Interactive comment on "Impact of wildfires on particulate matter in the Euro-Mediterranean in 2007: sensitivity to the parameterization of emissions in air quality models" by Marwa Majdi et al.

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:

A) This paper tries to evaluate model estimates of fire-related PM concentrations through evaluation with data from surface networks and satellite remote sensing. However, I think this work is flawed due to the decision to use only PM measurements. For some reason they do not make use of the rather extensive measurements which are available (Airbase,EMEP, or even AMS data) of sulfate, nitrate, ammonium, or other inorganic components. This is a serious problem I think. For example, Fountoukis et al (2011) suggested significant contributions of sulfate, nitrate and ammonium to PM1 mass, and backed up their analysis with comparison to measurements. Van Damme et al. (2014) showed enormous levels of NH3 from biomass burning, which presumably caused high PM2.5 also.

Figure 1 shows the PM2.5 composition for simulation "Poly-Nofires" over the Euro-Mediterranean region and during the summer 2007. Inorganics, mainly sulfate (23.5%), sea salt (23.6%) and ammonium (7.6%), contribute highly to PM2.5 composition. Similar results are found in Fountoukis et al. (2011) who showed also that sulfate, sea salt and ammonium contribute highly to the PM1 mass (30%, 14% and 13% respectively) over Europe during May 2008.
Several other studies evaluated the performance of Polyphemus to simulate sulfate, ammonium and nitrate concentrations (Sartelet et al., 2007; Zhang et al., 2013; Chrit et al., 2018). Chrit et al., (2018) evaluated the model Polyphemus over the western Mediterranean region during the ChArMEx campaign, by comparison to in-situ aerosol measurements performed during three consecutive summers (2012, 2013 and 2014). According to Chrit et al. (2018), sulfate and ammonium concentrations satisfy the performance and goal criteria, while sodium satisfies only the performance criteria. Chrit et al. (2018) found that chloride and nitrate were both underestimated compared to observations. They explained that this underestimation is probably caused by uncertainties in the measurements and difficulties in representing the gas-particle partitioning. Sartelet et al. (2007) showed that the concentrations of inorganics modeled with Polyphemus over Europe are consistent with observations (EMEP and AIRBASE). Model performance criteria are met for sulfate, nitrate and ammonium. Zhang et al. (2013) used Polyphemus to simulate air quality in July 2001 over western Europe. They evaluate the model's performance using surface measurements from EMEP and AIRBASE stations for inorganics. The simulated concentrations of inorganic PM are in a good agreement with EMEP observations, although sulfate and nitrate concentrations are underestimated.

The formation of inorganics because of wildfires is found to be low compared to the formation of organics. However, our simulation does take into account emissions of inorganic precursors such as ammoniac (NH3). Several studies (R'Honi et al.,2013; Van Damme et al.,2014; Whitburn et al.,

2017), show that large emissions of NH3 are released by biomass burning. Whitburn et al. (2017) studied the enhancement ratios NH3/CO for biomass burning emissions in the tropics using observations from the IASI satellite based instrument. They found a significant variability due to fire contribution. According to the Whitburn et al. (2017), the emission ratios NH3/CO in the tropics derived from IASI observations (as in Van Damme et al., 2014) are rather on the lower end of those reported in Akagi et al. (2011) that are used here.

If fire emissions are important for the regional budget of inorganics, more observations are required to provide emissions values of NH3 and concentrations of inorganics should be evaluated close to fire regions.

During the summer 2007, AMS data are not available. The PM data from AIRBASE and EMEP are scarce in our domain. We only have a few PM2.5 stations and only 3 stations (far from the studied fire regions: 2 in Spain and 1 in France) for inorganic concentrations. Evaluation with measurements is therefore not possible. However, we looked more closely at the contribution of inorganics to the simulated concentrations.

