

Comment on “Modeling organic aerosol concentrations and properties during winter 2014 in the northwestern Mediterranean region” by Chrit et al.

acp-2018-149

General Comments:

Chrit et al. have deployed the Polyphemus platform with expanded techniques for simulating organic aerosol formation and aging, particularly from residential heating sources, and applied it to the CharMEx campaign in winter 2014. The study design is generally sound and the sensitivity choices are informative. There is also adequate reporting of direct results. However, I found there to be a lack of further diagnosis or interpretation of results considering the amount of data the authors would have access to from the model. Considering this, I think the paper would be better suited in its current form for GMD, although I think it is of acceptable quality and scope for publication in ACP, given that the authors address specific concerns below.

Specific Comments

1. Section 3.4: I did not understand how profiles 1 and 2 are allocated to individual emissions. It should be made clearer why profiles 1 and 2 can be mismatched for volatility and O:C? Usually, I think of these as tied together by the molecular weight (i.e. carbon number) assumed for each model species of a given volatility. Are the assignments made using some feature from the emissions inputs, or are individual sectors assigned profile 1 or 2 based on some knowledge of their emissions (e.g. waste burning goes with profile 2, offroad diesel goes with profile number 1, etc)? If the latter, can the authors include a table that identifies these assignments? If the former, can the authors better describe what parameters and algorithm are used to make the assignments?

Profiles 1 and 2 are used to allocate emissions of I/S-VOCs into model surrogate species. This allocation depends on the emission sectors. In the profiles, volatility and O:C can mismatch for two reasons: the volatility range spans by one model species is quite large and the chemical compounds may have different functional groups. The profiles 1 and 2 are based on chamber measurements performed for different emission sectors: profile 2 for I/S-VOCs from residential heating sector and profile 1 for I/S-VOCs from traffic. For clarity, the beginning of section 3.4 was rewritten as follows:

“Emissions of I/S-VOCs are allocated into the surrogate compounds detailed in the above sections using emission distribution profiles, which are based on chamber measurements. The distribution of the emission profiles as a function of volatility (saturation concentration) is detailed in Table 1. Two emission profiles are used. The first one corresponds to the measurements of May et al. (2013a) for biomass burning, and it is similar to the emission profile used by Couvidat et al. (2012) for all sectors and by Ciarelli et al. (2017b) for residential heating. The second emission profile corresponds to an average of emission distributions from gasoline and diesel vehicles measured by May et al. (2013b, c), and it is used in Koo et al. (2014). Here, the volatility emission distributions are assigned to a profile number (equal to 1 or 2), depending on whether the volatility profile is similar to the profile from biomass burning emissions of May et al. (2013b) (profile number 2) or whether it is similar to the profile from vehicle emissions of May et al. (2013c) and May et al. (2013a) (profile number 1). As shown in Table 1, the emitted I/S-VOC are less volatile in the profile 1 than in the biomass-burning volatility distribution (profile 2).

Depending on the emission sector, the OM:OC and O:C ratios of the emitted surrogates may differ. For most sectors, such as traffic, the OM:OC and O:C ratios are assumed to be low (OM:OC is equal to 1.3 in Couvidat et al. 2012). However, for residential heating, the emissions may be more oxidized. The scheme of Ciarelli et al. (2017b) assumes higher OM:OC and O:C ratios, as described in Table 2. Here, the OM:OC and O:C ratios are assigned to a profile number (equal to 1 or 2), depending on whether the ratios are similar to the profile from biomass burning emissions of Ciarelli et al. (2017b) (profile number 2) or whether they are lower (profile number 1).”

In the simulation, the assignment to profile 1 or 2 is identified in Table 3.

