

## Responses to the comments of anonymous referee #1

Thank you for your comments which helped to improve our manuscript. Please find below your comments in blue, our responses in black and modifications in the revised manuscript in *italic*.

In the manuscript by Ciarelli et al. a modified VBS scheme for biomass burning-like OA is implemented in the chemistry transport models CAMx. The new VBS scheme was developed by the authors and is described in a paper under review in the GMD (Ciarelli et al., 2016b). CAMx is then used to simulate the wintertime OA mass concentration in Europe in Feb-Mar 2009. The model results are compared with model results from simulations using a different VBS scheme for biomass bring-like OA (Ciarelli et al., 2016a) and with AMS measurements from 11 stations around Europe. The manuscript addresses a very relevant and important topic: the contribution of small-scale residential (mainly wood) combustion to the OA mass loading in Europe during wintertime. My review mainly focuses on the method section, which I partly found quite hard to understand. I have a few critical questions concerning how the different VBS methods was applied which would like to get answered and also explained clearly in the manuscript. If this is done properly and the new VBS parameterization is considered to be scientifically sound by the reviewers of the GMD manuscript Ciarelli et al.,2016b, then I think the manuscript can be suitable for publication in Atmospheric Chemistry and Physics.

More general comments mainly concerning the method:

1.

Is it correct that the only difference between the base case model runs from Ciarelli et al., 2016a and this new study is that you use the new VBS sets (called VBS\_BC\_NEW) instead of VBS\_BC to describe the OA formation from biomass burning emissions? If the answer on this question is Yes, which I hope is the case, then please state this clearly in the manuscript. If e answer is No, you have to clearly explain all differences between the two different model runs.

The answer to this question is yes; all model input data prepared for Ciarelli et al. (2016a) were kept the same for this new application (VBS\_BC\_NEW). The model scheme to treat biomass burning like organic aerosol was updated based on Ciarelli et al. (2016b) which was accepted for final publication in GMD.

2.

Is it correct that you in total use 3 VBS sets to describe OA formation from biomass burning, 1 set for fresh HOA from fossil fuel combustion, 1 set for aged oxidized HOA, 1 VBS set for BVOC oxidation products (no ageing considered). Thus in total 6 VBS sets? I think you need to describe this more clearly in the manuscript and how this compares to the VBS sets used in Ciarelli et al., 2016a.

We agree with the referee that further description of the VBS sets is needed in the manuscript. The model deploys 3 sets to treat biomass burning-like aerosol (as shown in Ciarelli et al., 2016b) and 2 sets to treat HOA-like aerosol, based on Koo et al., (2014). In addition, it assumes that the primary semivolatile vapours from the HOA generate SOA, and not POA, upon oxidation with the OH radical and further condensation in the particle-phase. However, we don't have a separate set to allocate oxidation products from biogenic precursors, and they follow the same oxidation pathways of biomass burning-like aerosol as in the previous case (Ciarelli et al., 2016a), including aging. We are currently working on an updated version of CAMx which includes the separation of biogenic sources. In our reply to comment 8, we present a sensitivity test with no biogenic SOA formation in order to better address the importance of this source.

We further clarified this point as follows:

at line 179 of the revised manuscript

The third set allocates oxidation products from the traditional VOCs and biogenic precursors (xylene, toluene, isoprene, monoterpenes and sesquiterpenes)

and at line 185-186:

*This implies that also aging of biogenic products is implicitly taken into account.*

Moreover, we added Table 1, as suggested in comment 4, to clarify all the different sets used in the model (as also suggested by referee #2).

3.

In Ciarelli et al. (2016a) for further aging of ASOA and POA vapors from HOA-like emissions you use a reaction rate with OH of  $2 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . How about this new study? Was it  $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$  instead or is this only the reaction rate used for BBOA precursors?

A reaction rate of  $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$  was used to treat aging of biomass semivolatile SOA which we also applied to the rest of anthropogenic sources (referred to as HOA in the manuscript) in order to be consistent among all the other anthropogenic sources and as already proposed by more recent studies for the range of saturation concentrations used here (Donahue et al., 2013; Jo et al., 2013; Hodzic et al., 2016).

We added the following information at line 187 of the revised manuscript:

*A reaction rate of  $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$  was also applied to the rest of the anthropogenic sources (referred to as HOA ) in order to be consistent among all the other anthropogenic sources as already proposed by more recent studies for the range of saturation concentrations used here (Donahue et al., 2013).*

4.

