), and assuming that the NAEI inventory accurately reflects the AVOC:BVOC ratio of emissions; this suggests that biogenic emissions are some 8-9 times more effective in producing SOA than anthropogenic emissions. The other plots reflect more directly the changing chemical composition of the SOA and hence show the effect of individual compounds (or groups of chemically related compounds) that may dominate the SOA composition for a small number of scenarios. The effects of these specific compounds will be added to the overall trends across the range of scenarios and will be different for plots in S1 and S2 (particularly for the N:C ratio and molar mass plots due to the relatively small range of values). The combined plot (Fig. 1) where AVOC-SF = BVOC-SF should make**

the underlying trends clearer by averaging out some of the specific compound effects.

For the SOA mass plots the main differences between S1 and S2 are the different ratios at which the  $\text{NO}_x$  suppression of SOA formation becomes important and that the  $\text{NO}_x$  suppression seems to be more effective in the case where the AVOC-SF varies (S1) than when BVOC-SF changes (S2). The suppression of SOA formation by increasing  $\text{NO}_x$  has been well documented (see, for example Kroll and Seinfeld, 2008) and reflects whether the alkylperoxy radicals go on to form hydroperoxides or nitrates. In this work we find that SOA mass decreases with increasing  $\text{NO}_x$  for constant inputs (constant AVOC-SF or BVOC-SF) except at high VOC and relatively low  $\text{NO}_x$  levels where there is increasing SOA formation up to a peak. This is observed for AVOC-SF of 1 or greater (S1:- BVOC-SF = 0.01) and BVOC-SF of 100 or greater (S2:- AVOC-SF = 0.01). For S1 the peak occurs at a AVOC-SF:  $\text{NO}_x$ -SF ratio of 10:1, and for S2 the peak is at BVOC-SF:  $\text{NO}_x$ -SF ratio of about 100:1. The line of this peak roughly corresponds to the loss of hydroperoxide groups from the SOA (see Fig. S3 and S4 top left hand plot). If these ratios (10:1 and 100:1) are converted back to the inputs then the anthropogenic peak is at an AVOC: $\text{NO}_x$  ratio of about 8:1 and the biogenic peak is at a BVOC: $\text{NO}_x$  ratio of about 11:1. Hence the AVOC: $\text{NO}_x$  ratio for this work is in good agreement with the ratio of 10:1 reported for the degradation of 1-octene (Camredon et al., 2007), though rather higher than the ratios (1.5:1 to 4:1) reported for the oxidation of a mixture of 4 anthropogenic VOCs (Vivanco et al., 2011). The BVOC: $\text{NO}_x$  ratio of 11:1 is in good agreement with the 10-20 ppbC/ppb  $\text{NO}_x$  for  $\beta$ -pinene found by Pandis et al., (1991), and consistent with the high yields reported by Dommen et al., (2006) for isoprene: $\text{NO}_x$  ratios of 10.5:1 to 7:1 although other authors report maximum yields at BVOC: $\text{NO}_x$  ratios closer to 1:1 for both isoprene (Kroll et al., 2006; Chan et al., 2010) and  $\alpha$ -pinene (Capouet et al., 2008). However it has been noted that the different oxidant conditions used in these studies may affect the fate of the  $\text{RO}_2$  radical and impact upon the BVOC: $\text{NO}_x$  ratio for maximum SOA

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formation (Hoyle et al., 2011).

The amount of SOA formed with increasing VOC/NO<sub>x</sub> ratio at constant NO<sub>x</sub>-SF (= 0.1) was investigated. In Fig. S1 a factor of 10 increase in AVOC-SF causes a roughly similar increase in SOA formed. For the case where the biogenic input is increased (Fig. S2) the amount of SOA formed initially increases much faster (up to 100 times for a 10 fold increase in BVOC-SF) but then tails off until at the highest levels changing the BVOC-SF from 100 to 1000 only leads to double the mass of SOA formed. These results are similar to those reported by Capouet et al. (2008) but a detailed mechanistic investigation is outside the scope of the current paper, but should form the focus of a more comprehensive study.

