Atmos. Chem. Phys. Discuss., 11, C9257–C9264, 2011
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Atmospheric
Chemistry
and Physics
Discussions

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 #2

Received and published: 22 September 2011

Review of "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.

1. General comments

The objective of this paper is to test the sensitivity of secondary organic aerosol (SOA)

formation to estimated component properties. The distribution of organic species formed during gas phase oxidation was simulated using the Master Chemical Mechanism for a range of emission scenario under different temperatures, relative humidity and pre-existing aerosol mass conditions. The simulated distribution of organics was then used to calculate SOA formation using an absorptive partitioning. The sensitivity of SOA formation to vapour pressures and activity coefficients has been assessed for these various scenario and conditions with a particular focus on SOA properties (component masses, volatility, O:C ratio, molar mass and functionality distribution).

This work is relevant for publication in ACP, however I recommend some corrections before its publication to improve the scientific discussion of the paper. In particular and as already pointed out by Referee 1, the authors should compare their results with previous published work and should use the model to better explain their findings.

2. Specific comments

p. 21059 l. 2: "A fairly constant diurnal profile in simulated ozone and degradation intermediates was simulated after 9 model days"
How was the box model built to reach "the constant diurnal profile"? Is there a diurnal variation of the emissions, the photolysis, the temperature, the boundary layer height...? Is there any deposition or dilution of species included?

p. 21059 l. 7: "Further emission scenarios were simulated by independently multiplying the AVOCs, biogenic VOCs (BVOCs) and NOx component of the base case emissions by factors of 0.01, 0.1, 10, 100 and 1000"
Why is this range of variation selected? Is it representative of various conditions found in the UK or emission uncertainties?

p. 21059 l. 10: "To study the trends ... relevant scenarios were used."
If the simulations are not atmospherically relevant why are they used in Sect. 3 to discuss the sensitivity of SOA formation to emissions?

p. 21060 l. 4: "The temperature and RH values were selected to cover the range of typical conditions found in a temperate maritime climate such as that of the UK"
The relative humidity is set to 10, 30, 70 and 80

p. 21061: How is the uptake of water taken into account in the model?

p. 21064 l. 3: The base case scenario should be introduced here. The level of NOx and VOC simulated could be presented as well as the concentration of O3, SOA mass, average O/C ratio, average N/C ratio, and average molar mass.

p. 21064 l. 3: "These plots are analogous to the conventional isopleths used to illustrate the dependence of ozone production on VOC and NOx."
The ozone isopleths usually represent the ozone concentration as a function of VOC and NOx concentrations. Did the authors plotted in Fig. 1, Fig. S1 and Fig. S2 the logarithm of the concentration of VOC and NOx (if yes, please give unity) or the logarithm of the factor applied to the emissions of the base case scenario? If this is the case, the authors should be clearer in the descriptions of the plots, the discussions and the legends and axis of the figures.

p. 21064 l. 16: "All three figures show similar trends with rising VOC and NOx, suggesting a minimal dependence on the AVOC:BVOC ratio: i.e. a unit of AVOC is as likely to create SOA as a unit of BVOC"
The comparison of the potential of AVOC and BVOC to form SOA could be very interesting. All three figures show indeed the similar general trends of SOA with changes in NOx or VOC. However, from the figures shown, I don't see how it can be concluded that there is "a minimal dependence on the AVOC:BVOC ratio" or that "a unit of AVOC is as likely to create SOA as a unit of BVOC" because :
(i) if the yaxis are the logarithms of the factor applied to the emissions, the concentrations of VOC presented in the y axis are different between Fig. 1, Fig. S1 and Fig. S2. The concentration of VOC corresponding to log(10)VOC=3 in Fig. 1 is about equal to the one corresponding to log(10)Anthro=3 in Fig. S1 but about 10 times smaller than

the one corresponding to log(10)Bio=3 in Fig. S2 (as in the simulated base case scenario, BVOC emissions are about an order of magnitude lower than AVOC emissions).
(ii) the z axis color used for SOA mass in Fig. S1 and Fig. S2 doesn't look the same as in Fig. 1. It would help the discussion to have the same z axis.

