

Responses to the comments of referee #2

We thank Dr. Manish Shrivastava for the valuable comments that have greatly helped us to improve the manuscript. Please find below our responses (in black) after the referee comments (in blue). The changes in the revised manuscript are written in *italic*.

Jiang et al. provide a modeling study of organic aerosols in Europe using a volatility basis set approach. This study is important for this region and provides good insights about sources and formation of OA. Results are evaluated with measurements including PMF analysis of AMS/ACSM data. Below I have several suggestions for improvement and also citation of relevant papers that need to be considered by the authors.

General comments on modified VBS approach: VBS is a framework that represents gas-particle partitioning and multigenerational aging of SOA. But depending on SIVOC emissions, reaction rates, functionalization/fragmentation branching etc. different implementations of VBS can produce very different results. Thus, it is important to describe VBS developments in the context of previous studies, specifically acknowledging and documenting differences. The authors describe their VBS as a modified VBS approach. But use of a “modified VBS” terminology has been used in 2 previous papers from M. Shrivastava et al. 2013, 2015. Those papers included both functionalization and fragmentation of organics and compared model results to several field measurements (surface based and aircraft measurements). See:

<https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/jgrd.50160>

<https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2014JD022563>

The authors use the 1.5D VBS from Koo et al. To avoid confusion between author’s version of VBS and previous 2 papers (above), I recommend the authors add a few sentences about how their modified VBS differs from the modified VBS aging parameterizations developed by M. Shrivastava et al. It may be better to refer to their VBS as 1.5D VBS, since this is what they used. It would be also instructive to compare their modified VBS results with those from M. Shrivastava et al. Note that Cholakian et al. 2018 (cited in this paper) used a similar modified VBS as Shrivastava et al. 2013, 2015.

Actually the term “modified” in this study has a different sense. Shrivastava et al. (2013; 2015) modified the VBS framework to include gas-phase fragmentation reactions and a nonvolatile (semisolid) SOA paradigm, while the objective of this study is to perform OA source apportionment in Europe with a VBS-based air quality model. Thus, the major modification we made is to extend the volatility sets with split sources, together with minor adjustment of parameters for the sets of new diesel vehicles and biomass burning based on chamber experimental data.

In order to distinguish the modified 1.5-D VBS from previous studies, we added the description about VBS development, as well as a comparison of our work with literature in section 2.2.

(Section 2.2.1 P6 L3 – L7) “The 1.5-D VBS framework in CAMx is based on the one-dimensional (1-D) VBS, in which the organic species are grouped only by their volatility (Donahue et al., 2006). The 1-D VBS was later extended to a second dimension (2-D) to include the oxidation state – specifically O:C ratio (Donahue et al., 2011). In order to reduce the high computational burden of the 2-D VBS when implemented in CTMs, the 1.5-D VBS was developed, which combines the 1-D VBS and the multiple reaction trajectories defined in the 2-D VBS space, it can therefore account for changes in both volatility and oxidation state (Koo et al., 2014). The default VBS scheme in CAMx...”

(Section 2.2.1 P6 L16 – L21) “The VBS scheme has been modified in previous studies to improve the performance of air quality models. For example, Shrivastava et al. (2013; 2015) treated SOA as a non-absorbing semisolid with low “effective volatility” and added the fragmentation reactions. Using this method in the regional model CHIMERE, it was found that fragmentation could effectively reduce the SOA formation when further aging of biogenic SOA was allowed, leading to a better agreement with observations (Cholakian et al., 2018). Instead of a major modification of the chemical mechanism, this

study aims at modifying the 1.5-D VBS framework of CAMx to enable source apportionment of OA in Europe. As a first step to separate... ”

(Section 2.2.1 P6 L25 – L26) “The schematic diagram of the VBS with the modified basis sets (it will be referred to as PSI-VBS thereafter) is shown in Fig. 1”

(Section 2.2.3 P7 L17 – L23) “...While the standard VBS of CAMx disables the aging of SOA for the basis set PBS (biomass burning and biogenic sources) to avoid overestimation of biogenic SOA, the separated sets for biomass burning (BB) and biogenic (BIO) sources allow us to implement individual parameterization schemes. Therefore, we kept the default parameterization (without aging of SOA) for BIO as a compromise for the lack of gas-phase fragmentation, and enabled the oxidation of secondary gases from biomass burning (see BB in Fig. 1) with a reaction rate of $4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ according to previous studies (Ciarelli et al., 2017a; Ciarelli et al., 2017b; Denier van der Gon et al., 2015; Fountoukis et al., 2014; Murphy and Pandis, 2009; Theodoritsi and Pandis, 2019). For other basis sets, the default parameters of CAMx v6.3 were used.”

