
Anonymous Referee #2

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:**

Pg 2, line 15: the definition of OA\textsubscript{tot} is confusing, given that ‘aerosol’ usually refers to the particle phase concentrations only. If this is the sum of the particle and gas phase, do the authors mean that the gas phase species are only those who are low enough in volatility to participate in partitioning? Or all the gas phase species, including VOCs and IVOCs? Please clarify this.

We used the notation of Murphy et al. (2014), as now specified. In this notation, OA\textsubscript{tot} means the sum of particle and gas phase organic compounds of volatility lower than VOCs (i.e. of saturation concentration lower than C*=3.2 \times 10^6 \text{\mu g.m}^{-3}).

The sentence in page 2, line 15 is replaced in the revised version of the paper by:

« In the following, following Murphy et al. (2014), OA\textsubscript{tot} denotes the sum of gaseous and particle phase organic aerosol concentrations of volatility lower than VOCs. »

pg 3, line 27 Please qualify what is meant by “misclassified” here

For clarity, the sentence « Although primary gaseous I/S/L-VOCs are not considered or misclassified in emissions inventories » is replaced by « Although primary gaseous I/S/L-VOCs are not considered or classified as unspeciated NMOG in emissions inventories »
Section 2.1: the authors should consider adding more explanation as to what the original H$_2$O scheme was (and what its purpose is), and what additions/changes the authors are specifically making to H$_2$O. It’s a little unclear if the details being described on pg 4 through line 6 on pg 5 are of the original H$_2$O model?

The first 2 sentences of this section (starting on pg 4, line 18) would benefit from having the appropriate H$_2$O citations added.

The sentence “The new mechanism (H2Oaro) is an extension of hydrophilic/hydrophobic organic (H2O) SOA mechanism” is replaced by “The new mechanism (H2Oaro) is an extension of the hydrophilic/hydrophobic organic (H2O) SOA mechanism, which details the formation of organic aerosols from the oxidation of precursors (Couvidat et al. 2012). Laboratory chamber studies provide the fundamental data that are used to parameterize the atmospheric SOA formation under low/high-NOx conditions. The formed organic aerosols are represented by surrogate compounds, with varying water affinity (hydrophobic, hydrophilic). In the original H2O mechanism, the precursors are I/S/L-VOCs, aromatics (xylene and toluene), isoprene, monoterpenes, sesquiterpene. In the extension H2Oaro developped here, other VOCs are considered as SOA precursors (phenol, cresol, catechol, benzene, furan, guaiacol, syringol, naphthalene, methylnaphthalene).”

Because the list of VOCs is now detailed in the description of H2Oaro, the first sentence of section 2.1 is simplified and the sentence “This section presents a new SOA formation mechanism H2Oaro developed to represent the SOA formation from the main VOCs that are estimated to be SOA precursors (phenol, cresol, catechol, benzene, furan, guaiacol, syringol, naphthalene, methylnaphthalene).” is replaced by “This section presents a new SOA formation mechanism H2Oaro developed to represent the SOA formation from the main aromatic VOCs that are estimated to be SOA precursors.”

Pg 5, lines 23-24. The authors state that the one-product model correctly reproduces the experimental data; there is a small amount of spread between the model and experimental data. Can the authors briefly quantify that error? Same for the analysis given for fig 2 (lines 16-17 of pg 6)

To quantify the small amount of spread between the model and experimental data, we calculate the RMSE as follows:

\[
\text{RMSE} \% = 100 \times \left( \frac{\sum (\text{Yield}_{\text{exp}} - \text{Yield}_{\text{model}})^2}{N} \right)^{1/2}
\]

\text{Yield}_{\text{model}}: \text{The modeled SOA yield}

\text{Yield}_{\text{exp}}: \text{The experimental SOA yield}

N: number of experiments
For figure 1 page 6, RMSE=3.1%
For figure 2 page 7, RMSE= 2.87%

