Interactive comment on "Precursors and formation of secondary organic aerosols from wildfires in the Euro-Mediterranean region" by Marwa Majdi et al.

Anonymous Referee #1

The authors wish to thank the anonymous referee for the very helpful comments and corrections. All corrections have been included in this new version. A response to the general and specific comments is provided below (in blue).

General comments :

This study presents a new SOA formation mechanism developed to quantify the relative contribution of SOA precursors from wildfires in summer 2007 to organic aerosols in the Mediterranean region. The mechanism is an extension of an existing one by inclusion of some aromatic volatile organic compounds (VOC) emitted from wildfires. Since the wildfires have significant effects on the chemical composition of the atmosphere, a realistic representation of their emissions as well as their chemical fate in the models is important. Although I think such efforts might be valuable, this manuscript needs a major revision if accepted.

One of the weaknesses is that the manuscript presents simulations using an extended mechanism to quantify the relative contribution of precursors from wildfires to OA formation, but it does not provide any attempt to show how realistic the results are. It makes more sense to perform such studies during periods where detailed measurements –especially OA- are available to support the results, at least to a certain extent.
A general model evaluation (for both gaseous and particulate pollutants) to provide some confidence on the model performance during the selected period of time is the basis for all kind of modeling studies. Without such confidence it is impossible to get reasonable conclusions out of the simulations. In introduction, authors mention "a general good performance for PM2.5" citing another manuscript which is still under review.

Since the lack of available organic surface data close to the fire region during the summer 2007, we could not evaluate the organic gaseous and organic particulate pollutants which is in fact a limitation of our work. The paper of Majdi et al. (2019) is now published in ACP. It evaluates the simulated PM2.5 concentrations during the summer 2007 by comparison to available measurements of PM2.5 concentrations and aerosol optical properties. The general performances of the model for the PM2.5 concentrations during the summer 2007 are good, although they are slightly underestimated, compared to surface measurements at 8 AIRBASE stations. Besides, the new SOA formation mechanism developed in this work is based on measurement studies from smog chamber experiments. This gives confidence in the results,

although we agree that some further validation with organic concentrations close to fires is required.

Specific comments :

1) The title indicates that the study is for the "Euro-Mediterranean" region. Results, however, mainly focus on a sub-region over Italian peninsula, Greece and some Balkan countries, named awkwardly as *MedReg". I assume the name comes from the definition of different regions in the Mediterranean used in Majdi et al. (2018) as MedReg1, MedReg2, etc., but it sounds strange when it stands alone in this manuscript. Authors might consider changing it, for example simply as "sub-region".

In this work, we chose to focus more on MedReg which is considered to be the most affected subregion by fire according to Majdi et al. (2019).
Taking into account the referee's comment, MedReg is replaced by subregion in the revised version of the paper.

2) Page 1, line 23: Last sentence makes no sense.

The sentence in page 1, line 23 « Considering the VOC emissions results in a moderate increase of PM2.5 concentrations mainly in Balkans (up to 24%) and in the fire plume (+10%). " is replaced by "Considering VOCs as SOA precursors results in a moderate increase of PM2.5 concentrations mainly in Balkans (up to 24%) and in the fire plume (+10%). »

3) Page 2, line 10-11: please replace "intermediate organic compounds" with "intermediate volatility organic compounds"

« Intermediate organic compounds » in page 2, line 10-11 is replaced by « intermediate volatility organic compounds » in the revised version of the paper.

4) Page 12, Section 3: This section is too short. For the model set up authors cite Majdi et al. (2018) which is still under review. Even if that manuscript is accepted for publication, the modeling methods and detailed information about the model inputs must be described in this manuscript as well (meteorological parameters, anthropogenic and biogenic emissions (inventories, model, version), boundary conditions, deposition, etc).

A paragraph describing the model set up is added in page 12 line 23 in the revised version of the paper : « Here, the CTM Polair3D/Polyphemus (Mallet et al., 2007; Sartelet et al., 2012) is used with a similar set up as described in Majdi et al. (2019)

and summarized here.

A modified version of the Carbon Bond 05 model (CB05) (Yarwood et al., 2005, Kim et al., 2011) is used for gas-phase chemistry with the SIze REsolved Aerosol Model (SIREAM) (Debry et al., 2007) for aerosol dynamics (coagulation, condensation/evaporation). The meteorological fields are provided by the European Center for Medium-Range Weather Forecast (ECMWF, ERA-Interim). Boundary conditions of the nesting domain are obtained from the global chemistry-transport model MOZART-GEOS5 6 hourly simulations outputs (Emmons et al. , 2010). Anthropogenic emissions are generated from EMEP inventory for 2007 (European Monitoring and Evaluation Program, http://www.emep.int). Biogenic emissions are estimated with the Model of emissions of Gases and Aerosols for Nature (MEGAN-LHIV, Guenther et al., 2006). Sea-salt emissions are parameterized following Monahan (1986). Soil and surface database of Menut et al. (2013) is used to calculate the dust emissions considering the spatial extension of potentially emitted area in Europe described in Briant et al. (2017). The daily fire emissions are calculated using the APIFLAME fire emissions model v 1.0 (Turquety et al., 2014) as described in Majdi et al. (2019). »

5) The model domain covers an area where desert dust is very important. Some studies show significant dust contribution in the Mediterranean even below 2.5 micrometer (Fernandes et al., 2015; Denjean et al., 2016). Was dust included in the model simulations, in boundary conditions, how was dust distributed in model size fractions?