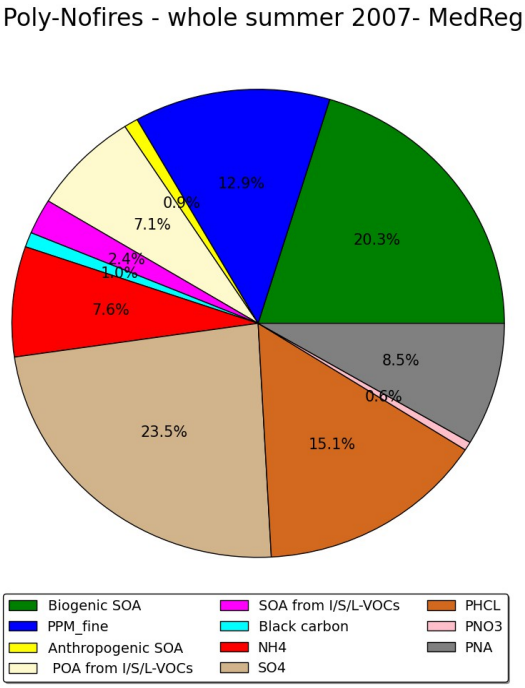


Figure 1: Composition of surface PM2.5 (simulation Poly-No-fires) over the Euro-Mediterranean region during summer 2007

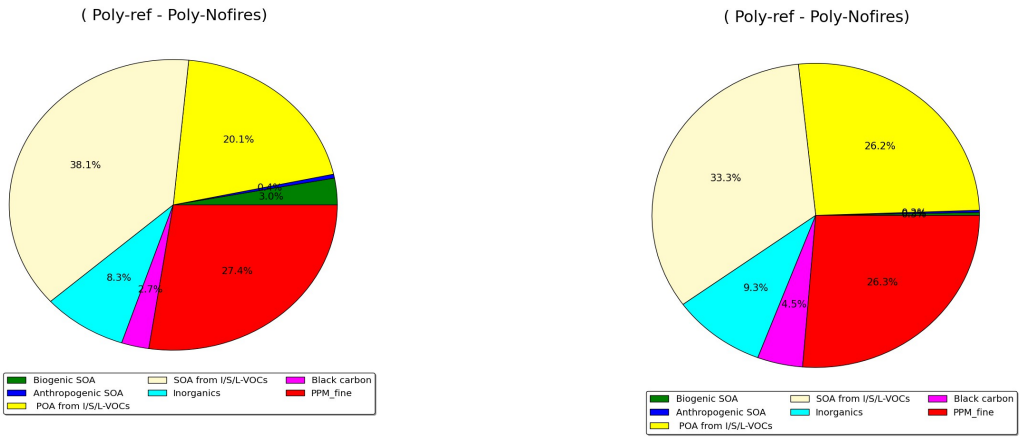
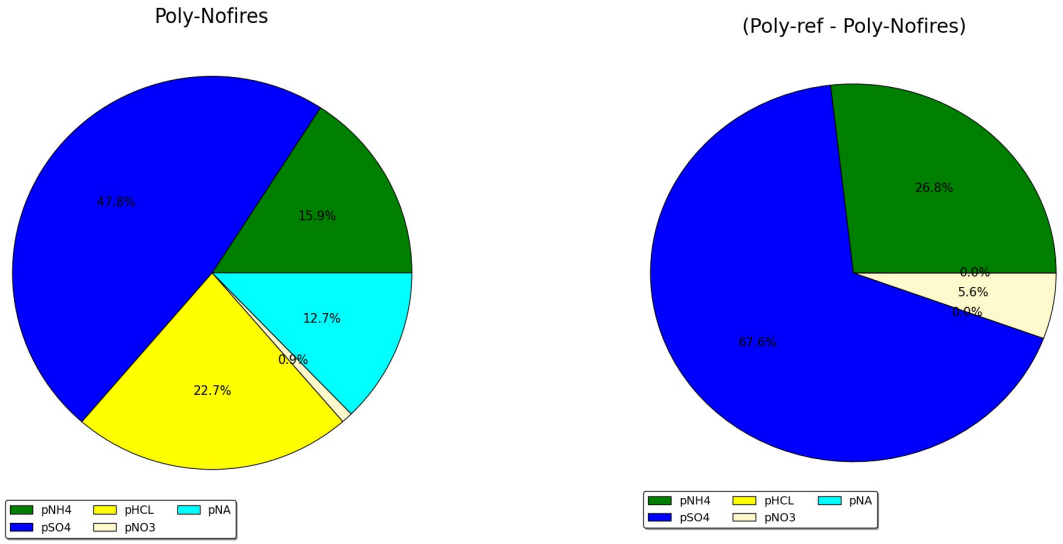


Figure 2: Composition of surface PM2.5 concentration due to fires (left panel: simulation Poly-ref over MedReg1 during the first fire event and right panel: simulation Poly-ref over MedReg2 during the second fire event).