For the N:C ratio it would be expected that at high VOC, low NO<sub>x</sub>, where a lot of SOA is formed then the N:C ratio would be very low and this is seen in both Figs. S1 and S2. On moving towards high NO<sub>x</sub> the amount of SOA drops and the N:C ratio increases but the shape of this change is determined by the distribution of nitro and nitrate groups (see Figs. S3 and S4). For the low AVOC case (Figs. S2, S4) nitro groups are limited to a small region at very low NO<sub>x</sub> and very low BVOC but nitrates make a significant contribution across a wide range of NO<sub>x</sub> values giving the plateau feature seen in Fig. S2 with no maximum. In Fig. S1 nitrates are more restricted to high NO<sub>x</sub> values (Fig. S3) and the N:C ratio at lower NO<sub>x</sub> are dominated by nitro groups. These nitro groups are associated with a limited number of compound types (for example, a series of multifunctionalized peroxybridged cyclohexene compounds with very low predicted vapour pressures) which dominate anthropogenic SOA composition across a range of scenarios and give the distinctive ridge feature (and maximum in N:C ratio) seen in S1. PAN groups make a small contribution to the N:C ratio for anthropogenic SOA (Fig. S3). Fig. 1 is an average of the plots in Figs. S1 and S2 so the ridge and maximum in N:C ratio are visible in this figure as well.

The molar mass plots in Figs. S1 and S2 show the expected broad trends:- re-

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gions with large amounts of SOA give the lowest molar mass (as more volatile, lower molar mass material is included in the condensation process) and conversely the regions with the smallest amounts of SOA tend to have the highest molar masses. This is most clearly seen in S2; in S1 (the low BVOC case) the effects of specific compounds are added to the overall trends. For example the pale blue region at  $\log(\text{NO}_x\text{-SF}) = 0$ ,  $\log(\text{AVOC-SF}) = -2$  to 0 is due to the large contribution to SOA of an alkene substituted with a nitro, aldehyde and acid group (molar mass = 159) in contrast to the red region immediately to the left which is dominated by the peroxybridged cyclohexenes mentioned above (molar mass = up to 290). The substituted alkene also makes a strong contribution to the maximum seen in the N:C plot mentioned above.

In the O:C ratio plots in Figs. S1 and S2 regions of high SOA mass (low  $\text{NO}_x$ /high VOC) show reduced O:C ratio due to the extra condensing material being more volatile, this being associated with fewer oxygenated functional groups. The pattern in the rest of the plot is not very clear (particularly in Fig. S1) and this is due to the effect of specific compounds. In Fig. S1 the pronounced ridge and maximum in O:C ratio occurs in the same region to the similar feature in the N:C ratio plot and will be due to the high O:C ratios of the peroxybridged cyclohexenes (O:C ratio = 1.7-2.0) and substituted alkene (O:C ratio = 1.0) which dominate the SOA composition in this region. In Fig. S2 there is a weak ridge structure with a maximum at very low VOC/very low  $\text{NO}_x$ . This is associated with SOA being dominated by C5 diols with ketone and hydroperoxide groups (O:C ratio = 1.0 -1.2). At higher  $\text{NO}_x$  ratios polyfunctional nitrates with O:C ratios of about 0.7-0.9 become important contributors to SOA. Fig. 1 is an average of the plots in Figs. S1 and S2 so the ridge and maximum in O:C ratio are visible in this figure as well. Significant differences are also seen in the high  $\text{NO}_x$ /low VOC region. For the low AVOC case (Fig. S2) the SOA composition in this region is dominated by three compounds:- a polyfunctional nitrate with an O:C ratio of 0.875; a cyclobutane derivative with a carboxylic acid and PAN group (O:C

ratio = 0.875- note increase in PAN at high  $\text{NO}_x$  in Fig. S4 ); and a cyclobutane derivative bearing carboxylic acid and nitrate groups (O:C ratio = 0.625). At low VOC and between a  $\text{NO}_x$ -SF value of 10 and 1000 the composition doesn't change much resulting in the large area in this plot with O:C ratio of about 0.7-0.8. The behaviour of the plot for low BVOC case is more complex and a detailed description of the limiting behaviour in this region is outside the scope of this work.

p. 21065, line 28. *Also the work of Valorso et al. (2011) and Compernelle et al. (2010) could be cited here, where different vapour pressure methods, including N-N/VP, JR-MY and N-MY, were compared and it was found that N-MY gives higher vapour pressures and consequently less SOA.*