I suggest that you create a table where you list all VBS sets used in the two different model simulations and if they represent SOA or POA, the sources (i.e. BVOCs, biomass burning or fossil fuel burning) and if they represent HOA, BBOA or Biogenic OA. As the manuscript is written now I get very confused about which organic compounds that are POA and SOA, their origin and if they are classified as HOA, BBOA or Biogenic OA. If I understand it correctly the BBOA is only the not atmospheric processed (oxidized) POA emission from biomass burning, and the POA from biomass burning sources that evaporates and then form more oxidized OA is treated as SOA (VBS\_BC\_NEW set 2) and the VBS\_BC\_NEW set 3 OA is always treated as SOA. I think you need to more clearly state that BBOA is only referring to the POA from biomass burning but not the SOA formed from biomass burning. I suggest that you change from BBOA to BBPOA. It is only in the abstract L40-41 that you mention that BBOA is referring to primary biomass burning-like OA and HOA primary hydrocarbon-like OA. I missed this and was confused about this when I was reading the manuscript the first time.

We agree with the referee and added Table1 listing all the sets/sources that we used. We also changed BBOA to BBPOA throughout the manuscript in order to clarify that BBOA refers only to the primary fraction.

*Table 1. Properties of the VBS space. Oxygen numbers for each volatility bin were calculated using the group-contribution of Donahue et al. (2011). Hydrogen numbers were calculated from the van Krevelen relation (Heald et al., 2010).*

	log (C*)	Oxygen number	Carbon number	Hydrogen number	Molecular weight
POA set1* (BBOA-like)	-1	4.11	11.00	17.89	216
Primary biomass burning (BBPOA)	0	3.43	11.75	20.07	216
	1	2.73	12.50	22.27	216
	2	2.01	13.25	24.49	216

	3	1.27	14.00	26.73	215
SOA set2*	-1	4.53	9.00	13.47	194
(BBOA-like)	0	4.00	9.25	14.50	189
SOA from SVOCs	1	3.40	9.50	15.60	184
biomass burning	2	2.83	9.75	16.67	179
SOA set3*	-1	5.25	5.00	4.75	149
(BBOA-like)	0	4.70	5.25	5.80	144
SOA from	1	4.20	5.50	6.80	140
VOC/IVOCs biomass	2	3.65	5.75	7.85	135
burning and biogenics	3	3.15	6.00	8.85	131
POA set1**	-1	2.69	17.00	31.3	278
(HOA-like)	0	2.02	17.50	33.0	275
Rest of primary	1	1.34	18.00	34.7	272
anthropogenic sources	2	0.63	18.5	36.4	268
	3	0.0	19.00	38.0	266
SOA set1**	-1	4.90	7.00	9.10	172
(HOA-like)	0	4.38	7.25	10.1	167
SOA from rest of all	1	3.84	7.50	11.2	163
anthropogenic in all	2	3.30	7.75	12.2	158
volatility range	3	2.74	8.00	13.3	153
(SVOCs,IVOCs,VOCs)					

\*Based on Ciarelli et al. (2016b).

\*\*Molecular structure as in Koo et al. (2014) and Ciarelli et al. (2016a).

5.

The new version of the model underestimates the OA to a less extent than the previous version. The only difference between the model runs is how the BBOA formation is treated. On L306-307 you write: “The modelled BBOA fraction on the other hand was generally higher than the measurements, with an average MFB of 50% (Table S3, Figs. 6-7)”. I interpret this as that the model improves the modeled total OA but at least partly for the wrong reason because it gives too much BBOA.

The model improves mainly because more SOA is predicted for the investigated period, whereas statistics for the POA fractions remained almost unchanged (Table 3 and Table 4 in the revised manuscript). The BBPOA fraction remained almost unchanged respect to the VBS\_BC scenario (Table S4).

We reformulated the sentence at line 321 of the revised manuscript as below and added Table S4:

*The modelled BBPOA fraction on the other hand was generally overpredicted as in our previous application (Table S4), with an average MFB of 50% (Table S3, Figs. 6-7)*

Table S4. Comparison of statistics for BBPOA in VBS\_BC\_NEW with VBS\_BC (average of all sites in February-March 2009)

	Mean obs ( $\mu\text{g m}^{-3}$ )	Mean mod ( $\mu\text{g m}^{-3}$ )	MB ( $\mu\text{g m}^{-3}$ )	ME ( $\mu\text{g m}^{-3}$ )	MFB [-]	MFE [-]
VBS_BC	0.36	0.60	0.24	0.45	0.47	0.98
VBS_BC_NEW	0.36	0.59	0.23	0.43	0.50	0.97

Moreover, PMF analysis is also affected by uncertainties, especially regarding the separation between the BBOA (primary) and SOA (secondary) fractions (Crippa et al., 2013).

6.