This is added in page 5 lines 23-24 in the revised version of the paper as follows :
« The one-product model with a stoechiometric coefficient $\alpha_1$ of 0.28 and a vapor pressure of 4.59 10$^{-8}$ torr correctly reproduces the experimental data with a small amount of spread between the model and experimental data (RMSE of 3.1%). » and in page 6 lines 16-17 : « Figure 2 plots the SOA yields against the SOA concentrations. A stoechiometric coefficient and a saturation vapor pressure 0.39 and 3.52 10$^{-6}$ torr respectively are found to fit accurately the experimental data with small differences between the model and experimental data (RMSE of ~ 3 % ). »

Pg 6, lines 1-2: can the authors briefly discuss what error might be anticipated to be introduced by using ACIDMAL as a high-NOx surrogate given the lack of data for this mechanism? Same for the cresol chemical mechanism, lines 13-15 of page 6?

In this work, for catechol and cresol, we did not differentiate low-NOx and high-NOx oxidation, because of the lack of data for high-NOx conditions. Because of the lack of data, it is difficult to estimate what is the error associated to this assumption.

Pg 11 lines 13-16: can the authors briefly explain their rationale for choosing USC$>$6 compounds to undergo the same OH oxidation mechanisms as phenol or naphthalene?

This assumption is based on the results of the smog chamber of Bruns et al. (2016) : they quantified the SOA yield from USC$>$6 and found that their yields are significant. However, because their OH oxidation mechanism may not be easily defined, we chose to represent it with a compound which also has high yields. Phenol and naphthalene are good candidates. Because the oxidation products of naphthalene and phenol are very different (e.g. volatility), a sensitivity simulation is performed on choosing the oxidation mechanism of naphthalene rather than phenol, to evaluate the impact of the changing the oxidation mechanism.

Page 11, line 15, the following sentence is removed : « In this study, USC$>$6 compounds are assumed to undergo either the same OH oxidation mechanisms as phenol or as naphthalene, which are previously discussed in sections 2.1.1 and 2.1.6 respectively. », and it is replaced by the following sentences: « Because Bruns et al. (2016) estimated that SOA yields for USC$>$6 compounds are high, they are represented in the model by a high-yield compound. Phenol and naphthalene are good candidates. Because the oxidation products of naphthalene and phenol are very different (e.g. volatility), a sensitivity simulation is performed on choosing the oxidation mechanism of naphthalene rather than phenol, to evaluate the impact of changing the oxidation mechanism. »
Section 2.2: The acronyms should be well defined: what are BBPOAlP, BBPOAmP and BBPOAhP? I strongly suggest making sure all acronyms in this work are well-defined the first time they are used. Also, consider re-defining major (uncommon) acronyms at the beginning of new sections for any readers who may be skipping sections. These aren’t defined to my knowledge until section 5.2. ‘P’ is never defined that I saw—pressure? There is a missing citation or statement on line 6 (currently shows up as a question mark). Also, it should be made clear in the text to which volatility bin BBPOA0, BBPOA1, etc belongs to.

The sentences in page 12 line 3 are replaced in the revised version of the paper by:

« The primary organic aerosols emitted by biomass burning (BBPOAlP for compounds of low volatility, BBPOAmP for compounds of medium volatility and BBPOAhP for compounds of high volatility, of saturation concentration $C^*$: $\log(C^*) = -0.04, 1.93, 3.5$ respectively) undergo one oxidation step in the gas phase, leading to the formation of secondary surrogates (BBSOAlP, BBSOAmP and BBSOAhP). »

The missing citation is added to line 6 page 12 as follows: « In the one-step oxidation scheme, used for example in Couvidat et al. (2012); Zhu et al. (2016); Sartelet et al. (2018) ... »

A reference to the volatility bins of the compounds BBPOA0, BBPOA1 etc are added page 12, line 15: « BBPOA0, BBPOA1, BBPOA2, BBPOA3, BBPOA4 refer to the primary surrogates and BBSOA0, BBSOA1, BBSOA2, BBSOA3 refer to the secondary ones (see Table D2 of Appendix D for their properties). »

Pg 12 lines 15-18: It’s not clear from the text or appendix D what the fragmentation and functionalization scheme is. It would be helpful to have the fragmentation and functionalization rates or fractions explicitly expressed. Or is the given reaction rate with OH of $4 \times 10^{-11}$ supposed to account a combined probability of fragmentation and functionalization?

