Interactive comment on "Aerosol composition and the contribution of SOA formation over Mediterranean forests" by Evelyn Freney et al.

Anonymous Referee #1

Received and published: 16 September 2017

The authors present airborne measurements of particles and gases above Mediterranean forests during the ChArMEx campaign. Offline TEM analysis is also presented. These measurements are used to investigate the sources of SOA in this forest. PMF and the Polyphemus model was also used to estimate the contribution of various sources to SOA. This manuscript employs a nice combination of measurements and modeling to investigate SOA. However, I find numerous major and technical corrections that need to be addressed prior to publication in ACP, as listed below:

The authors would like to thank the reviewers for their very constructive and informative comments. These comments and suggestions have helped us to improve the quality of our manuscript. Below we have responded to each of the reviewers comments. **The reviewers comments are in bold** and our reponses are in normal text.

Major Comments:

R1.1 P2 L7: You have defined "isoprene epoxydiols SOA" as "(IEPOX)", which is incorrect. Isoprene epoxydiols are compounds typically found in the gas phase and can be called IEPOX for short. They can go on to form isoprene epoxydiols-derived SOA, which is often called IEPOX-SOA.

Thank you for this correction. We have replaced IEPOX with IEPOX-SOA throughout the manuscript.

R1.2 P3 L15-18: I recommend that some of this information about what took place during this campaign be moved to the methods section, and replaced with a general description of what you investigated in this particular manuscript.

The text has been updated:

"In this work we present observations from four research flight over the forested Mediterranean region. The objectives of these flights were to characterize aerosol chemical and physical properties and investigate the origin of SOA over these forested areas.

R1.3 P3 L22: Is ATR an acronym? Please define if possible. Also, for readers who are unfamiliar with this aircraft, please provide more general information in this paragraph. E.g., what is the general size of the aircraft, how large is the payload, did it sample anything other than meteorological parameters and aerosols?

The accroynm ATR represents Avions de Transport regional. I have included additional information on the aircraft.

"The ATR (Avion de Transport Régional) is a turbo propeller aircraft of approximately 23 m long and 25 m wide, having a payload of about 4.6 ton (www.atraircraft.com)."

We moved the following sentence describing how aerosol measurements are made into section 2.2

"In order to sample aerosol particle species, a forward facing aerosol inlet was fitted in place of a side window. This inlet is designed with an outer sleeve for channeling air and a large tube radius with low curvature to limit particle losses due to deposition. This inlet is both isokinetic and isoaxial and has a 50% sampling efficiency for aerosol particles with diameters of 4.5 µm (Crumeyrolle et al. 2013). From the aerosol inlet the sampled aerosols are directed through a manifold to a number of different instruments"

The technical details of how gas-phase measurements are made are included in section 2.3.

R1.4 P4 L5: Provide a reference for the cToF-AMS instrument. Also, assuming it was the Aerodyne instrument, it should be referred to as the "Aerodyne compact time-of-flight aerosol mass spectrometer (cToF-AMS)" and called cToF-AMS instead of C-ToF-AMS to be consistent with previous literature.
We have included a citation to Drewnick et al., 2005, and changed C-ToF-AMS to cToFAMS.

> Drewnick, F., S.S. Hings, P.F. DeCarlo, J.T. Jayne, M. Gonin, K. Fuhrer, S. Weimer, J.L. Jimenez, K.L. Demerjian, S. Borrmann, D.R. Worsnop. A new Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS): Instrument Description and First Field Deployment, *Aerosol Science and Technology,* 39:637-658, 2005. PDF (July 2005)

R1.5 P4 L6: I think you mean "spatial" instead of "temporal"? What was your spatial resolution, i.e., how far does the plane travel in 40 s?
We changed temporal to spatial and added text

"(aircraft covers approximately 5 km in 40 sec)".

R1.6 P4 L26: Was it a high resolution (HR) or unit mass resolution (UMR) PTR-MS?
The PTR-MS is a unit mass resolution instrument. We have added this information.
"For measurements of volatile organic compounds (VOC), a unit mass resolution proton-transfer-reaction mass spectrometer (PTR-MS)…."