Dust was included in the model simulations, as now described in the model description (see reply to comment 4). Boundary conditions from the domain studied were obtained from the simulation on the larger domain (nesting domain).
Dust was distributed into 4 diameter bins (between 0.01 μm and 10 μm).

5) Page 12, line 27: Authors need to explain the reason of using CB05 mechanism by including additional compounds and reactions leading to SOA formation instead of using more advanced CB6 mechanisms (Yarwood et al., 2010) which have already some of these compounds.

CB05 and CB06 do not treat the SOA formation, they consider some SOA precursors, but the oxidation of the SOA precursors do not form semi-volatile organic compounds that can condense onto particles. In this work, we used a version of CB05 which was modified by Couvidat et al. (2012) and Kim et al. (2011) to integrate the formation of semi-volatile organic compounds from some VOCs that are SOA precursors. The purpose of this work is to develop further this modified version of CB05 to integrate the formation of semi-volatile organic compounds from more VOCs that are SOA precursors.

6) Page 15, Section 5.1: Uncertainties in VOC emissions are probably very high. As I understand, authors considered only two types of vegetation (crop residue and chaparral) of which the emission factors were available and also assumed that temperate forest and savanna have the same EF as chaparral for cresol, catechol, guaiacol, syringol, naphthalene and methylnaphthalene. Additional discussion about the variability of emissions from different vegetation with references is needed to justify this assumption.

We assume that temperate forest and savanna have the same EF as chaparral for cresol, catechol, guaiacol, syringol, naphthalene and methylnaphthalene. This assumption is made to not underestimate their emissions since temperate and savanna are the most burned vegetation in the Euro-Mediterranean region according to Akagi et al. (2011).

As described in the paper « Because the EF of VOCs emitted by wildfires of crop residue, chaparral, temperate forest and savanna in the inventory of Akagi et al. (2011) are often of the same order of magnitude (Table A1 of Appendix A), it is assumed here that temperate forest and savanna have the same EF as chaparral for cresol, catechol, guaiacol, syringol, naphthalene and methylnaphthalene. »

A discussion about uncertainties and the variability of emissions from different vegetation is added after page 16 line 12 :

« This assumption is justified by considering uncertainties linked to emissions : Turquety et al. (2014) estimated that the uncertainties on the emitted carbon related to fire emissions can reach 100%. They found that the database used for the type of vegetation burned plays a significant role on the emitted carbon (~ 75% associated uncertainty). Moreover, the inventory used in this work (APIFLAME (Turquety et al., 2014)) is mainly based on the emission factors of Akagi et al. (2011) using data from different field and laboratory experiments. Uncertainties related to these emissions factors are high. For example, Alves et al. (2011) measured carbon monoxide (CO) emissions for forest fires in Portugal 2.6 times higher than the values of Akagi et al. (2011) for extra-tropical forests. »

7) It is known that terpenoid emissions –especially monoterpenes- increase during forest fires (Ciccioli et al., 2014). Since monoterpenes are the essential precursors for SOA formation, their contribution to OA during wildfires might be larger when taken into account in addition to their natural emissions. Although not mentioned in the manuscript, I assume MEGAN model was used to estimate the BVOC emissions. At least some discussion about the contribution of the increased BVOC emissions to SOA formation during wildfires might be useful.

Yes, MEGAN is used (see reply to comment 4). Majdi et al. (2019) highlighted that during the fire episodes in summer 2007, SOA and POA from I/S/L-VOCs are the major PM2.5 component , their contribution to PM2.5 concentrations is larger than the SOA from biogenics (57% vs 0.3%). However, the potential increase of terpenoid emissions by forest fires is now specified in section 5.1 after line 11 page 15 : « Note

that although Biogenic VOC (BVOC) emissions may increase during wildfires, as suggested by Cicciolo et al. (2014), the potential increase of BVOC emissions from wildfires is not considered here due to lack of data. »

8) Page 13, Fig. 5: I assume that the MedReg is not another nested domain (same resolution as the red dotted domain). It has to be explained better in the text the choice of the green box named as MedReg -which is odd.

Indeed, MedReg is not a nested domain, it is the subregion where the most severe fire episodes occur according to Majdi et al. (2019).
The sentence « Since the largest fires in the Euro-Mediterranean domain occur mainly in Balkan and Eastern Europe (between 20 July and 31 July 2007), in Greece (between 24 August and 30 August) and in Southern Italy (between 9 July and 31 July 2007) (Majdi et al., 2019), we choose to focus on the subregion indicated in green box in Figure 5. » is added to page 12 line 26 in the new version of the paper.

