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Interactive comment on “Modeling meteorological and chemical effects of secondary organic aerosol during an EUCAARI campaign” by E. Athanasopoulou et al.

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We appreciate the positive comments and the valuable advice and suggestions.

(1) In general, I found some of the writing in the paper quite difficult to follow, often due to poor word choice or improper grammar. I would recommend careful copy editing for clarity and readability before resubmission. This observation is echoed by the other referee, who asks for clarification on some very basic/fundamental points concerning the model implementation.

Response: The text has been copy edited. Most corrections address the issues brought up by the two reviewers.

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Major issues:

(2) Like the other reviewer, I found the description of the SOA mechanism (Tables 1 and 2, P21822-21823) to be quite unclear and poorly documented and I have various questions concerning its implementation. I'm assuming the products with a postscript 'P' are the semivolatile products of reaction (e.g. OLTP) with bin-wise yields given in Table 2? The 'k' value given in the manuscript dictates the gas-phase reaction of the semivolatile vapors associated with SOA production, does that k also dictate the reaction rates of the SOA precursors? Finally, the VBS C* distributions in Table 2 are given with no references – from where are these derived?

Answer: We have added the requested clarifications to the revised paper. More specifically: The products of the reactions given in Table 1 with the postscript 'P', were the semivolatile organic products of the corresponding reactions with the yields given in Table 2. To avoid confusion we have named SOA1, SOA10, SOA100, and SOA1000 the four SOA species with the corresponding C* and combined Tables 1 and 2 into one new Table. This is now explained in the footnote of Table 1. The rates of the chemical reactions in Table 1 are the same as in SORGAM. The corresponding reaction rates are not equal to k (the aging rate constant). The aging rate constant is used for the aging reactions that is those converting the gas-phase SOA1000 to SOA100, the SOA100 to SOA10, and the SOA10 to SOA1. This is now clarified in the revised text. The C* distributions used are those suggested by Lane et al. (2008). A reference has been added to Table 1.

(3) The authors chose a particular implementation of a VBS modeling scheme for implementation in their model, but there are others possible. The model chosen includes a 1-bin shift in volatility per generation of oxidation and a 7.5% increase in mass. Other modeling studies have tried alternate implementations [Hodzic et al., 2010]. It should be acknowledged that the mechanism is primitive and uncertain (and in fact somewhat arbitrary) and that there may be large sensitivity to choice of parameters.

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Response: This is indeed a simple parameterization of the SOA chemical aging process, through the oxidation of the corresponding compounds in the gas phase by the OH radical. This approach was originally proposed by Robinson et al. (2007) who fitted the corresponding data during SOA formation from evaporated primary organic particulate matter. It does represent a net average change in volatility in a complex reactive system where both functionalization reactions (leading to decreases in volatility by more than one order of magnitude) and fragmentation reactions (leading to an increase in volatility are taking place). This approach has been found to give reasonable results in a variety of environments despite its simplicity. A number of more complex but also more realistic schemes has been recently tested by Murphy et al. (2012), but surprisingly this one-volatility bin shift scheme resulted in the best agreement with the observations. While it is clearly a first step in simulating chemical aging, it appears to capture some of the essential elements of the corresponding processes. This makes it a very good choice for models coupling on-line meteorology with atmospheric chemistry, such as COSMO-ART. We have added discussion on these points in the revised paper.

(4) Related to this, there is much evidence that a simple 1-d VBS cannot represent the multigenerational chemistry that SOA undergoes, as it will continually add mass while actual atmospheric oxidation will form less-volatile products via fragmentation reactions [Donahue et al., 2012; Jimenez et al., 2009; Kroll et al., 2011]. It would be good to include some discussion of the limitations of the 1-d approach and where it could potentially be improved.

Response: Murphy et al. (2012) recently tested an extension of this simple scheme in the 2D-VBS, together with more complex functionalization only, and functionalization/fragmentation schemes. This simple one-bin shift scheme had the best performance when compared to ambient measurements in Europe. Our explanation was that this scheme appears to represent the net change in volatility during the complex reactions that take place in the atmosphere. At the same time, our understanding

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of the details of the functionalization/fragmentation reactions remains incomplete, and thus the corresponding more complex models still have worse performance than the simple scheme used here. We have added discussion of this important point to the manuscript.

(5) The discussions of HOA/POA and OOA/SOA are somewhat confused and unclear in the manuscript, and this leads to some erroneous statements. HOA (“Hydrocarbon-like OA”, not Hydrogenated as stated at the top of P21817) and OOA are AMS factors and do not directly correspond to POA and SOA. HOA has been tied to primary combustion emissions (using tracers like CO and BC) and not necessarily to POA as it would be recognized in your model emission inputs. The fact that this model does not treat POA as semivolatile misses the fact that some components often counted as POA in models (SVOCs associated with combustion emissions) can contribute substantially to the OOA mass once they evaporate and oxidize in the atmosphere [Jathar et al., 2011; Murphy and Pandis, 2009; Pye and Seinfeld, 2010]. The fact that you are not treating semivolatile/aging POA is clearly stated, but I think discussions of and distinctions between HOA and POA (e.g. P 21823, L9-11; P21833, L5-7) need to be clarified and this identified as a potential shortcoming. HOA appears to be the fraction of POA from combustion engines and similar sources that is initially in the aerosol phase at ambient conditions, as measured by the AMS, and will likely not age substantially (as stated) – however, SVOC vapors often measured as POA in source testing will age and contribute to OOA.

Response: We have corrected the typo regarding HOA. We have added clarifications regarding our treatment of POA and the issues that this introduces when it is compared to the AMS HOA factor.