R1.7 P6 L13: Section 3.1 belongs as part of your Methodology section 2 above. This section describes where and when the measurements were taken (along with some information about general conditions of the atmosphere), but doesn't provide any science results.
This section has now been moved to section 2.6, and is highlighted in green.

R1.8 P6 L13: When you introduce the four RF's in this section (and then use them throughout the paper), please change it to use a uniform style. In this version, you have everything from, e.g., "RF20" to "RF20 03/07" to "RF 03/07 RF20" to "RF0307" (in Fig.S1) all referring to the same flight. I recommend providing the date of each flight in the methodology and then only use "RF20" in the results section.
Flight names have been changed throughout the manuscript to RF"flight number".

R1.9 P6 L20: Wherever you decide to specify the dates of the flights, I strongly recommend that you use a date format such as "3 July" instead of "03/07" throughout the manuscript and figures. 03/07 could mean 7 March or 3 July depending on where in the world the reader is.
This has been specified clearly in the tables and elsewhere we use only the flight number.

R1.10 P7 L11: When you say ". . .and aromatics)", do you mean C8- and C9-aromatics? This sentence doesn't make sense as is.

Yes, the text and tables have been updated to include this.
As written in the manuscript, Page 7, Line 15: "The principal VOC species measured by the PTRMS during all flights were acetone (*m/z* 59) and methanol (*m/z* 33), followed by isoprene (*m/z* 69) and its oxidation products (MVK + MCR + ISOPOOH) (*m/z* 71), and then VOC species representative of monoterpenes emissions (*m/z* 137). Anthropogenic VOC species (*m/z* 93 (toluene), *m/z* 79 (benzene), and C8- and C9 aromatics) never contributed more than 5% to the total VOC measured (Table 1)."

R1.11 Table 1: All of the VOC concentrations are in pptV, not ppbV, correct? Please check the units. Also what does the +- value represent? Range? Standard deviation?
The table has been updated to include the units. The +- values represents the standard deviation on the measurements during the flights. The table caption has been updated to make this clear.

Table 1. Mean concentrations of the different gas phase species measured aboard each flight. The error represents ± 1σ on all the measurements.

R1.12 P7 L27: ". . .was well oxidized" is a subjective statement that doesn't add scientific value or understanding, please change.
R1.13 P7 L28: "with little evidence of fresh primary organic aerosol": Please provide or cite your evidence for this statement. The O:C value of the bulk OA by itself does not provide information about what types of OA (primary vs secondary) constitute the bulk OA.

The sentence has been modified and additional text has been added.

P8, L8:The organic aerosol measured during all flights had high O:C ratios of 1.05 (± 0.05), high f44 > 0.2 and corresponding low f43 < 0.6, suggesting that the majority of the organic aerosol was secondary, with little influence from fresh primary organic aerosol.

R1.14 P8 L15: With the evidence that you've shown, I'm not really convinced that you can conclude that you're seeing organosulphates. You state that you don't have any visual evidence that there were other compounds e.g. ammonium sulphate present, but can you show evidence that NH4 (or N) was NOT present? That's what I would want to see to really back up your conclusion of organosulphates, particularly because you've included this conclusion in your abstract.

The particle does include N. However, we do not believe that this N is related to ammonium sulfate because ammonium sulfate particles can generally be easily distinguished using TEM as they have a well-defined crystal structure and are beam sensitive as seen in the particle Figure b. However, from TEM analysis we cannot be certain that these particles are organosulfates. Changes to the figure and the text are shown below.