In Ciarelli et al. (2016a) where you use the VBS\_BC method you write: “Further aging of BSOA is not considered in this study, based on previous modelling results showing overprediction of OA when such process is taken into account (Lane et al., 2008; Murphy and Pandis, 2009). This implies that also further aging of POA vapors from BBOA-like emissions was not considered since it is performed in the same basis set.” This is a large assumption which I think might be one of the main reason why you get much less OA (especially SOA from biomass burning sources) when you run VBS\_BC instead of VBS\_BC\_NEW. This needs to be discussed and explained in the manuscript. I also think that you should run a model simulation using VBS\_BC but separating the POA vapors from BBOA and allow them to be further oxidized in the same way as the HOA vapors. Then you compare the model results from this method with the model simulations with your new VBS sets (VBS\_BC\_NEW). To me this is a more fair evaluation of your new biomass burning-like OA VBS parameterizations compare to the old parameterization from Koo et al. (2014) that to my understanding allowed oxidation of evaporated POA from biomass burning sources. If your new biomass burning VBS parameterization still gives substantially better agreement with the observations than the Koo et al. (2014) VBS parameterization, then your contribution to the field can be considered substantial and important.

We thank the referee for this comment. We included Figure S4 in the manuscript where we compared the modelled OOA fraction as predicted by VBS\_BC, VBS\_BC with BBOA vapours allowed to be further oxidized as in Koo et al. (2014) and VBS\_BC\_NEW. The Koo et al. 2014 VBS approach with BBOA vapours allowed to get further oxidized (Figure S4 middle panel) also helped bringing model and observation in a better agreement, but to a lesser extent compared to VBS\_BC\_NEW (Figure S4 right panel). In order to emphasize the importance of aging processes we added the following statement at line 244 of the revised manuscript:

*Improvements in the modelled SOA fraction were also observed using the original VBS approach (Koo et al. 2014) when aging of the biomass burning vapours were taken into account (Figure S4).*

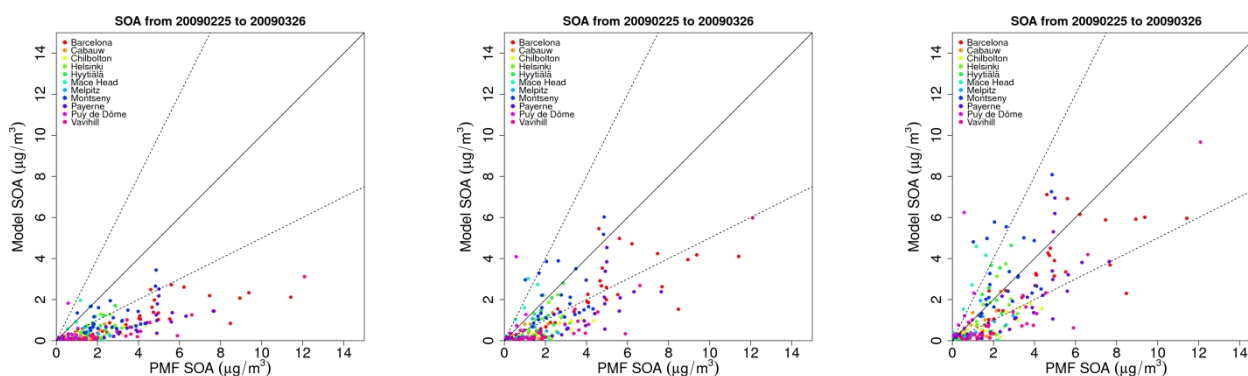


Figure S4. Modelled versus PMF SOA; with VBS\_BC (Ciarelli et al., 2016a) (left panel), with VBS\_BC where BBOA vapours were allowed to be further oxidized (Koo et al. 2014) (middle panel), and with VBS\_BC\_NEW (right panel).

7.

On L49-54 you write: “Contributions to OA from residential combustion precursors in different volatility ranges were also assessed: our results indicate that residential combustion gas-phase precursors in the semi-volatile range contributed from 6 to 30%, with higher contributions predicted at stations located in the southern part of the domain. On the other hand, higher volatility residential combustion precursors contributed from 15 to 38% with no specific gradient among the stations.”

I don't understand how you can separate the SVOC molecules in the gas-phase from the SVOC molecules in the particle phase. If we assume equilibrium partitioning between a condensed liquid

phase and the air, then the same molecule species are cycled back and forth between the gas-and particle phase because of evaporation and condensation. Do you mean: additional OA formed because of SVOC oxidation in the gas-phase as compared to additional OA formed as a consequence of IVOC oxidation in the gas-phase? Related to this I also wonder if all POA species (which are SVOCs) are allowed to evaporate (assuming equilibrate with the gas-phase at all times) and form more oxidized organic compounds that become SOA in the model when they re-condense. Thus, is it correct that all POA species eventually end up as more oxidized SOA species in the model? Or is only a fraction of the POA species allocated to the gas-phase and the rest is fixed in the particles based on the initial fresh POA VBS distribution (Fig S1)?