The units on this reaction rate seem incorrect, they are listed as molecules-1 cm3 s-1, where often reaction rates are expressed as molecules cm-3 s-1. Please comment on the units.

Also, a brief look through Donahue et al. (2013) does not show where the specific value of $4 \times 10^{-11}$ came from—perhaps another citation is also necessary here? Can the authors comment on this as well?

Finally, it should be stated what happens to fragmentation products—are they placed into higher volatility bins or are they “lost” and no longer tracked in the model? The authors should consider adding more details on all of the issues raised here in the text.

The unit of the reaction rate are molecule-1 cm3 s-1 because it is a second order reaction rate. Indeed, the reaction takes into account a combined probability of
fragmentation and functionalization, which are considered simultaneously in each oxidation reaction.

The experimental reaction rate of $4 \times 10^{-11}$ molecule$^{-1}$ cm$^3$ s$^{-1}$ is from Robinson et al. (2007). The sentences in page 12 line 16 is modified in the revised version as follows: « In the gas phase, the primary and secondary surrogates react with OH at a rate of $4 \times 10^{-11}$ molecules$^{-1}$ cm$^3$ s$^{-1}$ (Robinson et al., 2007). »

High volatility fragmentation products are not considered in the parameterisations. Since fragmentation and functionalization are considered simultaneously in each oxidation reaction, the oxidation products correspond to fragmentation and functionalization products which are placed into lower volatility bins than the precursor.

The sentences in page 12 lines 17-18 are modified as follows: « During each oxidation step, the oxidation of the surrogate increases the surrogate oxygen number and decreases its volatility and carbon number, due to functionalization and fragmentation which are considered simultaneously during each oxidation reaction. »

Section 3 lines 30-31: I suggest writing out what ISORROPIA and SOAP stand for.

The full names are added in the revised version of the paper as follows:
ISORROPIA refers to a thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols.
SOAP stands for Secondary Organic Aerosol Processor.

Page 13, line 6 and Table E1: I suggest adding 1 sentence explanation of what the reactivity factor is. In Table E1 this is listed as Reactivity f0, consider changing to something like Reactivity factor (f0).

This sentence in page 13 line 6 is modified as follows: « The reactivity factor (f0), which corresponds to the ability of a dissolved gas to oxidize biological substances in solution, may range from 0 for non-reactive species to 1 for highly reactive species. In this work, the f0 value is set to 0.1 (Karl et al., 2010; Knote et al., 2015). »

Reactivity fo in Table 1 is replaced by Reactivity factor (f0).

Section 4 page 13 line 12: It would be helpful to let the reader know that the emissions estimate of toluene and xylene will be discussed in the next section. Same for when NMOG is discussed in this section.

The sentence in page 13 line 11-12 is modified in the revised version of the paper as follows: « for VOC emissions, only toluene and xylene are considered (as detailed in section 5.1) ... »

The sentence in page 14 line 2-3 is modified in the revised version of the paper as
follows: « but the gaseous I/S/L-VOC emissions are calculated from NMOG (as described in section 5.2) ... »

Pg 14: What is Un in the Multstep-UnNMOG-withVOCs?
In the Multstep-UnNMOG-withVOC, Un stands for unidentified NMOG.
For clarity, the sentence page 14 line 3 « but the gaseous I/S/L-VOC emissions are calculated from NMOG » is modified to « but the gaseous I/S/L-VOC emissions are assumed to be unidentified NMOG and they are estimated from NMOG emissions. »

pg 14 lines 8-12: can the authors comment on by ~ how much (I assume a range) lower Donahue et al (2005)’s calculation of the enthalpy of vaporization was than the SIMPOL.1 calculations? I recommend including the range of delta(Hvap) s from SIMPOL.1 either in the text or in table 1.
The enthalpy of vaporization (ΔHvap) values from SIMPOL.1 calculations are presented in table B1 for each species considered in this work. These ΔHvap are always higher than 50 kJ/mol and they are in the range of 54 - 132 kJ/mol.
The sentence in page 14 lines 8-9 is modified in the revised version of the paper as follows: « This is lower than the ΔHvap values calculated for individual components using SIMPOL.1. The calculated ΔHvap values are in the range of 54 - 132 kJ/mol. »