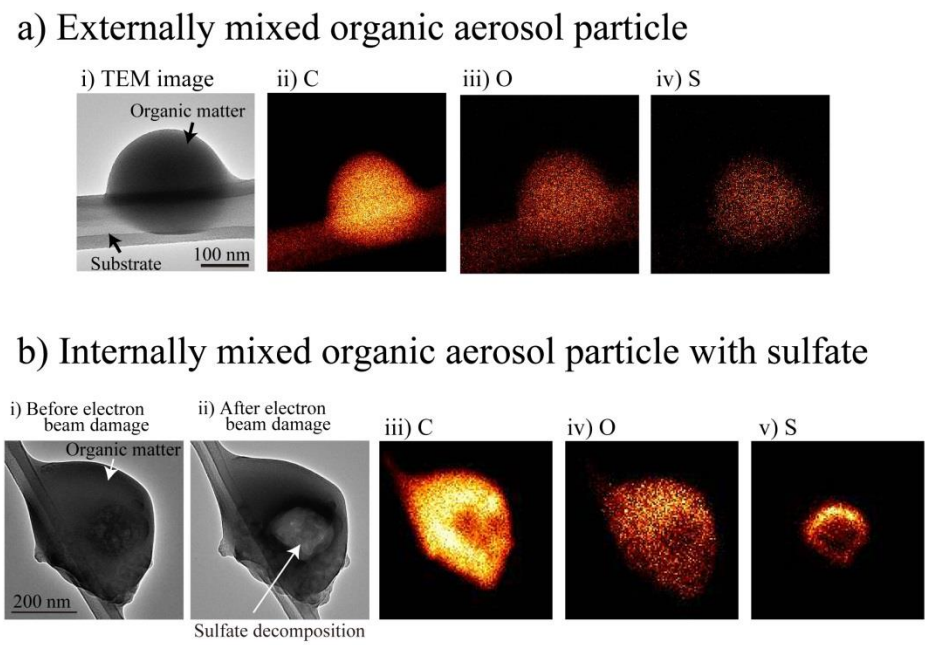

Figure 4. a) i)Example of an amorphous particle deposited on a carbon substrate. EDS mapping analysis showing signals for ii) C Carbon, iii) O Oxygen and iv) S Sulfur.; b) Internally mixed amorphous particles with signals, i) before and ii) after electron beam damage. EDS analysis showing signals for iii) C carbon, iv) O Oxygen, and v) S Sulfur.

"As described in section 2.5, the chemical composition of aerosol particles collected on TEM grids was determined using EDS. At least 230 particles were analyzed during each flight providing information of particle size and composition. The absolute number of particles analyzed using offline electron microscopy is small in comparison to what is measured by online particle counters, however this technique provides us with a qualitative snap shot into particle mixing state, morphology and composition. Only filters from the submicron stages are discussed here and showed that at least 35 (± 5) % of all aerosol particles measured was made up of homogenously mixed amorphous (no evidence of a crystal structure) particles. EDS analysis of these amorphous particles were composed of homogeneously distributed C, O, and S (Fig. 4a i) ii) iii). Externally mixed crystalline sulphate particles contributed 15 (± 5) % (likely ammonium sulphate) and 10 % were internally mixed amorphous C and crystalline sulphate (likely ammonium sulphate) species (Fig. 4b, Fig S4). The remaining fractions contained signals for sea-salt (Na Cl) and dust (Si, Ca) particles. "

R1.15 Figure 3: Please explain in the figure caption what each panel is showing. Also, in 3a), are all four panels showing the same particle? It looks to me like the substrate in the top left panel is at a different angle than it is in the other three panels (the substrate overlaps with the bottom left corner in all panels except the top left panel).

Yes, they are the same particle. In the microscopic analysis, two different imaging systems are used in the TEM and scanning TEM (STEM) for the EDS mapping. Switching between these two systems results in the images looking slightly rotated.

The figure and figure caption has been updated.

"Figure 3. a) i) Example of an amorphous particle deposited on a carbon substrate. EDS mapping analysis showing signals for ii) C Carbon, iii) O Oxygen and iv) S Sulfur.; b) Internally mixed

amorphous particles with signals, i) before and ii) after electron beam damage. EDS analysis showing signals for iii) C carbon, iv) O Oxygen, and v) S Sulfur."

R1.16 P8 L30: I do not see sufficient evidence to say that it is "likely" that the fine mode particles were linked to new particle formation. You haven't shown measurements of new particle formation or even particles <20nm in size (and it seems those measurements were not taken during these flights), nor have you discussed possible primary sources of particles such as cities, vehicular traffic, etc. Please change this text so that all of your conclusions are backed up with evidence, or change the strength of your conclusions to reflect the uncertainties.