Yes, in the sentence we refer to the amount of OA formed due to SVOC oxidation in the gas-phase, and further condensation, and amount of OA formed as a consequence of IVOC oxidation in the gas-phase followed by further condensation.

Not all the POA (SVOCs) species are allowed to evaporate in the model and end up to SOA. The POA species (SVOCs) at  $\log_{10}C^*=-1$  is used as a proxy for all non-volatile species and will only reside in the particle phase. We added this information in the caption of Fig. S1 as:

*The lowest bin ( $\log_{10}C^*=-1$ ) is used as a proxy for all non-volatile species which will only reside in the particle phase.*

For the other bins, the amount of SVOCs allocated to the gas-phase depends on the absorptive mass: e.g. a compound with a  $C^*=10 \mu\text{g m}^{-3}$  will reside 10%, 50% and 90% in the gas phase at  $C_{\text{OA}} = 100 \mu\text{g m}^{-3}$ ,  $10 \mu\text{g m}^{-3}$  and  $1 \mu\text{g m}^{-3}$ , respectively. Likewise, the proportion of this compound in the gas-phase increases with increasing temperature. As a consequence, at lower OA concentrations or at higher temperature, the oxidation of this compound is expected to proceed more rapidly.

We modified the sentence slightly (line 49) in the revised text as:

*Contributions to OA from residential combustion precursors in different volatility ranges were also assessed: our results indicate that residential combustion gas-phase precursors in the semivolatile range (SVOC) contributed from 6 to 30%, with higher contributions predicted at stations located in the southern part of the domain. On the other hand, the oxidation products of higher volatility precursors (the sum of IVOCs and VOCs) contribute from 15 to 38% with no specific gradient among the stations.*

8.

On L156-159 you write: "Hourly emissions of biogenic VOCs, such as monoterpenes, isoprene, sesquiterpenes, xylene and toluene, were calculated using the Model of Emissions of Gases and Aerosols from Nature MEGANv2.1 (Guenther et al., 2012) for each grid cell in the model domain."

But into what VBS scheme are the BVOC oxidation products added? In Koo et al., (2014) and Ciarelli et al. (2016a) you have a 4<sup>th</sup> VBS set for BVOC oxidation products which are not allowed to age because then you get too much SOA. According to Section 3.3 all of the modeled SOA can either be attributed to residential or non-residential combustion. What about the SOA from BVOCs? Did you not consider BVOCs when you calculated the SOA formation in this new study? I thought that the only difference between the base case model run in Ciarelli et al. (2016a) and in this work was the VBS setup for the BBOA and its transformation to SOA? This needs to be clarified. At least for the southernmost stations I would expect that BSOA formation also is substantial during the wintertime, and transport from south to north could bring this SOA to the northern latitudes too.

Certainly the SOA formation from BVOCs is very important and it was always considered in all the versions. There is, however, no separate set to allocate oxidation products from biogenic precursors, therefore they follow the same oxidation pathways of biomass burning like aerosol, including aging. We are currently working on an updated version of CAMx in which biogenic sources will be separated. In order to address the question of the referee, we performed a sensitivity test with no biogenic formation (where the reactions of isoprene, monoterpene and sesquiterpene against the OH, O<sub>3</sub> and NO<sub>3</sub> oxidants were turned off) and compared the results with the base case (VBS\_BC\_NEW). The contribution of biogenic SOA is then retrieved by calculating the difference between SOA in the

reference simulation (including biogenic SOA formation) and the one with no biogenic SOA formation. Based on this test, BVOC contribution to SOA was predicted to be around 20% for the stations at the lowest latitude (Spain) and a decreasing trend with increasing latitude (less than 5% in Helsinki and Hyytiälä) was found (Figure S5). This is consistent with higher temperatures and consequently more biogenic emissions at locations in the south than those in the north. However, the most predominant source was still predicted to be anthropogenic. We also included the snow cover for March 2009 as retrieved from the TERRA/MODIS instrument in Figure S6. Larger parts of the Scandinavian countries were almost completely covered with snow, partially suppressing the emission of biogenic precursors and in line with less contribution predicted from biogenic sources in Helsinki and Hyytiälä by the model (for the investigated periods).