In Valorso et al.,(2011) the predicted SOA masses were substantially larger than the experimental values (in contrast to our results where the prediction for the standard scenario is some 20-100x too low) and although the JR-MY method predicts more SOA than the N-N/VP method the difference is about 12% for the low  $\text{NO}_x$  case, 50% for intermediate  $\text{NO}_x$  and a factor of x4 for the high  $\text{NO}_x$  case (see their Figure 5); rather than the couple of orders of magnitude seen in Fig. 2. The two sets of results are not directly comparable as those from Valorso et al., use a fully explicit, automated chemical degradation mechanism (GECKO-A) on a single VOC; and the experimental systems being modelled are chamber studies with relative high concentrations of VOC (giving 5-30  $\mu\text{gram.m}^{-3}$  of SOA). There is some evidence from our results that for the higher emission scenarios (of the 27 used to generate Fig. 2) the factor difference between vapour pressure by JR-N/VP and by N-N/VP drops to less than x10 suggesting that the sensitivity to different vapour pressure methods decreases with increasing SOA mass. This would be expected as with increasing mass more volatile components would start to make a contribution to the SOA and the estimated vapour pressures by the two methods (JR-N/VP and by N-N/VP) would be more similar than for the less

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volatile components that dominate at low SOA mass.

p. 21065 l. 24: The following three sentences have been added after "...two Joback methods (JR-N/VP and JR-MY) show a significant bias towards increased mass." **Similar results have been reported by Valorso et al., (2011) where the JR-MY method consistently predicted more SOA than the N-N/VP method although the differences were much smaller than those shown in Fig. 2. The difference in sensitivity can be explained by the larger SOA mass reported by Valorso et al., (2011). The vapour pressure values predicted by the various models tend to converge as compounds become more volatile; so with increased SOA mass, more volatile components become included in the SOA and the sensitivity to the vapour pressure model is reduced.**

p. 21065 l. 28: The following sentence has been added after "...underestimating the slope of the vapour pressure curve (Barley and McFiggans 2010)". **Compernelle et al., (2010) also noted the large differences in estimated vapour pressures when using the MY and the N/VP vapour pressure equations, finding that the N-MY method under predicted their experimental SOA amounts while the N-N/VP method gave much better results.**

p. 21066, section 4.1 *Some comparison with Valorso et al. (2011) could be attempted. The spread in their Fig. 7 is much smaller than in Fig. 3 of this work, despite the fact that some methods are the same (JR-MY, N-N/VP). Is this due to the fact that only one VOC was oxidized? Or to the low NO<sub>x</sub> conditions there?*

The spread in Figure 7 of Valorso et al. (2011) is indeed rather smaller than the results we show here. The two simulations are however done under very different conditions, and in particular give very different amounts of SOA mass. The standard case we use (1.0/1.0/1.0 NO<sub>x</sub>-SF/AVOC-SF/BVOC-SF with T= 293.15K, 70% RH and 3.0 μgm<sup>-3</sup> involatile core) gives 0.0547 μgm<sup>-3</sup> of SOA when using the N-N/VP vapour pressure method. In contrast Valorso et al. (2011) low NO<sub>x</sub> case gave about 70 μgm<sup>-3</sup>. The

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change in the number of compounds seen in Fig. 3 with increasing SOA mass was investigated and it was found that at higher SOA masses there was less reordering. Hence the reduced sensitivity of the compound order to changes in the vapour pressure model, seen in their Fig. 7 compared to our Fig. 3 is most likely to be due to the higher SOA mass rather than the low  $\text{NO}_x$  conditions or the oxidation of only one VOC. Text to explain this point will be added to the paper.