We have changed this analysis to include particle concentrations measured using the condensation particle counters (CPC). We calculated the difference of the total number concentration measured by the CPC (cut-off diameter 5 nm) with the total particle concentration measured by the SMPS (starting diameter of 17 nm), giving us the total number concentration of the nucleation mode particles. The figure is now showing a plot of the nucleation mode particles against the ratio of Isoprene C and monoterpene C. This plot is showing that there is a higher fraction of nucleation mode particles measured when higher contributions of monoterpenes (relative to isoprene) are present.

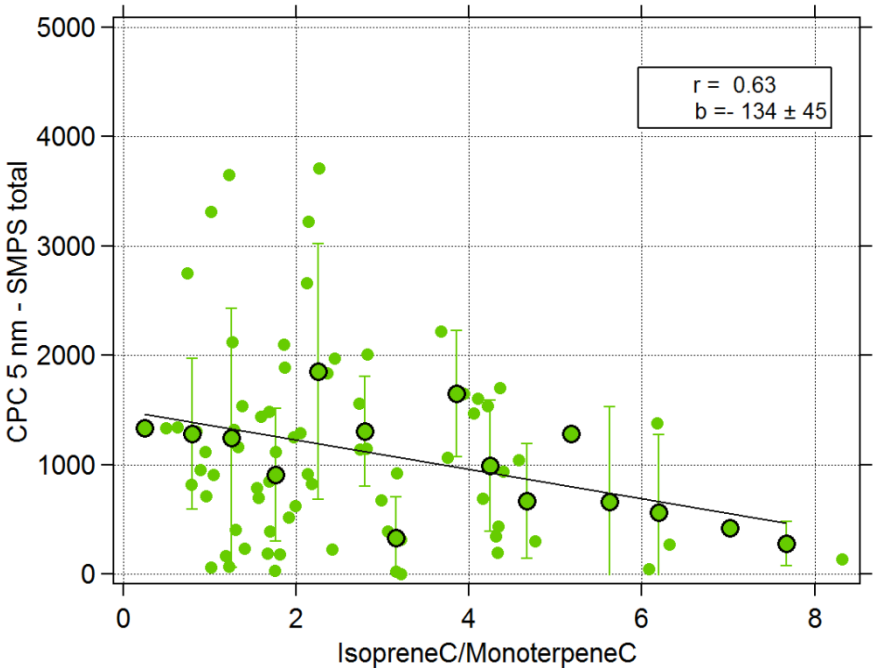

Figure 6. Ratios of IsopreneC/MonoterpeneC plotted as a function of the nucleation mode particles (difference between the CPC (cut off 5 nm) and the SMPS (cut off 17 nm)). Values for the four biogenic flights are included, as well as average values (black contained circles) calculated over a number of IsopreneC/MonoterpeneC ratios (size bins of 0.5), Error bars represent ± 1 σ of the average CPC5nm – SMPS values.

We have included throughout the manuscript discussion of the contribution of anthropogenic species. These are listed below.

P7, Line 19: Despite not contributing large quantities to the total VOC measured we cannot ignore the presence of the anthropogenic VOC species measured during all flights. We used the ratios of toluene to benzene to assess the contribution of anthropogenic emissions. The highest anthropogenic contributions were measured during RF15, when the ratio of toluene/benzene was 1.54. Values greater than 2 are generally found close to urban sources (Ait-Helal et al., 2014). Other evidence of

anthropogenic influence is the low enhancement ratios of HCHO (Formaldehydel)/CH_3CHO (Acetaldehyde), for RF15, this ratio was calculated to be +0.56, whereas for the other flights over forested regions, these ratios were calculated to be 4.8 (RF20) and 3.9 (RF23). For RF15, air masses arrived from the north of France (Fig. S2), likely bringing some anthropogenic influence from the mainland. The easterly flights were principally influenced by local or southerly airmasses, were possibly influenced by emissions from Marseille or from the Fos Berre industrial area. Full details of the VOC measurements aboard the aircraft will be provided in Waked et al. (in prep).

P10, Line 25: Plotting these two factors as a function of air mass age using anthropogenic VOC species (ratio of benzene/toluene), we observe a relatively flat and decreasing trend. These observations would suggest the contribution of anthropogenic precursors, although not insignificant, play a lesser role in the formation of the SOA measured during these flights.