p. 21064 l. 18: The evolution of SOA mass as a function of VOC and NOx level has been largely studied in chamber experiments (e.g. Kroll and Seinfeld, 2008). SOA isopleths as a function of NOx and VOC have also been plotted in several papers (e.g. Vivanco et al., 2011, Camredon et al., 2008, Capouet et al., 2008). Most of the results show (i) an increase of SOA with increasing VOC concentration and (ii) two regimes of SOA formation depending on NOx concentrations with an optimum reached at a given VOC/NOx ratio. Here, the authors have to compare their results with previous literature. The authors should also try to use the model to explain the simulated NOx / VOC limited regimes of SOA formation, together with the simulated average O:C, N:C and molar mass.

p. 21065 l. 1: "Figure 2 shows the sensitivity of condensed SOA mass to the methods used to estimate vapour pressure and the treatment of solution ideality across all conditions for 27 model scenarios."
Figure 2 also shows the sensitivity of condensed SOA mass to hydrolysis of acid anhydrides. Has hydrolysis also been applied for the scenario with low relative humidity?

p. 21065 l. 18: Comparisons with previous published results on the influence of activity coefficient on SOA formation have to be performed (see for example Compernolle et al., 2009).

p. 21065 l. 20: Comparisons with previous published results on the influence of vapour pressure estimates on SOA formation have to be performed (see for example Valorso et al., 2011 and Compernolle et al., 2010).

p. 21066: The order of the ranking of the top 200 species has been plotted in Fig. 3 and S3 to look at SOA sensitivity to estimated vapour pressures, activity coefficients and hydrolysis. It would be useful to report the contribution of these 200 species to the total SOA mass. Are a few species among the top 200 species needed to represent the total SOA mass or are all these species dominant but present in SOA at a low concentration?

p. 21066 l. 21: "It is not surprising that hydrolysis of anhydrides does not greatly change the compound ordering as the vast majority of compounds have the same vapour pressure as they have in the base case calculation."
Indeed the hydrolysis of anhydrides does not substantially change the compound ordering for the conditions simulated in Fig. 3. However large differences are observed in the vapour pressure distribution shown for the same simulation in Fig. 4, with most of the SOA components in the logC*=-2 bin for the simulation including hydrolysis. Why is this difference not observed in Fig. 3? Is it because the hydrated compounds are not present in the top 200 species of the base case simulation? It would be useful to clarify this in the manuscript and to specify, among the 200 species plotted in Fig. 3, the number of species that are identical between the base case simulation and the simulations performed to test the sensitivity of SOA.

p. 21068 l. 1: "If the hydrolysed case is compared to the base case then it is clear that the hydrolysis process reduces the concentration in bin logC*i=+2 and possibly some further bins of even higher volatility, while signficantly increasing the amount of material in bin logC*i=-2."
It can also be noted that the bin logC*i<-5 is largely reduced when hydrolysis is implemented. Does this mean that most of these species in this bin are formed from the oxidation of species that can be hydrolysed? If these species are hydrolysed, they are mainly in the aerosol phase and cannot be oxidized in the gas phase to give species in the logC*i<-5 bin. The contribution of these hydrolysed species to the total SOA mass could therefore be important. What is the contribution of the hydrolysed species to the total SOA mass?

p. 21069 l. 2: "If the right hand side of Fig. 6 (molar mass above 200 amu) is compared to the corresponding figure (Fig. 9c) in McFiggans et al. (2010) substantial similarities can be seen confirming that differences in predicted SOA composition with vapour pressure estimation techniques are not completely systematic and independent of functionality."