2. After going back to Ciarelli et al. (2017b), I am not convinced they included additional IVOCs, consistent with those being added in this simulation, in their parameterizations. It seems from Table 1 in that paper, that the authors included NTVOCs and also evaporated the existing POA into SVOC and IVOC bins. But I do not think they considered an additional IVOC category. Given this, I am not surprised that simulations here which include additional IVOCs and NTVOCs (S4 and S6) tend to over predict measurements. I would suggest the authors perform at least one run with R_RH set to 0 for residential heating sources and NTVOC turned on. This will probably look a lot like S5 so if the authors want to adjust the explanation of their cases to avoid doing more simulations, I think that is okay, but some detailed explanation should be added (i.e. R_RH could be defined as

adding NTVOC). Note this approach would not be perfect, because the SOA yields for the IVOCs would differ from those Ciarelli et al. (2017b) derived for NTVOC.

In Ciarelli et al. (2017b), NTVOCs have a saturation concentration of $10^6 \mu\text{g m}^{-3}$ falling with the IVOC saturation concentration range limit. These NTVOCs probably include some VOCs and some IVOCs. However, modelling IVOCs and SVOC emissions by multiplying POA by a factor accounts for the fact that in the emission inventory the gas-phase of I/S-VOCs is not given. We agree with the reviewer that some IVOCs are probably counted twice if NTVOCs are added to the emissions, as well as the factor to estimate I/S-VOCs from POA. Several changes are therefore made to the revised paper:

The sentence “but they are slightly over-estimated when the ageing of NTVOC is taken into account” is removed from the abstract.

On page 3, the sentence “Ciarelli et al. (2017b) modified the approach of Koo et al. (2014) by adding non traditional VOC (NTVOC) that have a limit saturation concentration between VOC and IVOC.” is replaced by “Ciarelli et al. (2017b) modified the approach of Koo et al. (2014) by considering non traditional VOC (NTVOC) that have a limit saturation concentration in the low range of IVOCs.”

On page 10, at the end of line 7, the following sentence is added: “Even though NTVOCs are added, emissions of I/S-VOCs as modeled by the factor R_{RH} are kept.”

On page 11, at the end of line 16, the following sentences are added: “Because I/S-VOC emissions as modeled by the factor R_{RH} are kept in those simulations, the IVOCs forming SOA may have been counted twice by adding NTVOCs, explaining the over-estimation.”

The sentences lines 18-20 on page 13 are removed.

On page 20, the words “ particularly those with NTVOC” are removed.

On page 20, the sentence “All the simulations tend to under-estimate the OA concentrations at Ersa, except for the two simulations where NTVOC are taken into account, which, however, over-estimate the OA concentrations.” is replaced by “All the simulations tend to under-estimate the OA concentrations at Ersa, except for the two simulations where NTVOC emissions are added to I/S-VOC emissions. These simulations over-estimate the OA concentrations, because some IVOC emissions are counted twice.”

3. Are the IVOCs from residential heating assumed to be the same composition (i.e. same SOA yields) as those from vehicle sources? If so, what is this based on?

In the one-step oxidation scheme, IVOCs from residential heating are assumed to have the same SOA yield as those from vehicle sources. This assumption is commonly made in 3D models (e.g. Couvidat et al. 2012). It is based on the work of Shrivastava et al. (2006), who show a very similar dilution curve behavior between diesel exhaust and wood smoke.

4. Do the authors have a sense for the variability of wood-burning fuels across the region and how well one volatility distribution would be at simulating their emissions? Are there varying practices for controlling emissions from chimneys or flues that would have an impact on the particle fraction from these sources?