P13, Line 24: The model results estimates overall contribution of 66% biogenic species and approximately 30% aromatic. This work provides a unique insight into the formation of SOA far from urban sources in biogenic dominated regions. It highlights how even at background forested sites throughout Europe, the impact of urban emissions of SOA formation is not negligible.

R1.17 P9 L14: This section 3.4.1 and also 3.4.2 are really part of aerosol chemical properties. I think they belong much better as subsections to 3.3 (aerosol chemical properties) rather than 3.4 (aerosol physical properties). Alternatively, they can be standalone sections.
The layout of the paper has been changed so that these sections are now stand alone sections

R1.18 P9 L26: Yes, isoprene oxidation is likely leading to some SOA formation, but what about other precursors? Is there any correlation with, e.g., monoterpenes? I would like to see a more thorough analysis here that considers all measured SOA precursor gases.

The contribution of monoterpene emissions is very weak in all of these flights, but the yield for the formation of SOA from monoterpene emissions is much higher.

Additional discussions are included throughout the manuscript. Please see response to question R1.16

R1.19 P9 L31: In Fig. 6a, m/z 80 is shown as an organic peak (green). It should be red (sulphate), correct?
This figure has been updated.

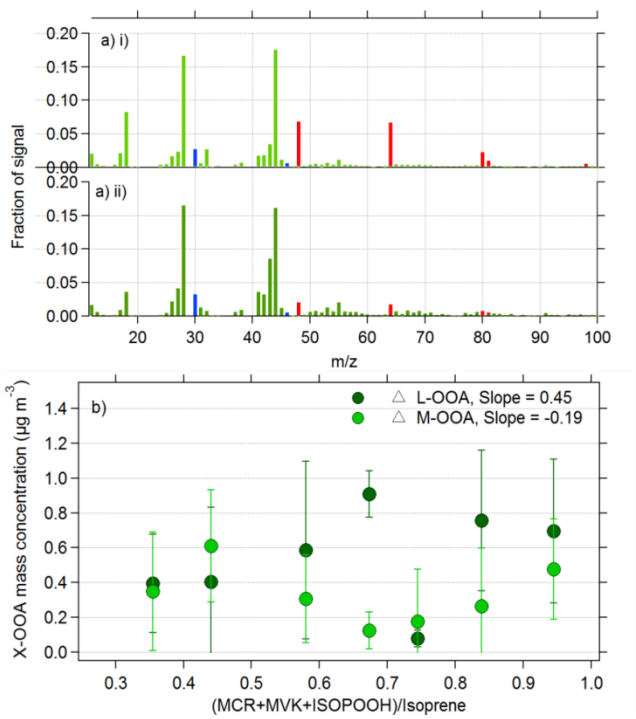

Figure 6. a) A two factor solution determined from PMF analysis of the biogenic research flights. a) i) The more oxidised organic aerosol (MOOA) associated with inorganic peaks for sulphate (red) and nitrate (blue) ,a)ii) the less oxidised organic aerosol (LOOA) with a lower contribution of inorganic peaks. b) Variations of these two species with aging airmass (using MCR+MVK+ISOPOOH over isoprene as a proxy for photochemical age of airmass.

R1.20 P10 L3: You state here and in other places that you are plotting as a function of photochemical age, which seems incorrect. Photochemical age would have units of time (hours or days), but you're plotting against the ratio of isoprene oxidation products to isoprene. It should be possible to convert this ratio to a unit of time, depending on whether the rate constants and all of the relevant reactions involving these compounds are known enough to do so. If not, I suggest that you say instead that you plot as a function of relative age, or simply as a function of the ratio which represents the relative age of the airmass.

We have changed the text throughout this discussion to make this clear.

Page 10, Line 1: "A time series plot of total organic aerosol (OA) with MCR+MVK+ISOPOOH shows a good relationship (Fig. S5a), and plotting the OA concentration against the ratio of (MCR+MVK+ISOPOOH)/isoprene provides us with a means to observe the evolution of the organic aerosol with the relative age of the air mass with respect to biogenic emissions. The ratios of (MCR+MVK+ISOPOOH)/isoprene measured during this flight are comparable to those measured over this forested area (0.4 to 0.8) (Zannoni et al., 2016)."

