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Interactive comment on “Functionalization and fragmentation during ambient organic aerosol aging: application of the 2-D volatility basis set to field studies” by B. N. Murphy et al.

Anonymous Referee #1

Received and published: 3 June 2012

This paper presents an interesting analysis of different forms of 2D-VBS methods compared to observations. Some of the results are counter-intuitive, in the sense that adding scientifically more realistic terms seems to degrade model performance in terms of O:C ratio. Much of the material discussing this is well written and worth presentation and discussion in the literature, but I do have some major concerns about this paper:

1) There is no discussion or presentation of the model's predictions of other, and better characterised, pollutants. One cannot discuss why a model does well or badly for the organic aerosol at a site without knowing how well the model performs for those pollutants with reasonably well-know emissions and chemistry.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Interactive
Comment

2) The analysis of the results is generally in terms of fractional error of OA mass and O:C ratio. Although O:C is a powerful diagnostic, OA mass itself has little value in my opinion - there are too many uncertainties involved. Some of the correlation coefficients (r) are very low, and no time-series are presented. I would like to see more discussion of the changes in r , and some illustration (possibly in Supplementary material) of the time-series performance of the model, for both OA and other pollutants.

3) It becomes clear that one of the major differences between the base-case functionalization scheme and the detailed functionalization scheme is that in the former the biogenic condensable gases are assumed to retain the same C^* values on aging, whereas in the latter BSOA and ASOA are treated in a more comparable manner. Thus, many things change when going from the base to the detailed scheme. I would have liked to see the intermediate step, so that one could isolate the effect of the BSOA assumptions from those of the more detailed functionalization treatment.

4) The paper discusses only OH oxidation, both in gas and particle phases. As OH is low in winter it is probably not surprising that particle-phase reactions driven by an OH rate give little effect on OA, but I would like to see a discussion of the role of other oxidants and particle-phase reactions.

5) The paper does not even mention a large amount of literature about the known characteristics of OA in Europe. Papers by e.g. Gelencser et al. (2007), Gilardoni et al (2011), Szidat et al (2006), or Yrri et al. (2011) clearly demonstrate that most OA in summertime is from BSOA. This finding is very important when evaluating model predictions, especially of the type presented in Fig. 4 of this paper. Previous modelling studies making use of such findings are also not mentioned or discussed e.g. both Simpson et al. (2007) and Gilardoni et al. (2011) compared model predictions of components (ASOA, BSOA, etc.) against long-term observational data designed to discriminate between modern and fossil-fuel sources.

6) The paper has no discussion of the uncertainties in the emission inventories being

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used. These uncertainties are significant, and much of the discrepancy between modelled and measured OA could plausibly be blamed on emissions, especially in winter (e.g. as demonstrated by Simpson et al. 2007 using levoglucosan comparisons).

7) P9880, lines 25 on. Some optimistic statements are made here that stand in conflict with the results presented in this study. It is incorrect to say that the added detail of functionalization brought the model into close agreement with the measurements. Indeed, many of the previous pages have been discussing the fact that this version performed worse in many ways than the base-version, in particular concerning the O:C ratio that this scheme was designed to capture. I also didn't understand the follow-up statement that it would be fair to hypothesize that this scheme would work well in a large scale 3-D CTM. This paper has provided plenty of evidence that this just isn't true.

Other points

P9860, first paragraph. Re-phrase "negative health outcome" in plain English.

P9861, line 28. The Jimenez et al. (2009) or earlier Donahue papers would be a better reference for the role of fragmentation.

P9862, 2nd sentence. Why mention urban enhancement in particular? Readers might be able to make a good guess as to what this means, but it seemed odd to bring up this rather specialist concept here, and in this way.

P9862, line 16. "performed reasonably well" is very vague. Quantify

P9865 What does "arrive directly from the North Atlantic" mean? These air masses did cross land at some point, they did not originate in the sea!

P9865, line 16. I would not call April a summer month in the Netherlands, rather spring.

P9866, line 11-12. A proper reference should be given for the emissions, the Kulmala et al papers are just an overview of the whole EUCAARI project. (The emission inven-

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tory developers would probably appreciate a better acknowledgement than a project deliverable code.)

P9866, line 20. Where did the chlorophyll-a data come from?

P9866. Deposition may play an important part in explaining OA mass arriving at sites such as Finnlakia and Mace Head, and even at sites closer to sources such as Cabauw (Bessagnet et al., 2010, Hallquist et al., 2009). Does the model apply the same deposition rates for all OA species? Which rates are used?

P9867. The terminology is confusing. It is strange to call the oxidation products of POA, "semi-volatile" SOA (sSOA)". Most of the BSOA and ASOA in this work is in fact semi-volatile. Find a better notation. (The terms ASOA and BSOA are well established also, why have these become aSOA and bSOA?)

P9868. Why is the OH rate four times higher for the IVOC-associated species than for the 'traditional' SOA?

P9869 line 15. The word aggressive is used without any quantification. This raises the question of the time-scale for this accumulation of mass - what is it, and does it justify the word aggressive?

P9870, line 12. The use of the summation notation here results in uneven formatting, without adding clarity. I would find it clearer to write something like ($\alpha_{2,j} = 0.5$, for all j) than having that equation with the \sum terms. Also, being picky, N_O should be defined earlier in the paragraph.

P9871, line 4. Be explicit about "previously". Do you mean above, or in another paper? P9873 on (Section 4.1) . As noted above, I missed a discussion of the correlation coefficients, and of how well the model performs for other compounds. I also wonder why the O:C results in Table 4 are 'encouraging'. The O:C results are way off, especially for the more detailed schemes that one would have hoped did best here. These problems are discussed well later in the paper, so I found this use of the word encouraging to be

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Interactive Discussion

Discussion Paper



surprising.

P9875, line 1. Why weren't the model predictions compared explicitly with SV-OOA and LV-OOA?

P9875, line 22. Quantify "faster".

P9880 on, Discussion. As noted at the start, this discussion fails to discuss many important factors, and much available literature and data. Table 1. No need for plurals on O I think, it looks strange.

Table 5 should be merged with Table 4. There is no reason to devise a new format for the same type of results, and it would be easier for the reader with one uniform Table.

Fig. 4. The notation here should match that used in the text.

Extra Refs

Bessagnet, B.; Seigneur, C. Menut, L. Impact of dry deposition of semi-volatile organic compounds on secondary organic aerosols Atmos. Environ., 2010, 44, 1781 - 1787

Gelencser, A et al., Source apportionment of PM_{2.5} organic aerosol over Europe: primary/secondary, natural/anthropogenic, fossil/biogenic origin J. Geophys. Res., 2007, 112, D23S04

Gilardoni, S. et al., Better constraints on sources of carbonaceous aerosols using a combined 14C - macro tracer analysis in a European rural background site Atmos. Chem. Physics, 2011, 11, 5685-5700

Simpson, D et al., Modeling Carbonaceous Aerosol over Europe. Analysis of the CAR-BOSOL and EMEP EC/OC campaigns J. Geophys. Res., 2007, 112, D23S14

Szidat, S et al., Contributions of fossil fuel, biomass burning, and biogenic emissions to carbonaceous aerosols in Zürich as traced by 14C J. Geophys. Res., 2006, 111, D07206

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Interactive Discussion

Discussion Paper

Yttri, KE et al., Source apportionment of the summer time carbonaceous aerosol at Nordic rural background sites Atmos. Chem. Physics, 2011, 11, 13339-13357

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 9857, 2012.

ACPD

12, C3192–C3197, 2012

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