(6) P21834, L17-27: How confident are you in the parameterization of cloud cover and the feedbacks between aerosols and cloud cover? Are the changes in average and spatially-resolved forcing due to changes in cloud cover actually significant relative to uncertainty in model output? Some discussion of this would be helpful to put these

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results in context.

Response: In order to address this issue, we have modified and lengthened the discussion in Section 4.3. The cloud cover parameterization used includes schemes for predicting grid-scale, diagnostic and convective clouds. While the first two schemes are quite robust, the initiation of a convective cloud within each grid cell is highly sensitive to several parameters. For example, changes in temperature due to the interaction of SOA with radiation could lead to the formation of clouds in cells that were cloud-free under a non-SOA regime. These changes in the cloud cover have a semi-direct effect on radiation and temperature and lead to nonlinear interactions among various processes. The result is a noisy-spotty pattern of SOA effects on cloud cover, which is indeed somewhat uncertain in terms of its spatial resolution. This is the reason that our analysis of the SOA radiative effects focused on the regional scale and not on specific areas. Local changes are mentioned in order to explain the interactions among processes and not to draw conclusions about the impact of SOA in specific areas. Vogel et al. (2009) found that during a cloud-free episode the aerosol radiative forcing is negative and spatially correlated to the aerosol field, whereas total-sky situations (as the case studied in the current article) result in smaller, even positive temperature changes, spotty and spatially uncorrelated to the forcing. The high spatial sensitivity of the cloud formation mechanism, poses some uncertainty in the spatially-resolved forcing. Nevertheless, the average regional radiation and temperature changes over Europe are robust. As shown in Table 5, aerosol mass affects radiation and temperature, without the interference of any cloud cover changes averaged over Europe during May 2008.

Minor Issues

(7) P21822, L2 – ‘saturation concentration’ – this usage doesn’t make sense to me, as this should not be affected by ‘a pre-existing internal mixture of aerosol compounds’. Unless you’re talking about the C^* of a given bin being dictated by the properties of the mixture of specific compounds that get lumped in the bin? In any case, this is not clear.

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Response: This is a valid point. Effective saturation concentration (C^*) is the appropriate term here. This has been corrected in the revised paper.

(8) P21822, L23 – ‘deprive the model’s capability’ – not clear.

Response: We have deleted this statement to avoid confusion.

(9) P21823, L26- ‘volatility concentration’ is not a meaningful term, maybe ‘effective saturation concentrations’?

Response: This has been corrected.

(10) P21824, L13 – ‘large increase in aerosol direct radiative forcing’ – won’t this typically cause a decrease (increase in the negative direction?).

Response: Corrected.

(11) P21824, L14-15 – It hasn’t been made clear at this point why this is an ideal period to model as you haven’t described it. You should qualify this statement with a brief description of the period.

Response: We added information about the simulated period at this point.

(12) P21824, L25 – OA isn’t ‘supposed to’ do anything, ‘observations suggest that OA reaches a stable oxidation state’

Response: The phrase has been corrected.

(13) P21828, L6 – ‘Section 4.4’ should read ‘Section 4.3’. Response: Corrected.

(14) P21829, L23-24 – Reading this I expected Fig. 3 will include results from other models. You should clarify that you’re just comparing domain averages here.

Response: We have rephrased to avoid confusion.

(15) P21830, L2-3- ‘differences: : : are not significant’ The difference between PM-CAMx and COSMO-ART for domain average OA seems to be about 30%, is this not

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significant?

Response: We have rephrased this sentence just mentioning an overall estimation for the predictions of the models without any comment regarding their significance.

(16) P21835, L18-23 – Probably a good place to also mention/discuss the potential for ‘missing’ contributions from the boundary (e.g. the intrusion of African OA observed for May 19-21).

Response: This point has been added.

(17) P21836, L1-16 – You make comparisons between the ‘base’ SORGAM model (Scenario 6) output with other model configurations at the different sites, but results are only shown for Cabauw. Why are these simulations not shown (but only summarized in text) for the other sites?

Response: Given the significant discrepancies between the SORGAM predictions and observations at these sites we did not think that the addition of more figures with these results would add much to the paper. Moreover and throughout the whole article, model results are schematically presented only when measurements are available (during this period, measurements existed only at Cabauw).

(18) P21836, L23 – PMCAMx also includes aging of POA (SVOCs), correct?

Response: Yes this is mentioned in the original manuscript and has been added to this section as well in the revised version.

(19) P21839, L1-2 – How do ‘nonurban sources’ contribute to the model if they are not explicitly included in the model?

Response: This has been now changed to ‘non-anthropogenic’. They contribute through SOA from the boundaries. This clarification has been added to the paper.

(20) P21840, L2- ‘biogenic activities’ should be ‘biogenic precursors’ or ‘biogenic emissions’

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Response: Corrected.

(21) P21841, L23 – ‘is now eradicated from COSMO-ART chemistry’ – this is an over-statement. It appears that the addition of this SOA ‘mechanism’ improves predictions of inorganic aerosol concentrations.

Response: This phrase is now changed to “nitrate overestimation and sulfate under-estimation found by Knote et al. (2011) are reduced after the current modifications in COSMO-ART chemistry”.

(22) Table 5 – I found this table very confusing at first – can this be reformatted? It could also be deleted as most of these values are included in the text.

Answer: The table has been reformatted.

(23) Figure 7 - It would be interesting to see change in OH expressed in a meaningful unit – perhaps molecules/cc?

Response: The units of OH values are now changed to molecules/cm³

(24) All multi-panel figures – it is helpful to have a short label (e.g. indicating the city or date) next to the panel letter to make it easier for the reader to quickly identify.

Response: We made this change to all multi-panel figures.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 21815, 2012.

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