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Interactive comment on "Organic aerosol concentration and composition over Europe: insights from comparison of regional model predictions with aerosol mass spectrometer factor analysis" *by* C. Fountoukis et al.

Anonymous Referee #2

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The authors compare model predictions from a regional chemical transport model to an extensive set of AMS measurements made over Europe. The key finding of this work is that the current treatment of OA (semi-volatile POA, SOA formation from anthropogenic and biogenic VOCs and the multi-generational aging schemes from the group at Carnegie Mellon University) appears to be sufficient in predicting the concentrations and [AMS-resolved] composition of OA. The paper also highlights that biomass burning OA emissions might not be well presented in the model.

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The paper is novel in that it undertakes a systematic evaluation of model predictions against AMS measurements made at several different locations and times. While I see no problems with the methods and the analysis, I feel the manuscript does not do justice in discussing the large model uncertainties. In fact, I am surprised that their model-measurement comparison is decent despite the fairly unconstrained and largely uncertain treatment of OA. This implies that the existing OA treatment mimics the average atmospheric chemistry of OA (or that it has compensating errors). I also think that their conclusion about an under-estimated biomass burning OA inventory is weak and encourage them to explore other explanations for their poor comparison at biomass burning sites.

I recommend the publication of this paper once the authors have addressed my comments below.

-Major comments-

1. Biomass Burning OA

One of the key findings based on the fPOA under-predictions is that biomass burning POA is not accurately represented in the model. As the authors point out, this could be because the emission inventories underestimate POA emissions from biomass burning sources and/or the volatility distribution of the POA used in the model (based off diesel exhaust) is not appropriate for use with biomass burning emissions. Given that, I find that the authors have only stated the former hypothesis in the abstract. Is there a reason why the authors think it could be an inventory problem and not a volatility distribution problem? Their reasoning in the 'Conclusions' section that a lower-volatility distribution compromises the OOA model performance is not strong enough to justify that the inventory underestimates biomass burning emissions (although it might be the most uncertain); see point (2) below for a discussion of other model uncertainties that could influence BBOA evolution or see point (3) below for an alternative explanation of how the OOA model performance could be improved through the inclusion of additional

SOA formation pathways.

I was excited to see what the application of the May et al. volatility distribution for biomass burning sources would do to model predictions but was disappointed to find out that the volatility distribution was applied to all the sources. Was this done because the model cannot be run in a source-resolved manner? Can PSAT be used to do this? If the model cannot track each source separately, it would still be possible to incorporate the source-resolved volatility distributions (from the May et al. papers) by building a source-weighted hybrid volatility distribution.

On a related note, what enthalpy of vaporization was used to capture the variation of fPOA with temperature? Was it treated as a function of the volatility (Epstein et al., 2010)?

2. Model Uncertainties

While the parameterizations to represent the emissions and thermodynamic and chemical behavior of OA have been used previously by various research groups (and hence well published), it is still prudent to think about where they come from, what they mean and how can they be improved for future modeling exercises. In this study the most uncertain representation, I believe, is the one for the multi-generational aging of fresh POA and semi-volatile SOA vapors (the one that marches organic mass down volatility street). First, the scheme has been fit to a smog-chamber experiment conducted on emissions from an uncontrolled diesel engine. Clearly, real-world sources are very different than uncontrolled diesels. Second, the parameters reproduce aging over the course of 12 to 24 hours. Real-world emissions spend a lot more time in the troposphere than simulated in that experiment. And finally, the scheme assumes that those same parameters would continue to form more organic aerosol over the timescale of days to week and ignores the role of fragmentation. I understand that this is a very general critique and addressing it might be beyond the scope of this work (since there are not a lot of data to constrain multi-generational aging). Despite that, I would like

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to see some discussion of this issue in the manuscript to avoid giving the reader the false sense that the parameterization to model multi-generational aging is robust and well-constrained. In fact, I would argue that it is much more uncertain than some of the other sensitivities (volatility distribution, factor analysis method) explored in this paper.

The next most uncertain parameter, given the conclusion from Figure 4 that OPOA is a dominant component of OA, would be the emissions of IVOCs. The current scaling of 1.5 was a guesstimate. Although there are no direct IVOC measurements to build an inventory, could the May et al. data be used to improve the '1.5' guesstimate? How sensitive would the model-measurement comparison be to the magnitude of the IVOC emissions?

Another uncertain input, is the volatility distribution of POA emissions and how they need to be applied to in-place POA emissions inventories. While the authors discuss the former, they do not address the later. Emission inventories are built on POA emission factors measured at varying organic aerosol concentrations and temperatures. When applying a volatility distribution to a POA emissions rate, one needs to be cognizant of the OA concentration and temperature at which the emission factor was measured to ensure that volatility distribution is applied to the right set of VBS bins. For example, a BBOA emission factor measured via a plume-chase study (lower OA concentrations) would need to be applied very differently to a given volatility distribution than if the BBOA emission factor were measured in say a dilution tunnel or a burn chamber (higher OA concentrations). Briefly, the task to divvy the POA emissions across the basis set bins is not trivial even if one knew the exact volatility distribution. I would expect the authors to discuss this issue when they explore the sensitivity of the model-measurement comparison to the volatility distribution.