- Cholakian, A., Beekmann, M., Colette, A., Coll, I., Siour, G., Sciare, J., Marchand, N., Couvidat, F., Pey, J., Gros, V., Sauvage, S., Michoud, V., Sellegri, K., Colomb, A., Sartelet, K., DeWitt, H. L., Elser, M., Prevot, A. S. H., Szidat, S., and Dulac, F.: Simulation of fine organic aerosols in the western Mediterranean area during the ChArMEX 2013 summer campaign, *Atmos. Chem. Phys.*, 18, 7287-7312, doi: 10.5194/acp-18-7287-2018, 2018.
- Ciarelli, G., Aksoyoglu, S., El Haddad, I., Bruns, E. A., Crippa, M., Poulain, L., Äijälä, M., Carbone, S., Freney, E., O'Dowd, C., Baltensperger, U., and Prévôt, A. S. H.: Modelling winter organic aerosol at the European scale with CAMx: evaluation and source apportionment with a VBS parameterization based on novel wood burning smog chamber experiments, *Atmos. Chem. Phys.*, 17, 7653-7669, doi: 10.5194/acp-17-7653-2017, 2017a.
- 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: a box-model study based on the VBS scheme of the CAMx model (v5.40), *Geosci. Model Dev.*, 10, 2303-2320, doi: 10.5194/gmd-10-2303-2017, 2017b.
- Denier van der Gon, H. A. C., Bergström, R., Fountoukis, C., Johansson, C., Pandis, S. N., Simpson, D., and Visschedijk, A. J. H.: Particulate emissions from residential wood combustion in Europe – revised estimates and an evaluation, *Atmos. Chem. Phys.*, 15, 6503-6519, doi: 10.5194/acp-15-6503-2015, 2015.
- Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics, *Environ. Sci. Technol.*, 40, 2635-2643, doi: 10.1021/es052297c, 2006.
- Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, *Atmos. Chem. Phys.*, 11, 3303-3318, doi: 10.5194/acp-11-3303-2011, 2011.
- 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, 9061-9076, doi: 10.5194/acp-14-9061-2014, 2014.
- 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.
- Murphy, B. N., and Pandis, S. N.: Simulating the Formation of Semivolatile Primary and Secondary Organic Aerosol in a Regional Chemical Transport Model, *Environ. Sci. Technol.*, 43, 4722-4728, doi: 10.1021/es803168a, 2009.
- Shrivastava, M., Zelenyuk, A., Imre, D., Easter, R., Beranek, J., Zaveri, R. A., and Fast, J.: Implications of low volatility SOA and gas-phase fragmentation reactions on SOA loadings and their spatial and temporal evolution in the atmosphere, *J. Geophys. Res.-Atmos.*, 118, 3328-3342, doi: 10.1002/jgrd.50160, 2013.
- Shrivastava, M., Easter, R. C., Liu, X. H., Zelenyuk, A., Singh, B., Zhang, K., Ma, P. L., Chand, D., Ghan, S., Jimenez, J. L., Zhang, Q., Fast, J., Rasch, P. J., and Tiitta, P.: Global transformation and fate of SOA: Implications of low-volatility SOA and gas-phase fragmentation reactions, *J. Geophys. Res.-Atmos.*, 120, 4169-4195, doi: 10.1002/2014jd022563, 2015.
- Theodoritsi, G. N., and Pandis, S. N.: Simulation of the chemical evolution of biomass burning organic aerosol, *Atmos. Chem. Phys.*, 19, 5403-5415, doi: 10.5194/acp-19-5403-2019, 2019.

Specific comments:

Page 3 Line 5-10: In addition to Hallquist et al. 2009, also cite M. Shrivastava et al. 2017 Review paper on SOA published in *Reviews of Geophysics*: <https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2016RG000540>

Done

Page 3 Line 15-20: For WRF-Chem please cite 2 of the more recent papers on VBS implementation of SOA in addition to Shrivastava et al. 2011: <https://www.nature.com/articles/s41467-019-08909-4>

Done

Page 7 Line 5: While several models underpredict OA from biomass burning, some models predict OA from biomass burning could be much more important. See <https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2014JD022563>. This should be acknowledged here in addition to Hodzic et al. 2010 for biomass burning.