Comparisons between VBS\_BC, VBS\_BC\_NEW and the sensitivity test with no biogenic SOA formation, showed similar improvement, with differences occurring mainly in the southern stations of Barcelona and Montseny (Figure S7). We revised the legends of Figures 11 and 12 to make it more clear that the biomass burning set also includes biogenic SOA and we added results from the sensitivity test at line 372 of the revised manuscript and at the last bullet point of the conclusions as below:

Line 372:

*Since biogenic SOA is included in the same set as the biomass burning (set3) for this model application, we performed a sensitivity test with no SOA formation from biogenic precursors (where the reactions of isoprene, monoterpene and sesquiterpene with OH, O3 and NO3 were turned off). Our results indicated that for this period, biogenic precursors contribute to SOA to a lesser extent (5-20%) than the anthropogenic ones, with higher contributions at southern stations consistent with higher temperatures, and consequently more biogenic emissions compared to the northern stations (Figure S5). The most predominant source was still predicted to be anthropogenic. Snow cover for March 2009 as retrieved from the TERRA/MODIS revealed that larger parts of the Scandinavian countries were almost completely covered with snow (Fig. S6), partially suppressing the emission of biogenic precursors and in line with very low contribution predicted from biogenic sources in Helsinki and Hyytiälä. Comparison of SOA from VBS\_BC\_NEW and the sensitivity test with no biogenic SOA formation showed similar improvement with respect to VBS\_BC, with differences occurring mainly in the southern stations of Barcelona and Montseny (Fig. S7).*

In the conclusions as last bullet point:

- *Model simulation performed with and without biogenic SOA formation revealed that, for this period, biogenic SOA contributed only to a small extent to the total SOA (5-20%), with an increasing gradient from north to south.*

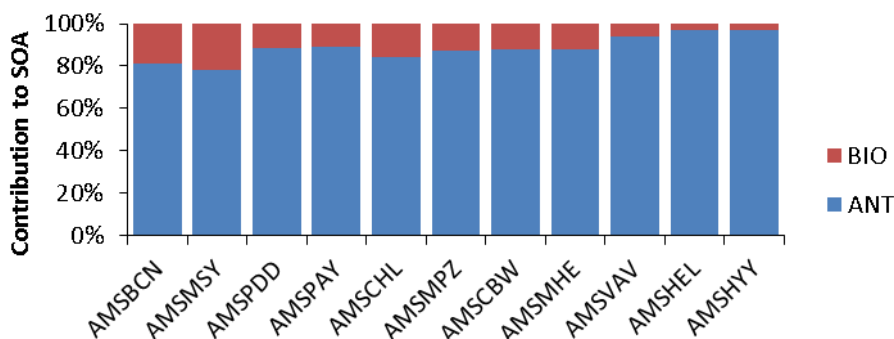


Figure S5. Biogenic and anthropogenic contribution to SOA at stations from south to north retrieved as a difference between the predicted SOA in the reference simulation (including biogenic) and a sensitivity test with no biogenic SOA formation.

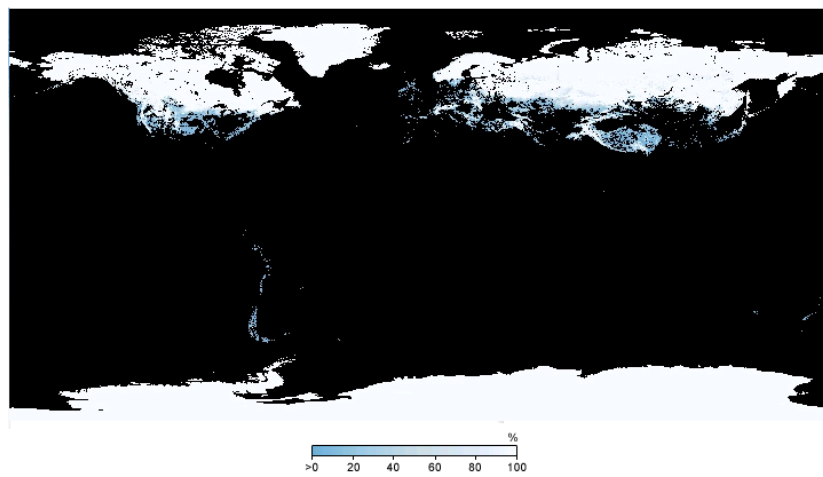


Figure S6. Snow cover for March 2009 as retrieved by the TERRA/MODIS instrument.