**The change in the JR-MY parameter with SOA mass was also investigated and was found to vary between 146 at the lowest SOA mass up to 164 at the highest masses, suggesting that at higher SOA masses there is less reordering of compounds with a change in vapour pressure model. This may explain why the degree of scatter seen in Fig. 3 (SOA mass =  $0.0547 \mu\text{g m}^{-3}$  by N-N/VP) is much greater than that seen in Fig. 7 of Valorso et al., (20011) (SOA mass  $>60 \mu\text{g m}^{-3}$ ).**

p. 21067, line 1-3. *This is indeed a very interesting result. Can the reordering be attributed to specific families of compounds? E.g. do acids become more important in SOA due to their interaction with water?*

Yes, there is clear evidence of this from the results. For the standard conditions using the N-N/VP method for vapour pressure, the relative ordering of the compounds is very dependant upon the their functionality when comparing the ideal and non-ideal calculation. So hydrogen bonding groups such as alcohols, acids and phenols become more important in the SOA when non-ideality is taken into account and nitrates and PANs become less important.

The following text was inserted into the paper at p. 21067 l. 6 after ..."the reordering must be the result of simultaneous positive and negative deviations from ideality in the multicomponent mixture.":- **This was confirmed by an analysis of how the representation of specific functional groups in the SOA changed with the inclusion of non-ideality. For the standard conditions (which includes 70% RH), the change from an ideal to a non-ideal calculation resulted in carboxylic acids on average**

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**moving up by 99 places, monoalcohols by 136 places and bis-phenols by 214 places. In contrast nitrates moved down by 202 places, mononitro compounds by 74 places and PANs by 308 places. This reordering clearly reflects the effects of negative deviations from ideality for the first set of functionalities in aqueous solution; and positive deviations from ideality for the second set of functional groups.**

p. 21067, line 6-7. *"This is further exaggerated under cooler, moister conditions" It should be discussed why this is the case. My guess is that the water-organic molecule interaction plays an important role in this, as it is, in general, more important than organic-organic interactions in SOA. Also in the study of Bowman and Melton (2004), it was found that activity coefficients of aerosol components are closer to unity if no water is present.*

The reviewer is quite correct in that the water-organic interactions will generally be more important than organic-organic interactions in SOA, certainly at medium and high %RH. From studies on the vapour-liquid equilibria of binary mixtures (including systems containing water) it is generally observed that solute deviations from ideality (whether negative or positive) tend to get larger, both at lower temperatures (Gmehling, 2009), and at higher dilutions (Gmehling et al., 2002). However the situation for complex multicomponent mixtures is much less clear. For a range of organic compounds in water, and providing only a single liquid phase is formed, then at say 70%RH, where 7 out of every 10 molecules in the condensed phase is a water molecule (for the ideal calculation), the interactions of a given solute molecule will be predominantly with water, rather than other solute molecules. The behaviour of the multicomponent mixture can be modelled as the product of the component binary mixtures and further dilution (i.e. increasing %RH) will cause the activity coefficients of the solutes to move away from unity as typically seen in the individual binary systems.

The following text was added to the paper at p. 21067 l. 7 after "...under cooler,

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moister conditions and only slightly less important under warm dry conditions." **For SOA mixtures formed at medium or high %RH the water-organic interactions will be more important than the organic-organic interactions. The more extensive reordering of compounds under cooler, moister conditions, is consistent with the movement of the SOA component activity coefficients away from unity. From studies on the vapour-liquid equilibria of binary mixtures (including systems containing water) it is generally observed that solute deviations from ideality (whether negative or positive) tend to get larger, both at lower temperatures (Gmehling, 2009), and at higher dilutions (Gmehling et al., 2002).**

p. 21068, line 18. *"highly optimistic" The sensitivity to the vapour pressure model is indeed high, for the models considered here. On the other hand, in your previous work, (Barley 2010), it was already shown that methods with JR systematically gave too low vapor pressures and the N-MY model a tendency to overestimate vapour pressure. For JR, also the cause of their anomalous behaviour, namely the treatment of  $T_b$  as a sum of group contributions, was identified. Based on this work, couldn't we dismiss these models as being unrealistic, such that they don't have to be included in a sensitivity test?*

In Barley et al. (2010) we showed that based on experimental vapour pressure data for a series of multifunctional compounds (all below 100Pa) that the JR method overestimated boiling points above about 500K and the MY vapour pressure equation underestimated the slope of the vapour pressure line (giving high vapour pressures). When these two methods are used together (JR-MY) some of the errors cancel out although in our opinion the results are still unsatisfactory as we made plain in our paper. The problem with the JR method is that it does *no more* than treat  $T_b$  as a sum of group contributions:- The SB method introduces an empirical correction and the Nannoolal method divides the sum of the group contributions through by the number heavy atoms to the power of 0.6583. Both these methods substantially reduce the  $T_b$  value for large, high  $T_b$  molecules from that predicted by a simple addition of groups. Hence there is

good reason to expect the predictions of the JR method to diverge from reality as the volatility of the compound is reduced.