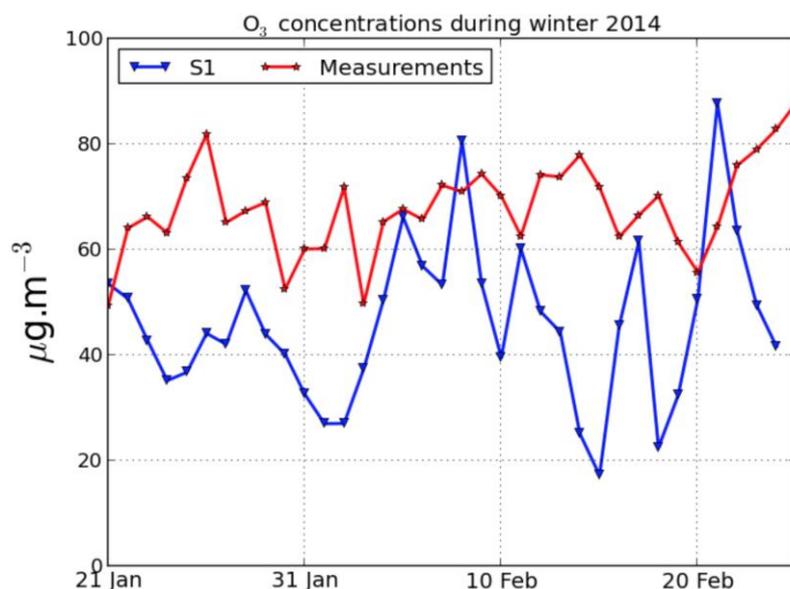
The volatility distribution of May et al. (2013) used for the wood burning emissions that is based on fitting data from thermodenuder measurements of the burning of 19 wood types. They found that the overall partitioning behavior of all the biomass fuel emissions considered in their study is similar enough to be represented in the model by one parameterization. Furthermore, we do not have data on the wood-burning fuels used across the region. Knowledge about wood-burning fuel may be complicated by the fact that the wood-burning fuel used may differ from official recommendations. The variability of wood-burning fuels may however be more important for very low-volatility emissions, which are difficult to measure. This point was added to the conclusion (see reply to comment 6).

5. The authors make the point that the winter time conditions are not favorable for oxidative aging of SOA or high formation of SOA from VOCs. However, the measurement data show relatively high O:C, out of reach of the model sensitivity cases. Can the authors demonstrate the model’s performance for relevant gas-phase oxidants to eliminate that as a factor?

Only ozone was measured at ERSA. We do not have other oxidants’ measurements.

The comparison of modeled and measured concentrations of ozone between January 21 and February 24 is added to the revised paper. This figure shows that the model tends to underestimate ozone concentrations (the modeled and measured mean concentrations are 46.2 and 68.0 $\mu\text{g m}^{-3}$). This suggests that the underestimation of the O:C ratio may be due to an underestimation of oxidants' concentrations and secondary aerosol formation. However, the O:C ratio is underestimated even during the days where ozone is well modeled.

These sentences are added to the revised paper in section 5, and the following sentences are added to the conclusion. : «... OM:OC and O:C ratios are underestimated at Ersa in all simulations. As ozone tends to be underestimated in the model compared to the measurements, the underestimation of the OM:OC and O:C ratios might partly be due to an underestimation of oxidants concentrations and secondary aerosol formation. »



6. I would urge the authors to consider adding more analysis of the relationship between model error and individual sources or chemical descriptions in the model. Are there correlations with other model species that would give some clues as to where the parameterizations are weak or better emissions data are needed (e.g. CO, POA, NO_x, etc)? What recommendations do the authors have for future work by experimentalists and other chemical transport model efforts? What pieces of the model description need the most work? One conclusion that comes out is that the results are more sensitive to the volatility distribution than the aging mechanism. I wonder if the authors could emphasize this point as an area in need of further research? Does more work need to be done on constraining the volatility, or on representing the diversity of wood burning fuels and conditions that exist?

Based on the paper of May et al. (2013), representing the diversity of wood-burning fuels does not seem to be influence the partitioning between gas and particle, although the emissions of low volatility compounds, which are not well characterized, may differ.

A paragraph emphasizing the future work and areas where the model needs more improvement is added at the beginning of the paragraph at line 23 in the conclusion of the discussion paper. “Because the volatility distribution at the emission is the parameter influencing the most the concentrations, further experimental research should therefore focus on characterizing it for the different sectors. The emissions and formation of very low-volatility compounds should also be further investigated to represent the aerosol characteristics observed.”

