

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.

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Received and published: 2 June 2014

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

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burning OA emissions might not be well presented in the model. 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.

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As stated in section 4.4 the use of another volatility distribution (which is used for all primary OA sources) should be viewed as a sensitivity test and not as a test of the actual volatility distributions. That being said, the hypothesis that the under-prediction of fPOA is due to the volatility distribution used in the base case simulations (based on diesel exhaust) cannot be fully tested here. However, we understand the reviewer's concern here and we have added this additional potential explanation in the abstract.

We think that the main problem with the deterioration of the model performance for OOA when using the May et al. BBOA volatility distribution for all sources is that this distribution covers saturation concentrations up to $10^4 \mu\text{g m}^{-3}$ while the base case volatility distribution in the model goes up to $10^6 \mu\text{g m}^{-3}$ with the total amount of emissions in the latter case being higher due to the addition of the IVOCs.

(2) *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.*

Unfortunately, the PMCAMx-2008 version used in this study assumes by default that all primary OA species have the same volatility distribution and thus simulates only one set of primary OA surrogate compounds together with their corresponding oxygenated forms. Therefore, we cannot vary the volatility distribution of the BBOA independently of that of the other primary OA emissions. PSAT cannot help here, because this is a limitation of the underlying CTM. The source-weighted distribution also is not helpful because the sources have very different distribution in space and time. Its results will be very similar to the sensitivity study presented in this paper. We have developed a source-resolved version of PMCAMx (called PMCAMx-SR) that relaxes this assumption.

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tion using different volatility distributions and aging schemes for each source. The description of PMCAMx-SR and its evaluation will be submitted for publication in the immediate future.

(3) *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)?*

Yes the enthalpy of vaporization that is used for fPOA is a function of the volatility. We use the values reported in Table S1 of Murphy and Pandis (2009). We have now added this information in the manuscript.

(4) 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 to see some discussion of this issue in the manuscript to avoid giving the reader the

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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.

We do agree with the above points. We did not intend to convey such a high degree of confidence on the aging parameterization of the model given its oversimplifying assumptions. As suggested by the reviewer we have now added text in Section 5 of the revised manuscript to discuss the various major uncertainties as well as relevant references. For example Murphy et al. (2011) explored a 2-bin reduction in volatility upon one oxidation step with a simultaneous decrease (by a factor of 2) of the aging rate constants and found a slight underprediction of the OA mass observed at Finokalia during May 2008 compared to the base case 1-bin shift. Hodzic et al. (2010) and Grieshop et al. (2009) investigated a 2-bin reduction (in addition to the 1-bin base case saturation concentration reduction) with a reduced OH reaction rate constant and found both to perform adequately. Murphy et al. (2012) added a detailed functionalization scheme that employed the fundamentals of group contribution theory to approximate the effect on volatility of adding relevant functional groups to the carbon backbone (Donahue et al., 2011). This approach alone resulted in a significant increase of OA mass. Adding fragmentation to the detailed functionalization scenario decreased OA mass concentrations to the approximate magnitude predicted by the base case (which employs a simplified scheme that is currently used in PMCAMx) and brought the model into reasonable agreement with the OA mass concentration measurements. In our base case aging scheme we use this simplified scenario that tries to describe the net effect of the chemical aging reactions (both functionalization and fragmentation) without treating any of the two types explicitly. The chemical aging scheme is an important source of uncertainty in the model and there is always the possibility of compensating errors.

(5) *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*

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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?

Unfortunately, the May et al. BBOA volatility distribution covers saturation concentrations up to $10^4 \mu\text{g m}^{-3}$ while the “1.5” estimate for the additional IVOC emissions covers a range of saturation concentrations between 10^3 and $10^6 \mu\text{g m}^{-3}$. There have been a number of studies (Tsimplidi et al., 2010; Hodzic et al., 2010) which have explored the sensitivity of VBS schemes to the IVOC emissions and have demonstrated their potential importance. We have added some text to discuss this important source of uncertainty.