We would make two points to defend the range of models we consider here. The first is that in Barley et al., 2010 we tested the models against multifunctional compounds with low experimental vapour pressures, which were however at least 3 orders of magnitude higher than the vapour pressure of compounds expected to condense into atmospheric aerosol and probably several orders of magnitude above the vapour pressure of the most complex products predicted by the MCM. The truth is that we need a much more sophisticated vapour pressure equation (one which can account for the behaviour of compounds with multiple hydrogen-bonding functional groups and for intramolecular hydrogen bonding between such groups due to their relative position) and the experimental data to fit to the model. We can't say for certain that the N-N/VP method gives better predictions than the JR-MY method for compounds with a volatility 6 orders of magnitude below those used in our test set because we don't know the validity of the extrapolation of the N-N/VP method to low volatility. Hence while we would recommend that researchers move away from the JR method for their main work it may be premature to drop the method from all comparisons and sensitivity studies. This leads onto our second point which is that people are still using JR-MY method in major studies (eg:- J Lee-Taylor et al., 2011, Valorso et al., 2011, Camredon and Aumont, 2006).

p. 21068, line 25. *There should be more discussion of Figure 5 at this point. For example, you could mention that the most abundant condensed molecules have a molar mass of around 200 amu and a O:C of around 0.5.*

The following text was inserted in line 27 after "...when the JR estimation method is used for Tb." **For both plots the most abundant condensed molecules have a molar mass in the range 150-220 and an O:C ratio of 0.5 to 1.0.**

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p. 21069, line 10-12. *"There may also be changes in the O:C ratio but this is not as clear" Comparing the figures, I think one can say that the extra material condensing has a somewhat lower O:C ratio. The peak in Fig. 6 is somewhat below 0.5, while in Fig. 5a,b the peak is above 0.5. The authors could add why the extra material peak is at a lower Mw, O:C. In my opinion, this is due to the lower p0 predicted by JR, such that more smaller and less functionalised molecules will also condense.*

Close examination of the figures confirm that the reviewer is quite correct. The main peak in Fig. 6 is at a molar mass of about 160 and an O:C ratio of about 0.45, while the peaks in Figs 5a,b are mainly at O:C ratio > 0.5. The reviewer is also correct in suggesting that the extra material will tend to have a lower molar mass and O:C ratio (on average) because the JR-N/VP method predicts lower vapour pressures. The JR-N/VP method predicts  $1.35 \mu\text{gm}^{-3}$  SOA compared to  $0.055 \mu\text{gm}^{-3}$  for the base case. With the additional SOA mass, more lower molecular weight and less functionalized molecules will contribute to the SOA.

The text on page 21069 will be changed...The sentence "There may also be changes in the O:C ratio but this is not as clear as the change in molar mass in these figures." was deleted and replaced by **Although it is difficult to see in these figures, close examination of Figure 6 shows that the main peak is at an O:C ratio of about 0.45 while the peaks in Figs 5a,b are mainly at O:C ratio > 0.5. The additional material predicted to condense when using the JR-N/VP model has a slightly lower O:C ratio consistent with less functionalized molecules contributing to the condensed material.**

p. 21069, line 17. *Why is there no box-whisker plot for the base case? One could take a black one.*

For clarity we have redone the figure to include black box-whisker plots for the base case (N-N/VP) and amended the caption and text in the main body of the paper appropriately.