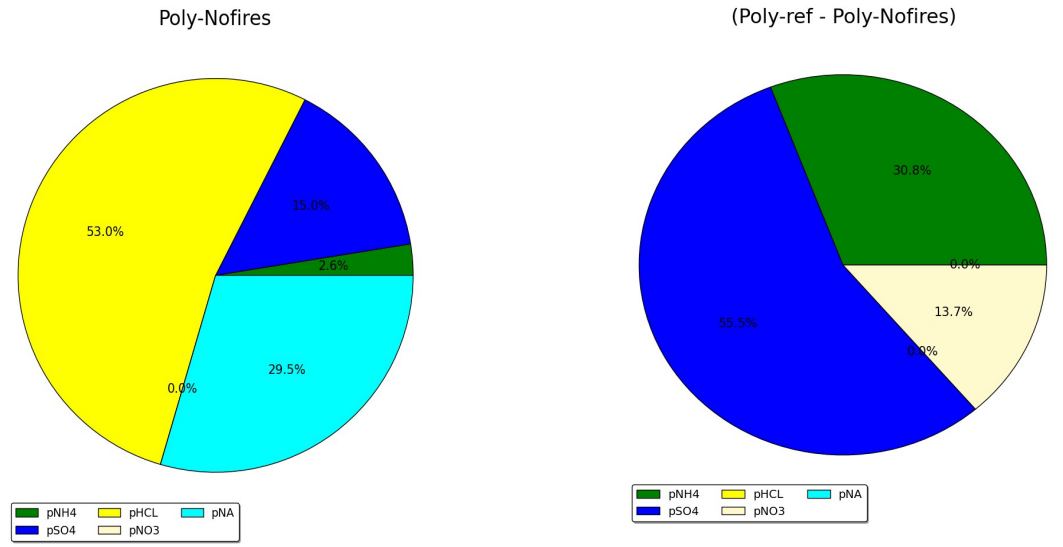


Figure 3: Composition of surface inorganic concentrations over Medreg1 during the first fire event (upper left panel, simulation Poly-nofires) and over MedReg2 during the second fire event (lower left panel, simulation Poly-nofires). Composition of surface inorganics due to fires over Medreg1 during the first fire event due to fires (upper right panel: simulation Poly-ref) and over MedReg 2 during the second fire event (lower right panel: simulation Poly-ref).

The contribution of inorganics is low compared to the contribution of organics. Figure 2 and Figure 3 show the composition of surface PM2.5 concentrations due to fires for simulation Poly-ref and the composition of surface inorganic concentrations respectively over MedReg1 for the first fire event and over MedReg2 for the second fire event.
The contribution of inorganics from fires varies between 8.3 and 9.3%. Focusing on the contribution from fires to inorganics, sulfate, ammonium and nitrate are the predominant components: between 55.7% and 67.6% for sulfate, between 26.8 and 38.7% for ammonium and 5.6 to 13.6% for nitrate.

These sentences are added to page 14 line 24 of the revised paper: "In our study, inorganics (mainly sulfate, sea salt and ammonium) contribute highly to PM2.5 composition, if fire emissions are not considered. Similar results are found in Fountoukis et al. (2011) who showed the high contribution of sulfate, sea salt and ammonium to PM over Europe during May 2018. However, when fire emissions are taken into account, the contribution of inorganics from fires is lower than the contribution of organics (8 to 9% of inorganics against 40 to 80% of organics). Focusing on the contribution from fires, sulfate, ammonium and nitrate are the predominant components of inorganics from fires: between 55.7% and 67.6% for sulfate, between 26.8 and 38.7% for ammonium and 5.6 to 13.6% for nitrate."

B) Further, on p10 they claim that by focusing on PM2.5 they avoid contributions from dust, but this simply isn't the case. The low-diameter tail of coarse-mode dust (and sea-salt) contributes of course to PM2.5, and measurements in southern Europe have shown that this can be a significant fraction even over long-periods (Putaud et al., 2010). (This same publication also demonstrates clearly the importance of non-organic compounds in contributing to PM2.5.)
I see no reason to believe that changes in model performance attributed here to various assumptions on OA emissions could not be masked or mistaken for problems with inorganic pollutants. As well as attending to the points raised below, I would encourage the authors to do a thorough analysis of the model performance for all the major compounds, and across many sites. I am afraid I cannot recommend this paper for publication without major revision.