Minor Issues/Typos/Suggestions

1. Page 1, line 10: Suggest replacing “whatever the parameterizations” with “in all parameterizations tested”. “Whatever the parameterizations” is replaced by “in all parameterizations” in the revised paper.
2. Page 2, line 3: Suggest replacing “primary fraction originates” with “primary fraction originates mostly”. “primary fraction originates” is replaced by “primary fraction originates mostly” in the revised paper.

3. Page 2, line 5: evidences should be evidence
“evidences” is replaced by “evidence” in the revised paper.

4. Page 2, line 8: I think the generally acknowledged IVOC range includes 10^3 - 10^6 while SVOCs are 0.1- 10^3 .

Theses ranges are corrected in the revised paper. “... (IVOC) (with saturation concentration C^* in the range 10^4 - 10^6 $\mu\text{g m}^{-3}$), semi-volatile organic compounds (SVOC) (with saturation concentration C^* in the range 0.1- 10^4 $\mu\text{g m}^{-3}$), or low-volatility ...” is replaced by “... (IVOC) (with saturation concentration C^* in the range 10^3 - 10^6 $\mu\text{g m}^{-3}$), semi-volatile organic compounds (SVOC) (with saturation concentration C^* in the range 0.1- 10^3 $\mu\text{g m}^{-3}$), or low-volatility ...” in the revised paper.

5. Page 1, line 16: Add “precursors” to read “main anthropogenic VOC precursors”.

This expression is actually in page 2 line 16.

“... main anthropogenic VOC ...” is replaced by “... main anthropogenic VOC precursors ...” in the revised paper.

6. Page 3, lines 19-22: The 2D-VBS can also accommodate oligomerization pathways, although most transport models don't take it into account.

The sentence “ ...taking into account two competing processes: functionalization and fragmentation (Donahue et al., 2012). ...” is replaced in the revised paper by “taking into account three competing processes: functionalization, oligomerization and fragmentation (Donahue et al., 2012).”.

7. Page 3, line 23: suggest rewording to “scheme that accounts for multigenerational ageing, including functionalization and fragmentation, and that...”

The sentence “... scheme that accounts for fragmentation, functionalization and multigenerational ageing, and that represents ...” is replaced in the revised paper by “scheme that accounts for multigenerational ageing, including functionalization, oligomerization and fragmentation, and that represents ...”

8. Page 3, line 35: Recommend the authors add more description of what the non-traditional VOCs are. In the past, the word nontraditional has been used to identify SOA from IVOCs and SVOC vapors. I was confused at first, but see from the sensitivity case descriptions that these NTVOCs are different compounds.

The following sentence is added to clarify the definition of NTVOCs in the revised paper. “... adding non traditional VOCs (NTVOCs). They are VOCs or IVOCs, not usually taken into account in CTMs, and with a saturation concentration in the low-range of IVOCs . Ciarelli et al. (2016) identified these NTVOCs as phenol, m-, o-, p-cresol, m-, 15 o-, p-benzenediol/2-methylfuraldehyde, dimethylphenols, guaiacol/methylbenzenediols, naphthalene, 2-methylnaphthalene/1- methylnaphthalene, acenaphthylene, syringol, biphenyl/acenaphthene and dimethylnaphthalene”.

9. Page 4, line 8: Are studies from 2001 and 2005 still recent? Obviously, this is the authors' call. Maybe everything after 2000 still ‘feels’ recent? It's certainly more recent than 1975.

The sentence “... , recent studies (Turpin and Lim, 2001; El-Zanan et al., 2005) show ...” is replaced by “..., numerous studies (Turpin and Lim, 2001; El-Zanan et al., 2005; Aiken et al., 2008, Couvidat et al., 2012, Tost and Pringle, 2012, Canagaratna et al., 2015, Tsimpidi et al., 2018) show ...”.

10. Page 5, line 11: Are the authors using ISORROPIA v1? Version 2 includes among other things interactions with crustal species. If the model includes version 1, a statement should be added explaining either the unimportance of dust sources during the campaign, and/or the unimportance of crustal cations on organic aerosol concentrations as they are modeled here. The output of ISORROPIA will affect things like water uptake and pH, but most OA models now probably aren't sensitive to parameters like these, at least first- or second-order. Is that true for this model as well?