Section 5.1: can the authors comment on how representative they believe woodfire stove smoke emissions are of wildfires?
We do not believe that woodfire stove smoke emissions are representative of wildfires. For example, smog chamber experiments do not take into account all the different types of the burned vegetation. However, the identification of SOA precursors from smog chamber experiments of woodfire stove smoke emissions is an indication of which SOA precursors may be involved in wildfires. The following sentence is added page 15 line 6: « Bruns et al. (2016) identified the most significant gaseous VOC precursors of SOA from residential wood combustion and presented their contribution to SOA concentrations. Although woodfire stove smoke emissions may not be representative of wildfires, they provide some indication of the SOA precursors involved during wildfires. »

Section 5.3, lines 32-33 (first sentence of the section): would the left panel of Fig 7 technically be showing POA_tot? Since these are the OAtot precursors?
No, the text is correct, and Fig 7 is showing OAtot. OAtot precursors are made of POA_tot and of the VOCs that are SOA precursors. In this study, POA_tot corresponds to I/S/L-VOCs in the particle and gas phase and do not include VOCs.
Technically, Figure 7 presents all the OAtot precursors: POA_tot (in the gas and
particle phase) represented in red and VOCs represented in blue.

Section 6.1. Pg 21 lines 3-5: Can the authors briefly justify the choice of using Multistep-withVOCs for this figure?
We choose to use Multistep-withVOCs for this figure because it is the simulation that represents the reference configuration and takes into account the added VOCs.

Page 21 lines 9-10: from which model run(s) does this data come from?
The data comes from Multistep-withVOCs run.

The sentence in page 21 lines 9-10 is modified as follows: « Figure 12 shows the distribution of the OA concentrations formed from the different VOCs emitted by wildfires in the simulation Multistep-withVOCs, over the sub-region MedReg during the summer 2007. »

Pg 23, lines 10-13: how were the differences within “the fire plume” determined? What’s meant by the fire plume here? How well can the model resolve an individual plume? Please explain this further.

We mean here by fire plume, the panache of fire emissions transported far from the fire region. As our model is an eulerian model, we do not follow the fire plume, but its location is determined visually. The differences within the fire plume are calculated by considering the relative differences of PM2.5 concentrations between the simulations Multistep-withVOC and Multstep-unNMOG-withVOC.

The sentence in page 23 lines 10-13 are modified as follows: « Estimating the gaseous I/S/L-VOCs emissions from POA rather than from NMOG results in higher local PM2.5 concentrations (+8 to +16% in Greece) and lower PM2.5 concentrations mainly in Balkans (-30%) and in the fire plume visually determined (-8 to -16%). »

Two more general comments:

A) Are the model results being compared to actual observations? If instead they are being compared to work done in the first author’s other ACPD paper, this should be made more clear and the comparisons could be spelled out more explicitly.

In this paper, the model results were not compared to observations. Comparisons to observations were performed in Majdi et al. (2019) (already published in ACP). They were not repeated here, because there was no observation of OA near the fire regions during the summer 2007.

The work done in Majdi et al. (2019) compared PM2.5 concentrations and optical
properties. Their reference simulation corresponds to the simulation onestepISLVOC of this paper. According to Majdi et al. (2019), good general performances of the model are shown for the PM2.5 concentrations during the summer 2007. However, the 8 AIRBASE stations used for the evaluation of PM2.5 are far from the fire regions, and they may not provide meaningful information for our study here.