I don't understand what the authors are trying to say.

p. 21069 l. 23: The author should discuss the results of Fig. 7 before comparing with McFiggans et al., 2010.

p. 21069 l. 24: "As expected this plot has a similar form to Fig. 10 in McFiggans et al. (2010),"
What do the authors mean by "a similar form" and why were the authors expecting to get a similar form? For a same case, nor the simulated median values of the molar mass or the O:C ratio, nor the spread of the box plots, are the same in the two figures. Only the relative evolution of the median values between all the sensitivity cases is comparable. What do we learn from this comparison?

p. 21071 - 21072: Comparisons with previous published results on the influence of activity coefficient on SOA formation have to be performed (see for example Compernolle et al., 2009).

3. Technical corrections

p. 21059 l. 9: "to give 206 emission scenarios"
Should it be 216?

p. 21064 l. 3: "The properties are logarithm of the average condensed mass (μgm-3); average O:C ratio; molar mass and average N:C ratio."
Should it be "condensed mass" instead of "average condensed mass" and "average molar mass" instead of "molar mass"? See also the legends and axis of the figures.

p. 21064 l. 12: "Figure S1 in the Supplement shows variability in the properties for the

35 scenarios with the lowest biogenic input (0.01); S2 shows them for the 35 scenarios with the lowest anthropogenic input (also 0.01)."
Should it be 36 including the base case?

p. 21064 l. 15: "All averages were calculated for the same atmospherically relevant case within a scenario T =293.15 K, It should also be specified that the SOA results are shown for vapour pressures calculated with N-N/VP and for the ideal case. See also the legends of the figures.

p. 21065 l. 5 "across all conditions for 27 model scenarios"
It would clarify the section to say that the 27 model scenarios were with emissions multiplied by factors of 0.1, 1.0 and 10.

Figures S1 and S2: Why are there no simulated data at high VOC and high NOx?

Too many references are made to McFiggans et al., 2010. It should be possible to read the two papers independently and most of the time, this reference is not useful and confusing for the reader. For example, the following references can be removed:
p. 21062 l. 16 : "As described by McFiggans et al. (2010)"
p. 21065 l. 5 "This figure is directly comparable to Figs. 3 and 4 in McFiggans et al. (2010)."
p. 21069 l. 16 "directly comparable to Fig. 10 in McFiggans et al. (2010)"

References

Camredon, M., Aumont, B., Lee-Taylor, J., Madronich, S., The SOA/VOC/NOx system: an explicit model of secondary organic aerosol formation, Atmos. Chem. Phys., 7, 5599-5610, 2007.

Capouet, M., Muller, J. -F., Ceulemans K., Compernolle, S., Vereecken, L., Peeters, J, Modeling aerosol formation in alpha-pinene photo-oxidation experiments, J. Geophys. Res. Atmos., 113, DOI: 10.1029/2007JD008995, 2008.

Compernolle, S., Ceulemans, K., Müller, J.-F., Influence of non-ideality on condensation to aerosol, Atmos. Chem. Phys., 9, 1325-1337, 2009.

Compernolle, S., Ceulemans, K., Müller, J.-F., Technical Note: Vapor pressure estimation methods applied to secondary organic aerosol constituents from α-pinene oxidation: an intercomparison study, Atmos. Chem. Phys., 10, 6271-6282, 2010.

Kroll, J. H., Seinfeld, J. H., Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593-3624, 2008.

Valorso, R., Aumont, B., Camredon, M., Raventos-Duran, T., Mouchel-Vallon, C., Ng, N. L., Seinfeld, J. H., Lee-Taylor, J., Madronich, S., Explicit modelling of SOA formation from alpha-pinene photooxidation: sensitivity to vapour pressure estimation, Atmos. Chem. Phys., 11, 6895-6910, 2011.

Vivanco, M. G., Santiago, M., Martinez-Tarifa, A., Borras, E., Rodenas, M., Garcia-Diego, C., Sanchez, M., SOA formation in a photoreactor from a mixture of organic gases and HONO for different experimental conditions, Atmos. Environ., 45, 708-715, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 21055, 2011.