Page 10, Line 25: "Plotting these two species as a function of the relative air mass age we observe a significant increase of the LOOA species with air mass age until a maximum is reached at ratios of 0.65. MOOA remains relatively stable, indicating an independent source. Plotting these two factors as a function of a proxy of air mass age using anthropogenic VOC species (ratio of benzene/toluene), we

observe a relatively flat and decreasing trend. These observations would suggest the contribution of anthropogenic precursors although not insignificant; play a lesser role in the formation of the SOA measured during these flights."

Page 11, Line 13: "The yield of formation of SOA from isoprene VOC precursor is relatively low compared to other biogenic species such as monoterpenes, and also compared with aromatics precursors (Ait-Helal et al., 2014). Given the lack of acidic aerosol and the measured NO concentrations (0.30 ppbV), we do not believe that isoprene-derived SOA contributed significant amounts to the OA measured during these flights. Therefore, although isoprene concentrations are in abundance during these flights, it is unlikely to have contributed large amounts to the formation of the measured SOA. Given the increase in OA with the relative "biogenic" air mass age, we could suspect that other sources of SOA during these flights could be from terpene precursors. This is also coherent with the increase in the number concentrations of fine particles at lower IsopreneC/monoterpeneC ratios. It should also be noted that the yield of SOA formation from aromatic precursors is similar to that of monoterpenes, and that some contribution of anthropogenic SOA can be expected."

R1.21 P10 L15: What is the value of f91 in your two spectra, and how does this compare with the other cited studies that investigated the contribution of monoterpenes or other pathways to m/z 91? The f91 in your spectra appear to be very small, suggesting these pathways aren't important.

The discussion in this section has been changed and this phrase has been removed.

"This m/z 91 was present in all OA mass spectra and was significantly higher for the LOOA than for the MOOA. In recent work, on the characterisation of aerosol particles over coniferous forests (mainly monoterpenes emitters) this has been shown to be due to the $C_7H_7^+$ fragment (Lee et al., 2016). It should be noted that m/z 91 can also be associated with fragments of primary OA and therefore other potential sources cannot be excluded."

R1.22 Table 3: Please fix the formatting, m/z 71 in the first column should not be bold. Also, what does Pr mean? Are these Pearson r correlation values? Or R^2? Please clarify.

The table formating is corrected. Pr represents the Pearson r correlation values. This is now clearly clarified in the table caption.

"Table 3: Pearson r (Pr) correlations for different time series during RF 20 and RF 23."

R1.23 P10 L34: ". . .we can conclude that the observed OA can probably be related to a non-IEPOX isoprene SOA.":

This conclusion as written is not backed up by the evidence you are presenting;

First, a given compound's contribution to photochemical activity (by which I think you mean OH reactivity, which is different) has little to do with it's ability to form SOA. Sure, isoprene may be the main contributor to OH reactivity (among the measured compounds), but what matters for SOA formation is the SOA yield, and you haven't discussed that in this work.

We have removed the paragraph discussing OH reactivity and have included additional text of the SOA yield associated with different VOC precursors. The formation of SOA from different precursor species is also discussed in the modelling section

Based on the reviewers comments we have modified the text in this section. These changes are included above in response to R1.20 "

Second, you are presenting some evidence that suggests that IEPOX-SOA was not present in substantial amounts, but then your only conclusion in this section of the manuscript should be that IEPOX-SOA was not an important contributor. You have presented no measure of non-IEPOX isoprene SOA, so you have no basis on which to speculate about the magnitude of the non-IEPOX isoprene SOA at this site, whether it is dominant, negligible, or somewhere between.

I suggest you clarify that you find that IEPOX-SOA appears negligible at this site, and that non-IEPOX isoprene SOA may play a role but it's unclear how much.

Thank you for your comments and suggestions. The text has been modified following your suggestion.