3. Additional pathways to SOA formation

While the gas-phase routes appear to be "well-represented" (see earlier comments (2)), there does not seem to be any mention of in-cloud or aqueous-phase SOA forma-

tion. Specifically, I am referring to the in-cloud oxidation of glyoxal and methylglyoxal (Carlton, ES&T, 2008), oligomer formation from semi-volatile SOA products (Kalberer, Science, 2004; it could be argued that the present aging scheme considers this) and organosulfates and tetrol formation from isoprene epoxide (Paulot, Science, 2009). Have these pathways been incorporated in this model or another model that simulates air quality over Europe? These pathways have been found to be quite important in the Southeast US that have large emissions from biogenic sources. Given the contribution of bSOA in Figure 4, I would expect these pathways to be important in this modeling study too and increase predictions of OOA concentrations (this increase might be sufficient to justify a lower volatility BBOA that would increase fPOA concentrations without compromising on OOA model performance). In the revised manuscript, I would expect the authors to include these pathways of SOA formation in their model or provide evidence for why these are not important for the episodes modeled in this study.

4. Model Evaluation

How does the model do on primary (CO, EC) and photochemical species (ozone, sulfate, nitrate) at these sites? Primary comparisons can shed light on mixing and transport while secondary comparisons can help build confidence in the oxidant pool that is an important driver of SOA formation.

The comprehensive model comparison against AMS data is novel but it would be helpful to also evaluate the model against speciated filter data across Europe. I see that filter measurements during the EUCAARI campaign were used to evaluate the model at four different sites. Are there pan-European air quality monitoring data to provide a more comprehensive evaluation. Would those comparisons support the conclusions in this paper? For example, an under-estimated biomass burning inventory should also result in poor EC performance.

5. Volatility Basis Set

The volatility basis set (1D and 2D VBS) is a very convenient and efficient framework

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to represent the thermodynamics and chemistry of organic gases and particles. However, the framework is separate from the processes it has been used to represent (semi-volatile behavior of POA, multi-generational aging, dependence of fragmentation with oxygenation and such). In other words, the VBS is just a framework to model processes and is separate from the scientific understanding/theory that the community has developed. That POA is semi-volatile and evaporates with dilution or heating is a theory and has nothing to do with the VBS. There are several instances in the paper that makes it sound like VBS and the process parameterizations are one and the same thing. For example, line 28 on page 7601: "Recently, CTMs have successfully implemented the VBS improving predictions of OA when compared to measurements (Murphy and Pandis, 2009; Tsimpidi et al., 2010; Fountoukis et al., 2011; Bergstrom et al., 2012; Zhang et al., 2013)." or line 17 on page 7602: "They found that implementing the VBS signiïňĄcantly improves model predictions of SOA, while depending on the emission inventory used, SOA levels tend to be overestimated." or line 11 on page 7603: "The OA treatment in PMCAMx is based on the Volatility Basis Set (VBS) approach". The VBS does not represent any approach; it merely represents a framework to model a particular approach, whatever that might be. If one desired, one could represent POA as non-volatile in the VBS. I would recommend the authors to revise the manuscript to address this distinction.

-Minor comments-

1. The terms OOA and C^* in the abstract have not been defined and might be difficult to follow for someone who is not familiar with the AMS and the VBS respectively.

2. On line 10 of page 7604, the authors write "The base-case simulation assumes that the chemical aging reactions of biogenic SOA (including both functionalization and fragmentation reactions) do not result in a net change of the bSOA concentration and thus it effectively neglects the chemical aging of biogenic SOA.". Although the concentration does not change, it will definitely change the distribution in the C^* bins and subsequently the distribution in the SV-OOA and LV-OOA categories.

3. Do the BBOA emissions used in this study represent the emissions for that particular year? I am mostly alluding to including the relevant year's wildfire emissions.

4. The trends in the diurnal profiles are not clearly visible given the range on the Y-axis; at present they appear flat. I would recommend relocating the legend and changing the range on the Y-axis.

5. Similarly to (1), I would change the X- and Y-axis range on the scatter plots so the data occupy more of the figure and trends/data points are more visible. Currently, there is a lot of white space.

6. I would recommend putting a legend on Figure 1 showing what the symbols mean.

7. I did not see a mathematical definition of fractional bias, fractional error, mean error and mean bias. Although fairly standard statistical metrics, it will not hurt to include them.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 7597, 2014.