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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.

B. N. Murphy et al.

spyros@chemeng.upatras.gr

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Responses to Referee #1

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:

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1) There is no discussion or presentation of the model's predictions of other, and better characterized, 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-known emissions and chemistry.

The model presented here is the 1-D version of the 3-D CTM PMCAMx-2008 using its modules and the corresponding emission fields. A detailed evaluation of PMCAMx-2008 has been presented by Fountoukis et al. (2011) for the same period and domain using measurements from the same field stations and also airborne measurements. They concluded that the model could reproduce well the observed fine PM concentrations and composition (e.g., 87% and 70% of the hourly OA and sulfate concentrations were within a factor of two). The main difference between the two models (other than the 1-D versus 3-D framework) is the treatment of the OA. The Fountoukis et al. (2011) study used the 1-D VBS framework for the description of the OA while here we investigate the ability of the 2-D VBS to reproduce the observations of OA.

The main weakness of the Lagrangian 1-D models is their inability to realistically account for horizontal dispersion processes. This together with the uncertainty introduced by the use of an altitude-independent wind speed increase the uncertainty of their hourly predictions (Seinfeld and Pandis, 2006). This is the reason that we have relied on comparisons of the average predictions and observations in this paper. This should be contrasted with our focus on the hourly comparisons in Fountoukis et al. (2011). Overall the performance of the 1-D model for the other fine PM species is similar but slightly worse to that of PMCAMx-2008. For example in Cabauw during the summer the average measured concentration was $1.7 \mu\text{g m}^{-3}$, the average predicted by PMCAMx-2008 was $2.4 \mu\text{g m}^{-3}$ and by the 1-D model $2.8 \mu\text{g m}^{-3}$. A detailed evaluation of the predictions of the 1-D species is outside the scope of the present work focusing on OA. We have added a brief discussion of the ability of the model to reproduce the concentrations of the other PM components in the revised paper.

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.

We agree with the reviewer that evaluation of models with just OA mass concentration is non-conclusive due to the many uncertainties involved. It is easy to get the right answer for the wrong reasons. If anything, the manuscript reinforces that point since two very different aging schemes result in similar prediction for mass concentrations. However, there is still significant value in the OA evaluation. If the model cannot reproduce the OA observations, it is clearly deficient.

We have removed the reporting of the correlation coefficients from the text as we feel this metric is not representative of the predictive power of this particular model and low correlation coefficients can be a symptom of the inherent physical limitations of the 1-D transport framework. Time series figures of organic aerosol mass and O:C predictions (for the base case and detailed functionalization-fragmentation case) against measurements have been added to the supplemental section. As the reviewer points out, this observation is a strong argument for use of O:C in model evaluation. We do not mean to definitively recommend one set of 2D-VBS parameters for use in large-scale models at this time. However, we do argue that certain model configurations, namely realistic functionalization routines without a fragmentation pathway, will lead to rampant overprediction under a variety of environmental conditions. The relatively low values of correlation coefficient are a feature of the 1-D model's physical simplicity. As noted above, horizontal dispersion is not accounted for. Moreover, only 6 hours of each observation day are simulated. Therefore, for every simulated point, there are four corresponding observation points (one each for the four closest hours). We have

added this discussion to the text.

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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.

This is a valid point. We have performed additional simulations for the intermediate case and added its results to the revised text.

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.

Particle-phase reactions and other oxidants (especially the nitrate radical) may be important in the wintertime for OA formation. This model does take into account oxidation of volatile organic precursors by the nitrate radical with the same yields applied as for OH and ozone reaction. However, aging by OH is assumed to be much more pervasive (even in the winter). We consider particle-phase reactions, although likely an important pathway for formation of low volatility organic compounds, to be outside the scope of this paper due to the uncertainty in forward and backward reaction rates at this time. It is also true that particle-phase reactions will not enhance O:C in the particle phase, unless significant fragmentation and volatilization of the more reduced fragment occurs. There is little to no data to constrain these processes at this time, but this will certainly

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be considered in future projects and can be easily incorporated into this general model framework. We have added this discussion to the text.