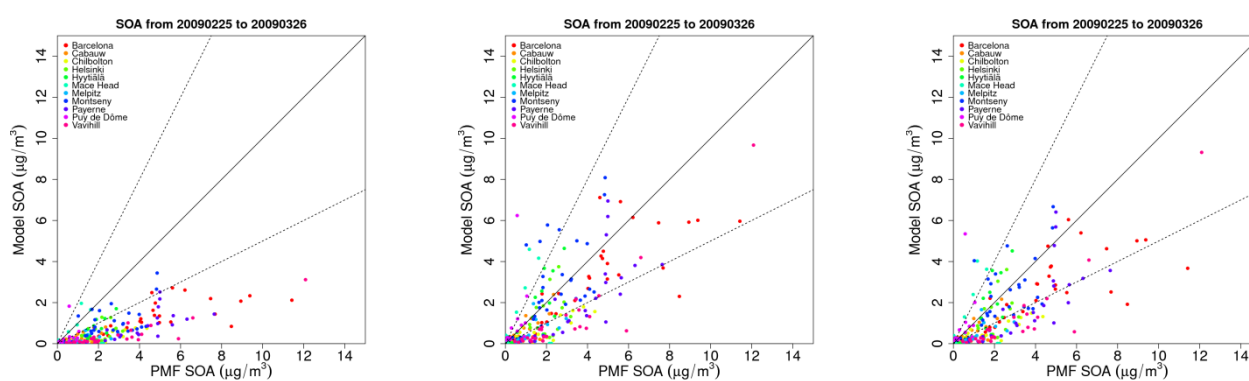


Figure S7. Modelled versus PMF SOA; with VBS\_BC (Ciarelli et al., 2016a) (left panel), with VBS\_BC\_NEW (middle panel), and with VBS\_BC\_NEW but without biogenic SOA (right panel).

9.

On L170-173 you write: “The third set allocates oxidation products from traditional VOCs (xylene, toluene, isoprene, monoterpenes and sesquiterpenes) and from non-traditional SOA precursors retrieved from chamber data (~4.75 times the amount of organic material in the semi-volatile range, Ciarelli et al., 2016b).” So do I understand it correctly that this 3<sup>rd</sup> VBS set for VOCs originating from biomass burning only considers the traditional VOCs emitted from biomass burning but not the traditional VOCs from other sources? I.e. the same traditional VOC species but from other sources (vegetation and fossil fuel) is added to other separate VBS sets. This, would be desirable since it allows you to distinguish SOA formed from biomass burning, biogenic VOCs and VOCs from fossil fuel sources?

For this application we don’t have a separate set to allocate oxidation products from biogenic precursors, and they follow the same oxidation pathways of biomass burning like aerosol, including aging. Fossil and non-fossil emissions are separated but biomass combustion from residential heating and biogenic precursors are treated in the same set (as in Koo et al., 2014). We strongly agree with the referee that a separate set, exclusively for biogenic precursors, would be highly desirable and we are currently working on an updated version of CAMx which includes such separation. The sensitivity test mentioned above suggests that BVOC emissions might contribute to the total SOA mass by ~5-20%.

10.

On L232-235 you write: “In spite of the improvements with respect to earlier studies, modelled OA is still lower than measured (mean bias MB from -0.1 µg m<sup>-3</sup> up to -3.1 µg m<sup>-3</sup>) at most of the sites, with only a slight overestimation at a few locations (MB from 0.3 µg m<sup>-3</sup> up to 0.9 µg m<sup>-3</sup>).” Here I think you also should mention that the model might underestimate the OA formation because no gradual BVOC

oxidation is considered. Or maybe even more if you did not consider any biogenic SOA formation?

As we stated earlier, we do consider SOA formation from biogenic precursors and they follow the same oxidation pathways of biomass burning like aerosol, including aging and as we wrote above, we strongly agree with the referee that a separate set, exclusively for biogenic precursors, would be highly desirable. However there could also be other reasons for the under-prediction of the modelled SOA fraction presented here (as also addressed in the reply to referee #2). Marine OA emissions are not included in our simulation. Gantt et al., (2015) showed that primary marine organic aerosol has a weaker coastal-to-inland concentrations gradient than sea-salt aerosol with some inland European cities having more than 10% of the submicron organic aerosol mass as a marine source. Fire emissions, which were not included for this study, are likely to be less important for this comparison since there were few fires activity data during the considered periods (as also addressed in the reply to referee 2). Moreover, aqueous phase SOA formation is not considered in this model application, which might be important for explaining the remaining discrepancies between model and retrieved OOA from measurements.

11.

Was the influence of NO considered when you divided the SOA precursors into the different VBS bins as was done by Koo et al. (2014)?

Yes, the influence of NO was considered as in Koo et al. (2014) and it was based on smog chamber data (Murphy and Pandis, 2009 and Hildebrandt et al., 2009).

To summarize: The model results looks reasonable and the agreement between the model and observations are as good as you could expect both when using the new VBS set and the old VBS set from Ciarelli et al. (2016a). But to me it still remain to be shown that the new VBS parameterization for biomass burning-like OA substantially improves the model performance as to compared to the VBS parameterization developed by Koo et al. (2014). I.e. you need to compare the model results from the simulations with your new VBS parameterization with a simulation using the Koo et al., (2014) VBS parameterization where you also allow the evaporated BBOA material to be further oxidized in the gas-phase. I also think you need to evaluate if not at least part of the reason why the model underestimates the OA is because it underestimates or maybe not even considers biogenic SOA formation.

We thank the reviewer for appreciating our model results. In the revised manuscript we improved the description of methods and added sensitivity tests to give a more comprehensive picture of this model application. The comparison of the results with those from Koo et al. (2014) clearly shows the improvement in the model performance (Fig. S4).