9) Page 25, Conclusions are very short, based only on model calculations without any supporting material or discussions. This section needs a revision.

The conclusion was modified to better stress out how this work improves upon previous work, and how it can be useful for other members of the community.

« This study quantified the relative contribution of OAtot precursors (VOCs, I/S/L-VOCs) emitted by wildfires to OA formation and particle concentrations, during the summer 2007 over the Euro-Mediterranean region. A new chemical mechanism H2Oaro was developed to represent the SOA formation from selected VOCs, namely toluene, xylene, benzene, phenol, cresol, catechol, furan, guaiacol, syringol, naphthalene, methylnaphthalene, the structurally assigned and unassigned compounds with at least carbon atoms per molecule (USC>6), based on smog chamber experiments under low and high-NOx conditions. This mechanism was implemented in the chemistry transport model Polair3D of the air-quality platform Polyphemus. Over the Euro-Mediterranean area, the OA concentrations emitted by wildfires originate mostly from I/S/L-VOCs. The OA concentrations from gaseous I/S/L-VOCs are about 10 times higher than the OA concentrations from VOCs. However, the contribution of the oxidation of VOCs to the OA concentrations is locally significant (it reaches 30% close to the area where wildfires are emitted and 20% in the fire plume). Air-quality models often represent SOA formation from only a few VOCs, such as toluene and xylene. This study points out the need to consider the contribution of a variety of VOCs, namely, phenol, benzene, catechol, cresol, xylene, toluene and syringol, when modelling SOA formation from wildfires. The contribution of these VOCs may even be underestimated here for two reasons. First, the yields from smoke chamber experiments were not corrected for wall losses, and they may therefore be underestimated leading to an underestimation of the SOA formation from VOCs in the model. Second, a large part of OA concentrations from

VOCs is in the gas phase (› 70%). This suggests that the influence of the VOC emissions on OA concentrations could be larger, if the surrogates from these VOC oxidations partition more easily to the particle phase. This could be the case if further ageing mechanisms are considered for these VOCs or if the particles are very viscous (Kim et al., 2019).

Emissions of gaseous I/S/L-VOCs are a large source of uncertainties. However, similar estimates were obtained here by using as a proxy POA emissions (with a factor of 1.5) or NMOG emissions (with a factor of 0.36). Sensitivity simulations were performed to quantify the uncertainties on OA and PM2.5 concentrations linked to I/S/L-VOCs emissions and chemical evolution (ageing). They are found to be lower than the uncertainties associated with SOA formation from VOC emissions. This stresses the need to consider a variety of VOCs in SOA formation model, and to better characterize their emission factors. »

10) Please change Giancarlo et al., 2017 to Ciarelli et al., 2017 in page 3, line 16, 29, 33, page 12, line 13, page 13, line 15, page 16, line 30, page 33, line 2

Giancarlo et al., 2017 is replaced by Ciarelli et al., 2017 in the new version of the paper.

11) Page 37, line 25: Please correct "Lowik, J." as "Slowik J."

Lowik, J. In page 37 line 25 is corrected to Slowik, J..

12) Page 38, line 27: Please correct the following reference: "Giancarlo, C.and El Hadad, I., Bruns, E., Aksoyoglu, S., Mohler, O., Baltensperger, U., and Pre- vot, A.: Constraining a hybrid volatility basis set model for aging wood burning emissions using smog chamber experiments, Geosci. Model Dev., 10, 2303–2320, https://doi.org/10.5194/gmd-10-2303-2017, 2017" as "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 cham- ber experiments: a box-model study based on the VBS scheme of the CAMx model (v5.40), Geosci. Model Dev., 10, 2303-2320, 10.5194/gmd-10-2303-2017, 2017"

The reference in page 38, line 27 is corrected.

References:

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and Formenti, P.: Size distribution and optical properties of mineral dust aerosols transported in the western Mediterranean, Atmos. Chem. Phys., 16, 1081-1104, 10.5194/acp-16-1081-2016, (2016).

A. P. Fernandes, M. Riffler, J. Ferreira, S. Wunderle, C. Borrego and O. Tchepel, Com- parisons of aerosol optical depth provided by Severi satellite observations and CAMx air quality modeling, The International Archives of the Photogrammetry, Remote Sens- ing and Spatial Information Sciences, Volume XL-7/W3, 2015, 36th International Sym- posium on Remote Sensing of Environment, 11–15 May 2015, Berlin, Germany

Yarwood, G., J. Jung, G. Z. Whitten, G. Heo, J. Mellberg and E. Estes. Updates to the Carbon Bond Mechanism for Version 6 (CB6). Presented at the 9th Annual CMAS Conference, Chapel Hill, October (2010).