Indeed, the low-diameter tail of coarse-mode dust (and sea-salt) contributes of course to PM10, but we choose not to consider PM10 in this paper (and therefore focus on PM2.5) in order to reduce the uncertainties related to dust emissions as much as possible.

Sentences page 10 line 5-7 "PM10 concentrations in the Mediterranean area are strongly affected by dust, which are difficult to simulate due to their sporadic nature and their main sources are located out of the model domain. Since dust is not in the scope of this paper, the analysis focuses on $PM_{2.5}$." are replaced by " PM10 concentrations in the Mediterranean area are strongly affected by dust, which are difficult to simulate due to their sporadic nature and the fact that their main sources are located out of the model domain. In order to evaluate more specifically the uncertainties associated with small particles (largest contribution from fires), and to minimize the contribution from dust, the analysis focuses on $PM_{2.5}$."

Other points:

0. The title is actually quite misleading. The paper only addresses some aspects of OM emissions, not emissions in general.

The title : "Impact of wildfires on particulate matter in the Euro-Mediterranean in 2007: sensitivity to the parameterization of emissions in air quality models." is replaced by : "Impact of wildfires on particulate matter in the Euro-Mediterranean in 2007: sensitivity to some parameterizations of emissions in air quality models."

1. The word dispersion, used in eg line 17 of the abstract, is usually associated with turbulent mixing in the air pollution context. Please use another term to make clear that here you mean statistical spread.

The word "dispersion" used in the paper is replaced by the "statistical dispersion" to avoid any kind of confusion.

2. p2, L20. Give reference for statements about anthropogenic origin.

The sentence page 2, line 20-21 : "Although ignitions are mainly of anthropogenic origin (negligence, arson, agricultural practices) , fire spread depends on meteorological conditions." is replaced by: "Although ignitions are mainly of anthropogenic origin (negligence, arson, agricultural practices) according to San-Miguel-Aynanz et al. (2013) and the European Forest Fire Information System (EFFIS) of the European Joint Research Center (JRC), fire spread depends on meteorological conditions."

3. p3, L8. Give reference for the volatility limits and definitions. Also, do you really mean from 1e4, or from 0.32e4 (see eg Table 4 of Murphy et al., 2014) ?

The volatility borders are very uncertain, but in this work we followed the volatility limits given in Robinson et al. (2007). The reference is added in the revised paper (page 3, line 8).

Reference:

- Robinson et al., 2007: Allen L. Robinson, Neil M. Donahue, Manish K. Shrivastava, Emily A. Weitkamp, Amy M. Sage, Andrew P. Grieshop, Timpthy E. Lane, Jeffrey R. Pierce, Spyros N. Pandis: Rethinking orhanic Aerosols: Semi volatile Emissions and Photochemical aging, Science, 315, 1259-1262, DOI:10.1126/science.113360

4. Units (e.g. p3. L8) should not be in italics.

All the units in italics are corrected in the revised version of the paper.

5. p3, L23. Change 'current CTMs' to 'two CTMs'. Your study says little about the many other CTMs used in Europe.

The sentences page 3, line 23: "The objective of this study is to evaluate the capabilities of current CTMs to simulate the impact of wildfires on the regional particulate matter budget (mainly

PM2.5).” is replaced by “The objective of this study is to evaluate the capabilities of two CTMs to simulate the impact of wildfires on the regional particulate matter budget (mainly PM2.5).”.

6. Table 1 is very vague and uses many acronyms that haven’t been explained yet. What is ECMWF, which version? What does ’from nesting simulations’ mean? Which version of MEGAN? Which version of EMEP emissions? Give more specific details and references here.

Table 1 summarizes the main characteristics of the Polyphemus and CHIMERE simulations. All the Acronyms used in this Table are explained in the text (from page 5 lines 1-21 to page 6 lines1-23). The clarifications below are added in the revised paper.

6-1 What is ECMWF, which version ?

The sentence page 5 line 20-21 “Both models (Polyphemus and CHIMERE) are driven by meteorological conditions simulated by the European Center for Medium-Range Weather Forecasts (ECMWF) model. ” is replaced by “Both models (Polyphemus and CHIMERE) are driven by meteorological conditions simulated by the European Center for Medium-Range Weather Forecasts (ECMWF, ERA-Interim) model.”

6-2 What does ’from nesting simulations’ mean?