More references were added in P7 L16 regarding the underestimation of OA from biomass burning.

Shrivastava, M., Easter, R. C., Liu, X. H., Zelenyuk, A., Singh, B., Zhang, K., Ma, P. L., Chand, D., Ghan, S., Jimenez, J. L., Zhang, Q., Fast, J., Rasch, P. J., and Tiitta, P.: Global transformation and fate of SOA: Implications of low-volatility SOA and gas-phase fragmentation reactions, *J. Geophys. Res.-Atmos.*, 120, 4169-4195, doi: 10.1002/2014jd022563, 2015.

Ciarelli, G., Aksoyoglu, S., El Haddad, I., Bruns, E. A., Crippa, M., Poulain, L., Äijälä, M., Carbone, S., Freney, E., O'Dowd, C., Baltensperger, U., and Prévôt, A. S. H.: Modelling winter organic aerosol at the European scale with CAMx: evaluation and source apportionment with a VBS parameterization based on novel wood burning smog chamber experiments, *Atmos. Chem. Phys.*, 17, 7653-7669, doi: 10.5194/acp-17-7653-2017, 2017.

Jathar, S. H., Gordon, T. D., Hennigan, C. J., Pye, H. O. T., Pouliot, G., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States, *Proceedings of the National Academy of Sciences*, 111, 10473-10478, doi: 10.1073/pnas.1323740111, 2014.

Page 11: Aqueous chemistry of organic aerosols (OA) in fog can also increase OA by 4-20% (see Gilardoni et al. 2014 PNAS for Po Valley Italy measurements of aqueous SOA). Since the authors underestimate winter-time OOA, missing aqueous phase SOA in fog would be an important source. Although they are overestimating OA during the autumn due to modeled bias in relative humidity and wet scavenging, the high bias could be due to other reasons like overestimation of SIVOC emissions, biases in aging parameterizations. This needs to be acknowledged as a caveat. The authors could also compare rain rates simulated by their model to measurements in that region to provide further evidence for model underestimation of rain rate/wet scavenging.

We thank the referee for comments on the possible explanations for model performance. The lack of aqueous-phase chemistry for SOA formation is definitely a potential reason for SOA underestimation. We added the explanation in P13 L19 – L21.

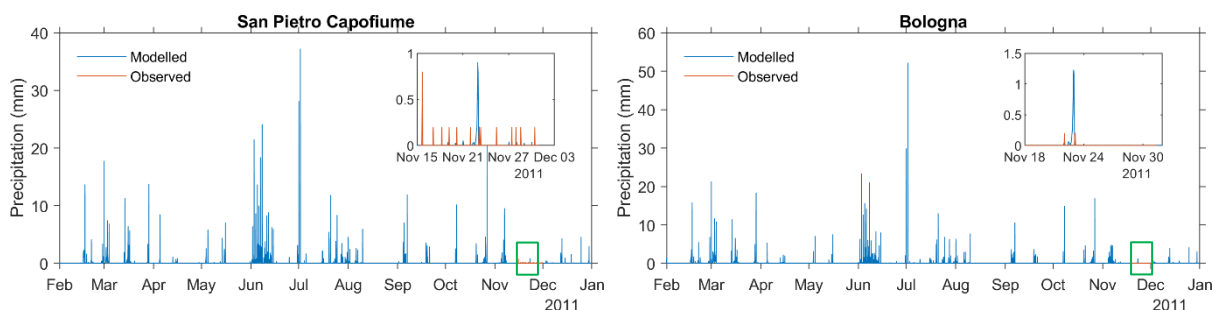
“It could come from the missing pathways of SOA formation such as the aqueous processing of water-soluble organics (Ervens et al., 2011), which was found to contribute up to ~20% of winter OA measured in Bologna (Gilardoni et al., 2016; Meroni et al., 2017).”