Minor specific comments:

L47, Page 1: Here you use the term “transportation precursors”. I think you mean precursors from the road transportation sector. I think you should change the formulation a bit to make this clearer.

Done.

L78-79 You write: “Moreover, numerous ambient studies of open burning plumes from aircraft do not show a net increase in OA, despite observing oxidation (Cubison et al., 2011; Jolleys et al., 2012).”

I suggest that you reformulate this sentence and instead write something like: *Moreover, numerous ambient studies with aircraft of open biomass burning plumes do not show a net increase in OA, despite observed oxidation (Cubison et al., 2011; Jolleys et al., 2012).*

When I first read this sentence I thought the open burning plumes came from the aircraft but then I realized that the aircrafts where only used for the measurements of the open biomass burning plumes.

Done.



L98-103: The sentence: "*Ciarelli et al. (2016a) showed that allowing for evaporation of primary organic particles as available in European emission inventories degraded OA performance (further under-predicted OA but with the POA to SOA ratio in a better agreement) whereas model performance improved when volatility distributions that implicitly account for missing semi-volatile material (increasing POA emissions by a factor of 3) were deployed.*" is hard to understand. I suggest that you split it into two or three sentences. What do you mean with "degraded OA performance"? Do you mean: degraded the model performance concerning the modeled total OA mass?

Yes. We modified the sentence to make it clearer:

*Ciarelli et al. (2016a) showed that allowing for evaporation of primary organic particles as available in the European emission inventories degraded the model performance for the total OA mass (further under-predicted OA but the POA to SOA ratio in a better agreement with measurements). In the same study, on the other hand, model performance improved when volatility distribution that implicitly accounts for missing semivolatile material (increasing POA emissions by a factor of 3) was deployed.*

On L112-115 you write: "*This indirect accounting of missing organic material could be used in the absence of more detailed gridded emission inventories, keeping in mind that the amount of higher volatility compounds was specifically derived from studies conducted with diesel engines (Robinson et al., 2007).*"

In fact I think the Robinson et al., (2007) study was only performed on one single diesel engine (a single-cylinder Yanmar diesel generator), which I expect do not represent modern diesel car engines very well.

I suggest that you instead of "diesel engines" at least write: a *single diesel engine*.

The sentence was modified as:

*This implies that, in these applications, the new emitted organic mass (POA + SVOCs + IVOCs) is 7.5 times higher than in original emissions (i.e.,  $OM = (3*POA) + (1.5*(3*POA))$ ) which could be used as an indirect method to account for missing organic material in the absence of more detailed gridded emission inventories.*

On L284-287 you write: "*On the other hand, the remote station of Mace Head showed a positive bias for SOA (MFB = 30%), even though model and measurement concentrations were very similar (0.54 and 0.35  $\mu\text{g m}^{-3}$ , respectively), which could be attributed to an overestimated contribution from the boundaries.*"

What do you mean by "overestimated contribution from the boundaries"? Is it the influence from the model boundary conditions?

Yes, in this case from the western boundary of the model domain.

On L337-340 you write: "*The model results indicate that non-residential combustion and transportation precursors contribute about 30-40% to SOA formation (with increasing contribution at urban and near-industrialized sites) whereas residential combustion (mainly related to wood burning) contribute to a larger extent, i.e., around 60-70%.*"

I suggest that you change to:

*The model results indicate that non-residential combustion and transportation precursors contribute to about 30-40 % of the SOA formation (with increasing contribution at urban and near-industrialized sites) whereas residential combustion (mainly related to wood burning) contribute to a larger extent, i.e., around 60-70%.*

We agree and changed the sentence as suggested.

On line L349-351 you write: "*In the southern part of the domain, the higher temperature will favour more organic material in the semi-volatile range to reside in the gas-phase, rendering it available for oxidation.*"

I would also expect that the higher UV-light intensity in the south caused more SOA formation because of higher OH concentrations.

We agree with the referee. In the southern part of the domain more OH should be available to react with secondary organic aerosol precursors. We revised the sentence at line L366-368 as below:

*In the southern part of the domain, where more OH is available, the higher temperature will favour more organic material in the semi-volatile range to reside in the gas-phase, rendering it available for oxidation.*

On line L351-351 you write: *“On the other hand, no south-to-north gradient was predicted for the higher volatility class of precursors.”*

Do you mean?

*On the other hand, no south-to-north gradient was predicted for the SOA formed from the higher volatility class of precursors.*

Yes. We thank the referee for this comment and we corrected the sentence as suggested.