Boundary conditions are from a simulation undertaken using a large domain (0.5°x0.5°, horizontal resolution) covering Europe and North Africa (see Figure G).
The Figure E is added in the appendix G of the revised paper.
The sentence page 6 line 1 : “ Simulations are undertaken using two nested domains.” is replaced by “ Simulations are undertaken using two nested domains (Figure 13 in Appendix A).”.

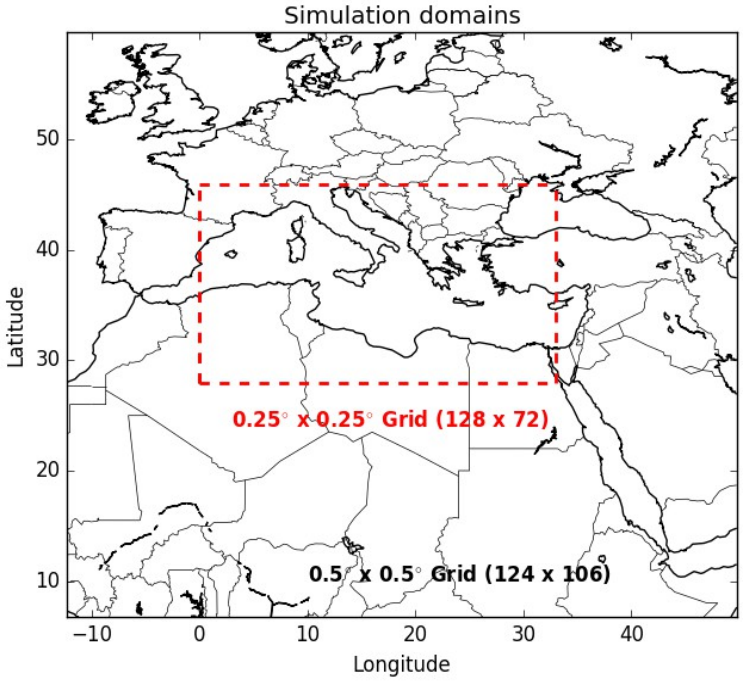


Figure G: Simulation domains including one large domain (with a 0.5◦ ×0.5◦ horizontal resolution) and a smaller domain (at a 0.25◦ ×0.25◦ horizontal resolution) delimited by the dotted red box.

6-3 Which version of MEGAN?

The sentence page 6 line 9-10 “Biogenic emissions are calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006).” is replaced by “ Biogenic

emissions are calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) with the standard MEGAN LHIV database MEGAN-L for Polyphemus and MEGAN v2.04 or CHIMERE (Guenther et al., 2006)."

6-4 Which version of EMEP emissions?

The sentences page 6 line 4-5 "Anthropogenic emissions are derived from the EMEP emissions inventory (European Monitoring and Evaluation Program, www.emep.int)." is replaced by " Anthropogenic emissions are derived from the EMEP emissions inventory for 2007. (European Monitoring and Evaluation Program,www.emep.int)"

7. P6, L3. The nesting factor is here given as 2:1, but usually one uses an odd ratio to avoid interpolation errors (e.g. https://earthscience.stackexchange.com/questions/8067/why-is-wrf most-often-configured-at-31-nesting-ratio). Have the authors checked if their results are robust?

The recommendation to use an odd ratio applies to WRF simulations. However, this is not required by Polyphemus nesting. Indeed the interpolation is done properly in 2D in Polyphemus, and it is accurate because the vertical levels do not vary with time/space.

8. p6, L9. Biogenic emissions of what? I assume isoprene and terpenes, but which?

The sentence page 6 lines 9-10 " Biogenic emissions are calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006)." is replaced by "Biogenic emissions of isoprene and terpenes (α-pinene, β-pinene, limonene and humulene) are calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006).

9. p6, L17-24. The explanation of the VBS scheme used is unclear. Firstly, where do the numbers -0.04, 1.93 and 3.5 come from? They are not suggested by May et al. 2013, and not obvious to the reader. Secondly, L21 suggests that OH+POA leads to SOA compounds in the same VBS bin, but L22-23 suggests a reduction in volatility equivalent by a factor of 100. Which is it?