The overestimation of SIVOC emissions is also a possible explanation for overestimated OA in SPC. As we mentioned in P8 L26, “... *this factor (SVOC/POA ratio) presents substantial inter-country variability due to different combustion type, fuel parameters and operation conditions, indicating a potential over- or underestimation for a specific area by using the factor of 3 in the whole domain*”. Since the calculation of SIVOC emissions is still with very high uncertainty, one can hardly conclude if it is over- or underestimated. That is why we attribute the major reason to the missing fog scavenging process in the model (which we can clearly observe from the comparison of measured and modelled relative humidity in Figure 2). However, we agree that it is important to highlight the potential effects of the highly uncertain SVOC emissions as a caveat for future studies. A general statement for all sites is added in Section 3.2, P13 L24-L27.

“Another potential limitation is related to the uncertainties in SVOC/IVOC emissions. We adopted a factor of 3 for the SVOC and POA ratio for the whole domain, however, the substantial spatial and temporal variability of the factor could lead to over- or underestimation of SVOC emissions at site scale (Denier van der Gon et al., 2015) and therefore over- or underestimation of the SOA, as well as of POA.”

Both measured and modelled precipitation in Bologna and SPC during the observation time was very low (see the zoomed subplot below, total observed precipitation <3.8 mm for SPC and < 1 mm for Bologna). Although the model performance to reproduce such low precipitation amounts are not as

good as at other sites, we think the effects from such low precipitation amounts should be negligible. Scavenging at SPC was controlled by fog, as highlighted by the significant decrease of PM1 mass during night-time, in concomitance with the fog inset (Gilardoni et al., 2014). The lack of scavenging mechanisms in the model during night-time is evident in Figure 2, showing that the modeled OA is not able to follow the diurnal trend of the measured OA during the fog period.



Denier van der Gon, H. A. C., Bergström, R., Fountoukis, C., Johansson, C., Pandis, S. N., Simpson, D., and Visschedijk, A. J. H.: Particulate emissions from residential wood combustion in Europe – revised estimates and an evaluation, *Atmos. Chem. Phys.*, 15, 6503-6519, doi: 10.5194/acp-15-6503-2015, 2015.

Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 11069-11102, doi: 10.5194/acp-11-11069-2011, 2011.

Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., Costabile, F., Gobbi, G. P., Pietrogrande, M. C., Visentin, M., Scotto, F., Fuzzi, S., and Facchini, M. C.: Direct observation of aqueous secondary organic aerosol from biomass-burning emissions, *Proceedings of the National Academy of Sciences of the United States of America*, 113, 10013-10018, doi: 10.1073/pnas.1602212113, 2016.

Page 12 Above line 5: Instead of “biomass density” the authors could probably just say increasing biogenic emissions here?

Here we used “biomass density” to refer to the increased biomass leading to increased biogenic emissions. We rephrased the sentence in P12 L16 – L17 to avoid misunderstanding.

“The OOA from biogenic sources (OOA-BIO) begins to increase from April, when the biogenic emissions increased with increasing temperature and biomass density”

Page 12 Line 20: From Figure 6 it seems the authors could have applied a site specific scaling of POA emissions based on PMF HOA+BBOA. This could improve their POA, its diurnal variation and also IVOC emissions for biomass burning that are calculated as 4 times BB-POA. Please comment on use of a site-specific scaling of BB-POA and IVOC emissions based on PMF HOA+BBOA.

We totally agree that a site-specific scaling of POA would improve the model performance. However, the challenge for now is whether the coverage of OA measurements and PMF studies can support the site/region-specific POA emissions scaling and IVOC emissions for the whole domain. Meanwhile, we should note that the PMF studies are also associated with relevant uncertainties (as mentioned in P12 L20–L21). Developing a site-specific S/IVOC emission estimation method requires further improvements on measurement and analysis techniques, as well as more field measurements. We added a discussion about future works in section 3.2, P13 L24 – L31.

“Another potential limitation is related to the uncertainties in SVOC/IVOC emissions. We adopted a factor of 3 for the SVOC and POA ratio for the whole domain, however, the substantial spatial and temporal variability of the factor could lead to over- or underestimation of SVOC emissions at site scale (Denier van der Gon et al., 2015) and therefore over- or underestimation of the SOA, as well as of POA. It could also partially explain the differences in model performance for the temporal variation of HOA and BBOA for each site. To further improve the model performance, it is necessary to continuously update the chemical mechanism in models by introducing the missing processes and improving the parameterization based on the advanced knowledge; as well as to improve the emissions by including more site-specific sources, IVOC and SVOC estimates, and updated diurnal variation profiles.”