The text has been updated.
Page 11, Line 13 "The yield of formation of SOA from isoprene VOC precursor is relatively low compared to other biogenic species such as monoterpenes, and also compared with aromatics precursors (Ait-Helal et al., 2014). Given the lack of acidic aerosol and the measured NO concentrations (0.30 ppbV), we do not believe that isoprene derived SOA contributed significant amounts to the OA measured during these flights. Therefore, although isoprene concentrations are in abundance during these flights, it is unlikely to have contributed large amounts to the formation of the measured SOA. Given the increase in OA with the relative "biogenic" air mass age, we could suspect that other sources of SOA during these flights could be from terpene precursors. This is also coherent with the increase in the number concentrations of fine particles at lower IsopreneC/monoterpeneC ratios. It should also be noted that the yield of SOA formation from aromatic precursors is similar to that of monoterpenes, and that some contribution of anthropogenic SOA can be expected."

R1.24 P11 L4: It will be very difficult for the editor, reviewers, and future readers to properly interpret this modeling work if the full model details are not yet published in this work or elsewhere! It would seem improper for this manuscript to be published before the Chrit et al. manuscript (in which you say the details can be found) at least appeared in ACPD.

This manuscript is now published in ACPD, in the same CHARMEX special issue.
Chrit, M., Sartelet, K., Sciare, J., Pey, J., Marchand, N., Couvidat, F., Sellegri, K., and Beekmann, M.: Modelling organic aerosol concentrations and properties during ChArMEx summer campaigns of 2012 and 2013 in the western Mediterranean region, Atmos. Chem. Phys., 17, 12509-12531, https://doi.org/10.5194/acp-17-12509-2017, 2017.

R1.25 P12 L11: This final paragraph should be removed; it is repeated information and doesn't add to the manuscript. In its place, you could consider strengthening this section by adding a paragraph to compare the model results with your measurements that were presented earlier in the paper. Are your measurements consistent with the model? What new information have we

learned? What are the next steps, e.g., what other model or measurement results would we need to learn more?

This has been removed and the discussion on what are the next steps etc are included in the conclusion.

Technical Corrections:

R1.26 P3 L23: Please change "preformed" to "performed".
This has been changed.

R1.27 P3 L29: Please change "chaneling" to "channeling".
This has been changed.

R1.28 P4 L2: Please change to "scanning mobility particle sizer".
This has been changed.

R1.29 P4 L17: Please specify explicitly which standard temperature and pressure, to eliminate any possible confusion.
This information has been added.
All reported concentrations are in standard temperature and pressure (used here 22^{o}C, 950 hPa).

R1.30 P4 L26: Update the Waked et al. citation if possible.
This paper is still in preparation

R1.31 P4 L26: Add "(VOC)" after the word "compounds" to define this acronym.
This has been changed.

R1.32 P4 L27: Add references for the PTR-MS instrument.
A reference is already included in the text.
Full details of the PTR-MS configuration on-board and operating conditions are provided in Borbon et al. (2013)

R1.34 P5 L16: I believe the proper name to use here in the "PMF Evaluation Tool (PET)".
This has been changed.

P5 L20: SQUIRREL is an acronym and should be capitalized.
This has been changed.

P7 L18: Please change from Fig. A6 to Fig. S6.
This has been changed.

Table 2: Specify the units, as well as what the +- values represent.
Units have been added to the table and the caption has been updated.
Table 2. Concentrations ($\mu g\ m^{-3}$) of the different chemical species measured aboard each flight during level low altitude legs., error values are standard deviations calculated on the mean values of the measurements.

P8 L15: Change from A7 to S7. There are other locations in the manuscript with similar
A instead of S, please correct all instances.
This has been changed, and the manuscript has been searched for similar corrections.

P9 L5: Please define what isopreneC and monoterpeneC are.
Additional information has been included
isopreneC/monoterpeneC (Carbon associated with Isoprene/Monoterpene)

P9 L11: Change "rations" to "ratios".
This has been changed.

P10 L7: m/z should be italicized in all places in the paper.
This has been changed.

P11 L6: Your supplemental figures are not referenced in order. Your Fig. S3 was just referenced here for the first time. I'm not sure if ACP has strict guidelines about this, but it's common to number them in the order they appear in the manuscript.
The supplementary figures have been reorganized to be consistent with the text.

Many figures: The text and labels in a lot of the figures are too small to read. I suggest you make the font larger for clarity.
The figures have been updated.