In this work, we didn't use a VBS scheme. We used the one-step oxidation scheme developed by Couvidat et al. (2012) where the emission distribution is based on the fitting of the curve of dilution of diesel exhaust from Robinson et al. (2007). This emission distribution is approximately similar to the one measured by May et al. (2013a) for biomass burning (see Table A). According to Couvidat et al. (2012), I/S/L-VOCs emissions are assigned to 3 surrogates species: POAlP, POAmP and POAhP (for compounds of low, medium and high volatilities respectively), of saturation concentration $C\pi$: $\log10(C\pi) = -0.04, 1.93, 3.5$ respectively.

C* (µg/m^3)	Couvidat et al. (2012) emissions distribution	May et al. (2013a) emissions distribution for biomass burning
$10^{-0.04}$	0.25	0.20 0.20
$10^{1.93}$	0.32	0.10 0.20
$10^{3.5}$	0.43	0.4

Table A: the emission distribution of I/S/L-VOCs given by Couvidat et al. (2012) and May et al. (2013a)

The sentences in page 6, lines 17-24: "I/S/L-VOCs emissions are assigned to 3 surrogates species: POAlP, POAmP and POAhP (for compounds of low, medium and high volatilities respectively), of saturation concentration Cπ : log(C*) = -0.04, 1.93, 3.5 respectively. The volatility distribution at emissions of I/S/L-VOCs is detailed in Couvidat et al. (2012) (25%, 32%, and 43% of I/S/L-VOCs are assigned to POAlP, POAmP and POAhP respectively). It corresponds to the volatility distribution measured by May et al. (2013) for biomass burning aerosol emissions. Each primary aerosol undergoes one OH-oxidation reaction in the gas phase with a kinetic rate constant equal to 2.10−11 molecule−1 .cm3 .s−1 , leading to the formation of secondary surrogate in the same volatility: SOAlP, SOAmP and SOAhP. The ageing of the primary aerosols reduces the volatility of the secondary product by a factor of 100 and increases the molecular weight by 40% (Couvidat et al., 2012). " are replaced by : "I/S/L-VOCs emissions are assigned to 3 surrogates species: POAlP, POAmP and POAhP (for compounds of low, medium and high volatilities respectively), of saturation concentration Cπ : log(C*) = -0.04, 1.93, 3.5 respectively. The volatility distribution at emissions of I/S/L-VOCs is detailed in Couvidat et al. (2012) (25%, 32%, and 43% of I/S/L-VOCs are assigned to POAlP, POAmP and POAhP respectively). It corresponds to the volatility distribution measured by May et al. (2013a) for biomass burning aerosol emissions. Each primary aerosol undergoes one OH-oxidation reaction in the gas phase with a kinetic rate constant equal to 2.10−11 molecule−1 .cm3 .s−1 , leading to the formation of secondary surrogates: SOAlP, SOAmP and SOAhP. The ageing of the primary aerosols reduces the volatility of the secondary product by a factor of 100 and increases the molecular weight by 40% (Couvidat et al., 2012)."

10. p6, L17. The use of 'log' is ambiguous. In most VBS papers it means log10, but in other papers (especially mathematical) and common programming languages (eg python) it means the natural logarithm, log_e (or ln). I suggest using log10 to be clear.

The sentence page 6, line 17 : "I/S/L-VOCs emissions are assigned to 3 surrogates species: POAlP, POAmP and POAhP (for compounds of low, medium and high volatilities respectively), of saturation concentration Cπ : log(Cπ) = -0.04, 1.93, 3.5 respectively." is replaced by: "I/S/L-VOCs emissions are assigned to 3 surrogates species: POAlP, POAmP and POAhP (for compounds of low, medium and high volatilities respectively), of saturation concentration Cπ : $\log_{10}(C\pi)$ = -0.04, 1.93, 3.5 respectively.

11. p6, L33-34. Akagi provides emission factors for several ecosystems, but non are a close match to Mediterranean landscapes. And some of these emitted isoprene and terpenes, which also form SOA. Which emissions were in fact used?

The sentence in page 6 line 33 "Emissions for each species are derived from the carbon emissions using the emissions factors from Akagi et al. (2011)." is replaced by "Emissions for each species

are derived from the carbon emissions using the emissions factors from Akagi et al. (2011). These emission factors are provided in terms of g species per Kg DM burned ($g.kg^{-1}$) for all relevant species observed in biomass burning plumes and for different standard vegetation types that match to Mediterranean landscapes (chaparral, temperate forest, crop residue, pasture maintenance and savanna). The contribution of these vegetation types to the burned area detection over the Mediterranean region during the time period studied is 37.2% for temperate forest, 32.7% for savanna, 9.6 % for chaparral and 19.9% for crop residue."
The isoprene and terpenes (α-pinene, β-pinene, limonene and humulene) emissions from fires are considered in this work.