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 Yttri 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 modeling 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.*

We have added a discussion of this literature to our analysis of Fig. 4. We disagree with the statement that these papers “clearly demonstrate” that most OA in summertime is from BSOA. We think that they make a strong case that most of the OA is of biogenic origin and that BSOA is a significant component. Each one of these studies has their potential weaknesses. For example, the source-apportionment studies neglect the oxidation of levoglucosan in the summer. This may have resulted in an underestimation of the summer wood-burning contribution to OA.

6) *The paper has no discussion of the uncertainties in the emission inventories being used. These uncertainties are significant, and much of the discrepancy between modeled and measured OA could plausibly be blamed on emissions, especially in winter (e.g. as demonstrated by Simpson et al. 2007 using levoglucosan comparisons).*

We completely agree with the reviewer about uncertainties in the emissions inventories. Especially uncertain are the biogenic VOC inventories from MEGAN (Guenther et

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al., 2006) and the wood-burning emission inventories as pointed out by Simpson et al. (2007). These uncertainties can lead to well more than a factor of 2 uncertainty in the model's final OA mass prediction. We have added this important point to the text. We would further reiterate, though, that our focus is on the uncertainty introduced by the aging mechanism. Regardless of the magnitude of emissions from various sources, compounds begin their atmospheric residence time relatively reduced. Thus the inability of the model to capture moderately high O:C when fragmentation is introduced is likely a result of inaccurately modeling a chemical process as opposed to an emission factor.

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.

There may be some confusion here arising from the discussion in the text. We do not argue that the detailed functionalization case on its own performs well for predicting OA mass. Rather, it is necessary to include fragmentation in order to bring the model back into the vicinity of realistic OA mass predictions. We have changed this text to add clarity, and emphasize that the good performance for the detailed functionalization/fragmentation case is in relation to the poor performance of the functionalization case, and to the agreement with the base-case configuration, which has been shown to perform well in 3-D CTMs. The reviewer's point about O:C is correct and well-taken. The next paragraph goes on to discuss this issue. We have added a statement

cautioning readers about the possibility of this model missing important OA formation pathways that would enhance O:C (and possibly OA mass) predictions.

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Other points

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

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We have changed "negative health outcome" to read "increased mortality and morbidity rates."

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

Added.

10) 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.

We have removed the phrase.

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

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We have added performance statistics from the previous work.

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12) 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!

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When performing the back-trajectory calculation, HYSPLIT predicts these air masses to cross the western edge of the PMCAMx European domain and thus no input data is available to characterize their origin before that time. They may have originated further west, which presumably would allow the use of the 3-D model boundary conditions, assuming enough model time passes before the parcel arrives at the observation site. However, it is also possible that these trajectories turn south, for instance, just passed the western boundary and actually originate from the European continent. There is not enough information to constrain this so we ignore these days. We have added this detail to the text.

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

Corrected.

14) *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 inventory developers would probably appreciate a better acknowledgement than a project deliverable code.)*

This carbonaceous aerosol inventory was provided by Denier van der Gon and collaborators at the TNO. This has been added to the manuscript.

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

Chlorophyll-a data were acquired using the GES-DISC Interactive Online Visualization And aNalysis Infrastructure (GIOVANNI), part of NASA's Goddard Earth Sciences (GES) Data and Information Services Center (DISC). This has been added to the text.

16) P9866. Deposition may play an important part in explaining OA mass arriving at sites such as Finokalia 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?

Both wet and dry deposition are accounted for by the model. Dry deposition is a function of meteorological parameters and land use (not as important for particulate mass), while wet deposition is calculated from the precipitable water input from the WRF simulations. Since black carbon and sulfate seem to perform well for this model (see above), it is fair to assume deposition of OA is treated reasonably. However, scavenging of organics gases is an uncertainty. Here, we assume all organic gases have an effective Henry's Law constant of 2700 M atm-1. This sensitivity of mass predictions to this assumption has been explored in previous studies, but is still quite uncertain.

17) 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?)