Page 4, the sentence « Through comparisons to both ground based and satellite remote sensing (MODIS) observations, a general good performance for surface modeled PM2.5 with a clear improvement of PM2.5 is found when including fire emissions » is removed. It is replaced by the following sentence at the end of section 3: «The reference simulation uses the same setup as Majdi et al. (2019). The evaluation of Majdi et al. (2019) of the simulation includes both ground based and satellite remote sensing (MODIS) observations. Ground-based observation of PM2.5 at 8 AIRBASE stations and of aerosol optical depth at 6 AERONET stations are used. The evaluation shows good performances of the model, especially when wildfires are taken into account in the simulation. Enhancements in PM concentrations due to wildfires are simulated at ±1-day uncertainty in the timing compared to satellite observations (MODIS), with a strong contribution from organic compounds (~61%) (Majdi et al., 2019).»

Page 13, line 11, the words « The simulation onestepISLVOC » are replaced by « The reference simulation onestepISLVOC ».

B) This work would benefit from a discussion of the pros/cons of each model simulation type, and whether or not any model simulations appear to better represent the real atmosphere. Much work was clearly done here, but the paper currently does not seem to have the “why this matters/how it improves upon previous work” factor yet that will allow it to become an easily useful guide and reference for other members of the community.

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.

Figures/tables:

Figures 1-4 would benefit from being made in a higher-quality format rather than the excel default graphs.

Figures 1-4 are reproduced in a high quality format in the revised version of the paper.

Figure 11: It should state in the figure caption and/or on the figure which model simulation is being used to make this figure.

The caption of figure 11 is modified in the revised version of the paper as follows: «Daily mean surface OA concentrations from wildfires (left panel) and the relative contribution of VOCs to OA from wildfires (right panel) during the summer 2007 (simulation Multistep-withVOCs).»

Figure 12: from what data/model simulation(s) was this pie chart constructed? This should be stated in the figure caption and in the text.

The caption of Figure 12 is modified in the revised version of the paper as follows:
« Distribution of OA concentrations formed from the different VOCs emitted by wildfires over the sub-region MedReg during the summer 2007 (simulation Multistep-withVOCs).»

Figure 13: the colorbars should have units with them (% and mass concentrations?). This colorbar is a little hard to interpret, are we to take that the tan regions are anywhere between 0-5 or 8% different? Can the authors make the colorbars for each % difference plot the same, they’re currently changing by between 5 and 11 units. I suggest considering a non-linear colorbar to see more structure within the -5 to 5% difference range.

Units on the colorbars (% and μg/m$^3$) are added to Figure 13 in the new version of the revised paper.

Similar colorbar for each % difference plot are considered in Figure 13 in the new version of the revised paper.

Technical comments:

Page 2 line 7: suggest rewriting to PM is composed of organic and inorganic compounds, dust, and black carbon (Jimenez et al., 2009).

The sentence in page 2 line 7 is modified in the new version of the revised paper as follows: « PM is composed of organic and inorganic compounds, dust and black carbon (Jimenez et al., 2009).»

Page 2 line 13: do the authors mean that both POA and SOA are composed of compounds of different volatilities? Suggest clarifying this sentence.

Indeed, we mean that both POA and SOA are composed of compounds of different volatilities.

The sentence in page 2 line 13 is modified in the revised version of the paper as follows: « Both POA and SOA may be composed of components of different volatilities such as S-VOCs, L-VOCs which may partition between the gas and particle phases (Robinson et al., 2007). »

Page 20 line 11: un should be Un in the simulation name.

Multistep-unNMOG-withVOCs in page 20 line 11 is replaced by Multistep-UnNMOG-withVOCs (as in the simulation name) in the revised version of the paper.

Page 20 line 21: this would make more sense if it was written something like “Across our cases, 28 to 42%...”
The sentence in page 20 line 21 is modified in the revised version of the paper as follows: « Across our cases, 28 to 42% of the OA concentrations from I/S/L-VOCs emissions are primary. »