12. Also, L33 suggests that only carbon emissions were used, but many studies suggest that fires are a major and sometimes huge source of gases including NH3 (eg van der Werf et al., 2017, Van Damme et al., 2014), and hence of inorganic PM. Were such emissions examined for their impact on PM? Were they checked?

According to the Whitburn et al. (2017), the emission ratios NH3/CO in the tropics derived from IASI observations (as in Van Damme et al., 2014) were rather on the lower end of those reported in Akagi et al. (used here). Therefore, we believe we did not underestimate NH3 emissions. However, the impact on inorganic concentrations is low, as discussed previously in comment 1.

13. p7, The notation PPMfine is very confusing. This is usually used to represent emissions of any primary particulate matter including OM, BC and inorganics. Am I right in saying that your PPMfine is PM2.5 - OC - BC - SIA? In which case I would expect most of be essentially OM-OC - is that what you mean? To further the confusion with this PPMfine notation, you introduce PPMcoarse which is more traditional, just PM10-PM2.5. So, PPMfine excludes OC, BC and SIA, and consists largely of O and H, whereas PPMcoarse consists of OM+BC+SIA. As I said, confusing.

PPMfine corresponds to all the unidentified fine particles emitted by wildfires which are incorporated to consider the differences between PM2.5 emissions and the total of all PM included in specific species. Therefore, PPMfine corresponds to PM2.5-OM-BC-SIA.
This is why we believe that PPMfine includes actually OM and I/S/L-VOCs.
For clarity, the following sentence line 1 page 7:
"For aerosols, the difference between emission factors provided for the main primary emissions (organic and black carbon, small amounts of inorganics) and for the total PM2.5 is modelled as a specific, inert and unidentified species grouping other fine mode primary particulate matter PPMfine"
is replaced by:
"For aerosols, all unidentified fine particle compounds emitted by wildfires are affected to an inert compound PPMfine. It corresponds to the difference between the emission factor of total PM2.5 and the emission factors of speciated PM2.5 compounds (organic and back carbon, small amounts of inorganics)."

14. p7, Figure 1. It is difficult to see the yellow fire labels on top of the yellow background. Change the colors.

In the revised paper, the Figure 1 page 7 is replaced by the Figure A below.

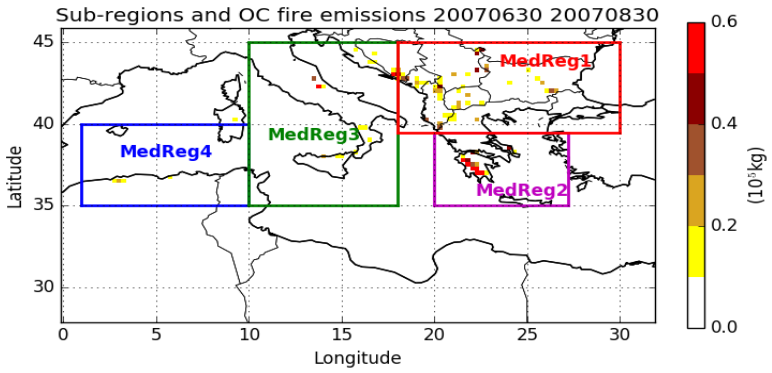


Figure A: Map of the nested domain over the Mediterranean area with a spatial resolution of 0.25°×0.25°. The total organic carbon emissions(kg. (grid cell)−1) from fires during the summer of 2007 are presented. The sub-regions used in this study are also indicated in colored boxes: MedReg1 (Balkan + Eastern Europe), MedReg2 (Greece), MedReg3 (Italy) and MedReg4 (Algeria).

15. p9. Table 2.

- The Poly-ref emissions are said to be introduced between 1km and the PBL. I assume you mean between ground level and min(PBL,1km)? If not, I have a serious problem with your base-case!

Indeed, we meant that fire emissions in the simulation Poly-ref by are injected in min (PBL, 1km).

- What is PB?

We mean by PBL : Planetary Boundary Layer.
“PB” in Table 2, page 9 is replaced by “PBL (Planetary Boundary Layer)”.