The ISORROPIA version used in this study is ISORROPIA v1 (Nenes et al. 1998). Crustal cations are not taken into account in this work, although they may affect water uptake and pH. However, as a first approximation, I/S-

VOCs are assumed to be hydrophobic, and therefore their concentrations would not be influenced by crustal species.

11. Page 5, line 15-16: The authors reference Chrit et al. (2017) for their grid configuration details, but I think it would still be useful to put it here. What is the grid resolution and layer resolution of the nested and large domains?

The spatial resolution and the vertical resolution used here are added to the revised paper: "...in Chrit et al. (2017). The spatial resolutions used for the European and Mediterranean domains are 0.5°x0.5° and 0.125°x0.125° along longitude and latitude. 14 vertical levels are used in this study for both domains from the ground to 12 km. The heights of the cell interfaces are 0, 30, 60, 100, 150, 200, 300, 500, 750, 1000, 1500, 2400, 3500, 6000 and 12 000 m. Boundary conditions...".

12. Page 5, lines 28-30: Is the total [I/S-VOC + POA] equal to 2.5 or 1.5 times the original POA? Could the authors adjust the wording of this sentence to make this clearer?

The total [I/S-VOC + POA] is equal to 2.5 times the original POA. For clarity, the sentence "I/S-VOC gas-phase emissions are estimated from the POA emissions from residential heating by multiplying them by a constant factor assumed to be 1.5 in the default simulation." is replaced by "I/S-VOC gas-phase emissions are estimated from the POA emissions from residential heating by multiplying them by a constant factor assumed to be 1.5 in the default simulation. The total (gas + particle) I/S-VOCs is therefore equal to 2.5 the original POA."

13. Page 6, line 9: remove "the" to read "at the model cell closest to the station"
"the" is removed from that sentence.

14. Figure 1: Could the authors adjust the color scales so it's a bit easier to assess them in relation to each other? For example, 0.01 for the left and 0.05 for the right?
The color scale of this figure is adjusted in the revised paper.

15. Page 7, line 9: Suggest changing "different parameterizations are compared" to "different parameterizations, described in the following sections, are compared".

"different parameterizations are compared" is replaced by "different parameterizations, described in the following sections, are compared" in the revised paper.

16. Page 7, line 16: How are the saturation concentrations for the S/I-VOCs chosen? Are they from a previous study? Are they fit to something?

These saturation concentrations for the I/S-VOCs are chosen to fit the curve of dilution of POA from diesel exhaust of Robinson et al. (2007) with three molecules. This point is added in the revised paper: "... different volatilities chosen to fit the dilution curve of POA from diesel exhaust of Robinson et al. (2007) and characterized by their saturation concentrations (0.91, 86.21 and 3225.80 $\mu\text{g m}^{-3}$ respectively) ...".

17. Table B1: Why is it that for the SOA vs. POA species, the enthalpies of vaporization are the same even though the molecular weights are higher, the saturation concentrations are somewhat lower and the O/C ratios are somewhat higher? I would guess the SOA species should have larger enthalpies of vaporization.

The enthalpies of vaporizations are assumed to be the same for SOA as for POA because of lack of experimental data. It is difficult to estimate what the enthalpy of vaporization of SOA should be. A recent study of Majdi et al. (2018) found that the sensitivity of AOS concentrations formed from fire emissions to variations in the modeled enthalpy of vaporization is low compared to other sensitivities, such as the ageing scheme.

18. Tables D1 and D2 look to be repeated?
Yes, the table D2 is removed from the revised paper.

19. Page 11, line 6: Should "SOA" be "POA"?
Yes, "... 31% of SOA from ..." is replaced by "... 31% of POA from ..." in the revised paper.

20. Table 5: What is the uncertainty reflective of? One standard deviation?

Yes, it is the standard deviation to the measurements.

21. Page 20, line 24: The authors have cited May et al. 2013a (biomass burning emissions) twice. The second A in the name of May is removed from that reference in the revised paper.