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Comment

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.

Anonymous Referee #1

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In this work, box modelling results, of SOA formation by VOC oxidation, are presented with a near-explicit model (the MCM), with a large variation of the parameters: emissions, vapour pressure model, non-ideality and to a limited extent chemistry (hydrolysis of anhydrides) are varied and the impact on SOA quantity and properties are given.

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General points

This work presents interesting results, but there is a lack of discussion and exploring the reasons for the results. The advantage of explicit models is precisely that the impact of parameter change on calculated properties can be traced back to specific processes, and this should be exploited. Also, reference to literature is too limited. I can only recommend publication in ACP if these issues are addressed.

Specific points

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?

p. 21064, section 3. General:

This is of course not the first study investigating the VOC/NO_x 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 discussion on the reasons why the results have this specific form.

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_x/low VOC seems to be virtually nonexistent, and both N:C and O:C maxima are much weaker than compared to Fig. 1.

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line 19. "has a more complex NO_x-dependence."

One could be more specific: the most important trend is a decrease of SOA mass with NO_x increase. The region of SOA mass increase with NO_x 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_x ratio. For example, Pandis et al. (1991) find a maximal SOA yield at HC/NO_x = 10-20 ppbC/ppb NO_x for β -pinene. Limitation of SOA formation at high NO_x could be due to the formation of relatively higher volatility compounds (e.g. nitrates). Also the change of reaction mechanism with NO_x concentration will have an important influence, as NO_x reacts with peroxy radicals. In the modelling work of Capouet et al. (2008), for α -pinene, a decrease in SOA yield with increasing VOC/NO_x is seen at high VOC concentrations, and this was attributed to an inefficient ozone production from VOC oxidation at low NO_x, 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_x-dependence?

line 21-23. The O:C ratio.

No reasons are given for the limitations at high VOC/low NO_x and low VOC/high NO_x. 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_x?

line 24 "showing less NO_x limitation than VOC limitation."

Is it not the other way around? NO_x limitation means that the considered property (here N:C) is limited by the limited presence of NO_x. From figure 1, one can see that in the VOC limited region there is less N:C than in the NO_x limited region.

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

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compared and it was found that N-MY gives higher vapour pressures and consequently less SOA.

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, NN/VP). Is this due to the fact that only one VOC was oxidized? Or to the low NO_x conditions there?

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?

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.

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?

p. 21068, line 25.

There should be more discussion of Figure 5 at this point. For example, you could

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mention that the most abundant condensed molecules have a molar mass of around 200 amu and a O:C of around 0.5.

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 p_0 predicted by JR, such that more smaller and less functionalised molecules will also condense.

p. 21069, line 17.

Why is there no box-whisker plot for the base case? One could take a black one.

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?

p. 21070, line 12-13. "the spread... is much smaller for the two methods that use T_b 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 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?

Fig. 1, caption.

"for those scenarios with AVOC=BVOC". This suggests that AVOC emissions are taken

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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?

Technical corrections

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.

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.

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.

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