On L 291-294 you write: *“Mostly traffic-related HOA was underestimated at the urban site Barcelona (Table S2, Fig. 6), with the model not able to reproduce the diurnal variation of HOA at this urban site likely due to poorly reproduced meteorological conditions or too much dilution during day time in the model (Fig. S2).”*

Can it not also be because of too weak diurnal variations in the HOA emissions from traffic in the model?

Reflection: But in the case of Helsinki it seem as if the model instead gives substantially more HOA during the morning (6 UTC, 8 am local time, and 15 UTC, 5 pm local time), which is what you would expect if the HOA mainly came from the local traffic. But surprisingly to me the observations do not indicate any increased local HOA contribution during the morning and afternoon rush hours in Helsinki. Could it be related to the vehicle fleet in Helsinki (i.e. is the road traffic very much dominated by gasoline cars which do not emit much primary HOA but precursors for SOA formation) ?

HOA in Barcelona as determined by PMF analysis displays an atypical diurnal variation with a late peak in the morning and no clear increase in the night. The reason for this behavior is still unknown and is not captured by the model. The site of Barcelona is located in a complex area, i.e. on the coast and close to mountains, which is difficult to model with such a coarse model resolution (0.25x0.25 deg).

On the other hand, it is possible that emissions for Helsinki are not realistic in the model (Karvosenoja et al., 2008). Fountoukis et al. (2014) also reported similar over-prediction at the site of Helsinki for the primary organic fraction during the February- March 2009 period.

## REFERENCES

Ciarelli, G., Aksoyoglu, S., Crippa, M., Jimenez, J.-L., Nemitz, E., Sellegri, K., Äijälä, M., Carbone, S., Mohr, C., O'Dowd, C., Poulain, L., Baltensperger, U. and Prévôt, A. S. H.: Evaluation of European air quality modelled by CAMx including the volatility basis set scheme, *Atmos. Chem. Phys.*, 16 (16), 10313-10332, doi:10.5194/acp-16-10313-2016, 2016a.

Ciarelli, G., El Haddad, I., Bruns, E., Aksoyoglu, S., Möhler, O., Baltensperger, U. and Prévôt, A. S. H.: Constraining a hybrid volatility basis set model for aging of wood burning emissions using smog chamber experiments, *Geosci. Model Dev.*, accepted, 2016b.

Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, *Atmos. Chem. Phys.*, 13, 961-981, doi:10.5194/acp-13-961-2013, 2013.

Donahue, N. M., Chuang, W., Epstein, S. A., Kroll, J. H., Worsnop, D. R., Robinson, A. L., Adams, P. J. and Pandis, S. N.: Why do organic aerosols exist? Understanding aerosol lifetimes using the two-dimensional volatility basis set, *Environ. Chem.*, 10(3), 151, doi:10.1071/EN13022, 2013.

Fountoukis, C., Megaritis, A. G., Skyllakou, K., Charalampidis, P. E., Pilinis, C., Denier van der Gon, H. A. C., Crippa, M., Canonaco, F., Mohr, C., Prévôt, A. S. H., Allan, J. D., Poulain, L., Petäjä, T., Tiitta, P., Carbone, S., Kiendler-Scharr, A., Nemitz, E., O'Dowd, C., Swietlicki, E. and Pandis, S. N.: Organic aerosol concentration and composition over Europe: insights from comparison of regional model predictions with aerosol mass spectrometer factor analysis, *Atmos. Chem. Phys.*, 14(17), 9061-9076, doi:10.5194/acp-14-9061-2014, 2014.

Gantt, B., Johnson, M. S., Crippa, M., Prévôt, A. S. H., and Meskhidze, N.: Implementing marine organic aerosols into the GEOS-Chem model, *Geosci. Model Dev.*, 8, 619-629, doi:10.5194/gmd-8-619-2015, 2015.

Hodzic, A., Kasibhatla, P. S., Jo, D. S., Cappa, C. D., Jimenez, J. L., Madronich, S., and Park, R. J.: Rethinking the global secondary organic aerosol (SOA) budget: stronger production, faster removal, shorter lifetime, *Atmos. Chem. Phys.*, 16, 7917-7941, doi:10.5194/acp-16-7917-2016, 2016.

Jo, D. S., Park, R. J., Kim, M. J., Spraklen, D. V., Effects of chemical aging on global secondary organic aerosol using the volatility basis set approach, *Atmos., Environ.*, 81, 230-244, 2008

Karvosenoja, N., Tainio, M., Kupiainen, K., Tuomisto, J. T., Kukkonen, J. & Johansson, M. Evaluation of the emissions and uncertainties of PM<sub>2.5</sub> originated from vehicular traffic and domestic wood combustion in Finland. *Boreal Env. Res.* 13: 465-474, 2008.

Koo, B., Knipping, E. and Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, *Atmos. Environ.*, 95, 158-164, doi:10.1016/j.atmosenv.2014.06.031, 2014.