(6) *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.*

This is a valid point and we completely agree with the reviewer here. We have added some text in section 4.4 to point this out as another source of uncertainty.

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(7) 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 formation. Specifically, I am referring to the in-cloud oxidation of glyoxal and methylglyoxal (Carlton, EST, 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.

Murphy et al. (2012) explored the contribution of aqueous-phase (in-cloud) SOA formation by glyoxal and methylglyoxal in several European sites (Mace Head, Cabauw, Finokalia) that are also studied in our work during both May 2008 and February/March 2009. They found small enhancements to both average OA mass loadings (< 3 percent) and O:C (< 10 percent) at the surface. Their estimated absolute OA production from this pathway was lower (in absolute magnitude) than that estimated by Carlton et al. (2008) or measured during the CalNEX campaign but the contribution to total SOA formed was similar (a few percent). Please note that the predicted biogenic SOA concentrations shown in Figure 4 are partly background OA coming from the boundary conditions and are not due to local production. Also the bSOA concentrations are quite lower (by approximately a factor of three) than those in the Southeastern US. Aqueous-phase SOA formation from glyoxal and methylglyoxal was also investigated

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by Myriokefalitakis et al. (2011) in the global 3-D chemistry/transport model TM4-ECPL. The estimated effects over continental Europe were modest to small. We have added text summarizing these points in the revised manuscript.

(8) 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.

This is true provided that the primary emissions are well represented in the corresponding inventory. If not, then the comparison for primary and photochemistry-driven species will be inconclusive. To address the reviewer's point we have added a discussion of the model performance for particulate sulfate and elemental carbon during all three periods. Briefly, the model compares well with the AMS measurements for fine particulate sulfate concentrations in all three periods and sites. The best performance is seen in May when the model reproduces 70 percent of the data within a factor of 2 (FERROR=0.4, FBIAS=0.1). The largest discrepancy is seen in the winter period (FERROR=0.7, FBIAS=0.3) when the model overpredicts sulfate in Mace Head and Finokalia and underpredicts in Melpitz while the comparison is more encouraging at the rest of the sites. During the September/October 2008 period the comparison is better than during winter with the model reproducing 60 percent of the data within a factor of 2 (FERROR=0.6, FBIAS=-0.1). For EC the model tends to under predict concentrations (FERROR=0.8, FBIAS=-0.35) during all periods especially at suburban sites influenced by local pollution (e.g. Melpitz) although the number of available data were limited for May and fall (27 data points for fall, 95 for winter and 26 for the May period).

(9) The comprehensive model comparison against AMS data is novel but it would be

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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.

Unfortunately there is no pan-European network that systematically provides filter-based data for all these species. We have collected however EC data for these periods and have added this comparison in the manuscript (see reply to the above comment). Indeed there seems to be a systematic underprediction of EC concentrations that supports the conclusion about the underestimated biomass burning emission inventory. However, this could also be due to incompatibilities of the semi-empirical EC definition used in the emission inventory and that used by the various European sites.

(10) Volatility Basis Set

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

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the VBS significantly 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.

This is a valid point. The framework is different from the actual parameterizations of the various physical and chemical processes. We have re-phrased all such sentences in the revised manuscript accordingly.

Minor comments

(11) *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.*

The C* has now been defined in the revised version of the abstract. The OOA was defined in the initial version.

(12) *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.*

Further gas-phase oxidation of bSOA vapors (aging reactions of bSOA) do not result in the one-bin volatility shift that is assumed for the primary OA and aSOA. We have added this to the text to further clarify this assumption.

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(13) 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.

Yes, the wildfire emissions are representative of the specific year, month and day.

(14) 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.

We have redrawn the figures following the reviewer's recommendation.

(15) 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.

We are using a scale that tries to cover the full range of measurements and predictions.

(16) I would recommend putting a legend on Figure 1 showing what the symbols mean.

Done.

(17) 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.

We have now added the definitions in the revised text.

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