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p. 21069, line 25-29. *I notice another difference. In the Part 1 figure 10, N-MY, SB-MY have a lower Mw than the base case, while in figure 7 of the current work Mw is higher. In principle, due to the higher vapour pressures N-MY and SB-MY predict, I would expect a higher Mw; the molecule must be larger/more functionalised before it will condense. Can the authors explain this difference?*

Due to the uneven difference with vapour pressure methods with regards to changing functionality, as displayed in both papers, generalised distributions of molar mass, for example, are likely to be sensitive to:- 1) the chosen complexity of the functionality; and 2) the prescribed abundance of said compounds. Therefore, with regards to this issue, it is important to note that in the first paper the upper and lower quartiles of molar mass spanned up to 200 g/mol, whereas the Figure 7 in this paper shows a much tighter distribution, sometimes less than 50 g/mol. This is an indication that in this work we are breaking the functionality into much smaller fragments, or perhaps more accurately, using less 'first order representations' in this paper. Indeed, in the first paper we used 19 UNIFAC groupings to construct the functionality of each compound, whereas in this instance we are using a collection of SMILES representations for each compound and parsing into 58 maximum functional groups using the method of Nannoolal et al., 2004. Also in the first paper, the median molecular weight values are more uniformly distributed than this paper. In short, one has to be careful with regards to slight nuances in the observations in both papers which might be a function of the inputs used. The general trends remains the same in both papers (e.g. higher mass loading for predictive techniques that biased toward lower volatility), but in this paper we are more tightly constrained with regards to composition.

p. 21070, line 12-13. *"the spread... is much smaller for the two methods that use Tb by JR." You could notice also that the methods using MY (but not JR) show the largest spread, both in O:C and Mw. So it seems that methods predicting higher vapour pressures show a larger spread. Why is this the case? Intuitively, I would think*

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*that in a method predicting low vapour pressures, both the heavy, largely oxygenated, and the light, less oxygenated products would condense, giving a larger spread on Mw and O:C. Clearly this reasoning is wrong, but could the authors explain why?*

The calculations for this figure are done over a range of 27 scenarios and 32 cases. The spread of the O:C and molar mass values seen in Fig. 7 reflect the range of SOA mass. For the vapour pressure methods that give the lowest vapour pressures (eg. JR-N/VP) the range of SOA mass over this set of calculations is from 0.0022 to 40.54  $\mu\text{gm}^{-3}$  (a factor of about 18,000). For the method that gives the highest vapour pressures (N-MY) the corresponding factor is about 6,000,000 (0.00000132 to 7.8  $\mu\text{gm}^{-3}$ ). As the distribution of the components of the SOA are heavily influenced by the mass of SOA formed (with low SOA mass giving high molar mass and O:C ratio and high SOA mass giving lower average values) the spread in O:C ratios and molar mass seen in Fig. 7 are directly related to the spread of condensed SOA mass. Hence the low vapour pressure method gives a more limited range of O:C ratios and molar masses because the very low SOA mass cases are missing from the sample.

Fig. 1, caption. *"for those scenarios with AVOC=BVOC". This suggests that AVOC emissions are taken equal to BVOC emissions. But from sect. 2.1 I learn that the standard scenario has 1510 ktonnes VOCs, of which 1330 ktonnes, (hence the large majority) being anthropogenic. Can the authors clarify?*

The reviewer is quite correct to point out this inconsistency in terminology and as a consequence we have introduced AVOC, BVOC and  $\text{NO}_x$  scaling factors (shortened to AVOC-SF, BVOC-SF and  $\text{NO}_x$ -SF) to distinguish between the number of times average UK emissions and the UK emissions themselves (see beginning of this response). Hence the caption for Fig. 1 has been changed to "AVOC-SF = BVOC-SF".

## Technical corrections

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p. 21069, line 1. The use of 'consistent' could be taken wrongly to mean 'systematic'. This is clearly not true, given the following sentences and also the fact that fig. 6 is not featureless. But I would reword to avoid confusion.

This section has been reworded and the word "consistent" has been dropped.

Fig. 1. *A small notation inconsistency. In the figures O/C, N/C is used, while in the text O:C, N:C is used.*

The titles in Fig 1 and in the Supplementary material have been changed to O:C Ratio and N:C ratio to be consistent with the caption and the text of the paper.

Fig. 3. *Symbols '+', '\*\*', of SB-N/VP, SB-MY are hard to distinguish. Similarly for JR-N/VP, JR-MY. Use different colors (light blue for example), and/or more different symbols.*

Fig 3. has been redone with SB-N/VP as blue open circles and JR-N/VP as red open circles.

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