We agree with the reviewer about the confusing nature of the acronym sSOA as it relates to the rest of the SOA system. An alternative name used in the past is oPOA to denote oxidized products of POA. However, this is in itself a contradiction. Because this manuscript directly follows Murphy et al. (2011), we prefer to keep the naming convention consistent with the previous work. In the near future, though, we will recommend a more generalized and self-consistent naming convention that should be helpful for the field to communicate without such confusing acronyms.

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

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The parameterization for IVOC aging is based on the work of Grieshop et al. (2009), where the rate of $4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ was found to predict smog-chamber formation of SOA from a diesel engine and wood cook-stove. In previous work (Murphy et al., 2009) we assumed that the traditional SOA compounds would have smaller carbon number and thus to first order, smaller reaction rate with OH. This is not strictly true as the presence of oxygenated functional groups will affect the rate constant. Note that the first generation of oxidation of traditional VOCs moves mass to volatility bins up to 8 orders of magnitude away in a single stage. Thus it's possible that the higher reaction rate for IVOCs is offsetting the erroneous fast initial formation of traditional VOCs. These uncertainties will be evaluated in future work and discussion has been added to the text.

19) *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?*

Aggressive is perhaps the wrong word-choice here and the reviewer's point about time scales is well-taken. As mentioned at the end of the sentence, this phenomenon is not faster than it should be. Instead, it may lead to overprediction at medium to long time-scales. At $4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $[\text{OH}] = 1 \times 10^6 \text{ molec cm}^{-3}$, the time-scale of oxidation is about 7 hours. Thus after 2 days, significant mass has reached from even the highest volatility bins to the volatility bins atmospherically relevant for partitioning to the particle phase. A better word for this phenomenon is then 'unyielding.' The change has been made.

20) *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 S terms. Also, being picky, N_O should be defined earlier in the paragraph.*

Changed.

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21) P9871, line 4. Be explicit about "previously". Do you mean above, or in another paper?

This refers to Murphy et al. (2011). We have updated the text.

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22) 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 surprising.

We have rephrased the sentence referring to Table 4. We originally added correlation coefficients for completeness, but due to inherent physical limitations of the 1-D trajectory model, we do not believe they effectively communicate information about the model's predictive power. Thus, we have removed them from Tables 3 and 4 and the rest of the manuscript.

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

PMF analysis of AMS data, as the reviewer points out, is certainly a valuable product that can be used to evaluate CTM predictions. Its application to the current work, though, is somewhat problematic. Because the base-case model predicts OA mostly in the semi-volatile range of volatility but across the full modeled range of O:C, it is difficult to group bins into LV-OOA and SV-OOA unless one draws a line at a particular

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O:C value. This has the same effect as comparing the observed O:C to the weighted-average predicted O:C. For the more detailed models, OA fails to approach the high O:C characteristic of LV-OOA and instead stays mostly in the SV-OOA range. Thus comparing these cases to PMF would only show again the inability of the corresponding scheme to predict high O:C. We chose not to use the comparison for this work. A thorough comparison to thermodenuder data appears in Murphy et al. (2011) and sensitivity to unknown parameters is quantified. This approach can help answer questions regarding the ability of the model to predict volatility.

24) *P9875, line 22. Quantify "faster".*

It is difficult to quantify this process since the base-case configuration will lead to build-up of products (which are reactants for the next generation) and then faster reaction rates. The nature of absorptive partitioning complicates the issue further as compounds that start in the semi-volatile range will be almost completely contributing to particle mass after one generation of oxidation under the detailed scheme. However, that same mass will still oxidize and contribute to the particle phase under the base-case scheme. We have rephrased the statement.

25) *P9880 on, Discussion. As noted at the start, this discussion fails to discuss many important factors, and much available literature and data.*

Discussion has been added as addressed above.

26) *Table 1. No need for plurals on O I think, it looks strange.*

Changed.

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27) 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.

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Changed.

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

Changed.

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 PM2.5 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 ^{14}C - 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 CARBOSOL and EMEP EC/OC campaigns *J. Geophys. Res.*, 2007, 112, D23S14

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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.

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

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