**Interactive comment on "Aerosol composition and
the contribution of SOA formation over
Mediterranean forests" by Evelyn Freney et al.
Anonymous Referee #3**
Received and published: 14 September 2017

**Authors present the results obtained during an airborne measurement campaigns over 2
Mediterranean forested areas (South of France). More precisely, they report results combining c-
ToF-AMS, HS-PTR-MS, SP2, SMPS/OPC, Aerolaser (for formaldehyde measurements) as well as
offline TEM analysis, from 4 flights (2 for each forest). Simulations performed with the Polyphemus
model and comparisons with the measurements are also presented.**

**While the paper is well written with a clear structuration, significant work is still needed to make it
suitable for publication in ACP. Important details are missing and some major issues can also be
found here and there throughout the manuscript (despite 21 co-authors).**

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.

Main comments:
**1- There are major inconsistencies between VOCs concentrations reported in the text (p2 line 6, for
instance), in figure 1 and in table 1. Not only a question of units. Must be checked very carefully
and corrected.**
P2, Line 6 has been corrected and the remainder of the text has been verified for inconsistencies.

2- Regarding PMF analysis, much more details are needed (at least in the SI)
Additional details are now included into the supplementary material, including figures S9 to S11
(Factor profiles, scaled residuals, Q/Qexp and fpeak analysis), as well as correlation with time series
for 3 and 4 factor solutions.

**3- It's not clear if the average values reported in the text and tables refers to the whole flight or
only to the low altitude legs. This should be clarified and homogenized throughout the text.
Considering the vertical profiles presented in figure S4, whole flight averages make no real sense.
These vertical profiles and their implications are not discussed in the text except for boundary
layer heights (p6, line 20).**
The average values reported in the text represent only the low and constant altitude legs of the
flight. This has been clarified in the text.

The vertical profiles are only used to determine the boundary layer heights, only data collected
during the vertical profile measurements are used for the plots shown in Figure S3. The caption in
Fig. S3 has been changed to clarify this.

Page 8, Line 2:
"In the following section we will report average values for different chemical species during low and
constant altitude parts of the flights."

Figure S4. Vertical profiles of RH, formaldehyde, and isoprene + its oxidation products (MVK+MCR) for research flights: a) RF15 , b) RF20, c) RF21 , d) RF23 . Only data collected during the vertical profile measurement are used in these plots.

4- Either the definition of externally mixed aerosol has recently changed either I don't understand the difference between fig 3a and b. This leads to important confusions in the discussion and conclusions.
This paragraph has been re written to avoid confusion.

"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 externally 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), the molecular structure of these particles is unknown. Externally mixed crystalline sulphate particles contributed 15 (± 5) % 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. "

Other comments
R3.1 : P1 line 30-31. Direct comparisons between AMS and TEM analysis are not relevant. AMS refers to a mass concentration without distinction between internally and externally mixed aerosol particles and TEM analysis refers, at best, to a number concentration. Authors state that at least 50 particles per gird have been analysis. What is the representativeness of the analyzed particles with respect to the total particles population? (SMPS/OPC measurement can help to assess this representativeness)

Yes, the authors agree that direct comparisons between AMS and TEM are not possible and therefore the text has been modified to avoid misleading the reader. In regard to the representativeness, total particle concentration observed during flights were in the range of 3289±1942 cm^{-3}, considering each sample was collected for approximately 15 minutes, this leads to about 14394 particles that could have been trapped by the grid. Given that TEM analysis of a substantial fraction of those particles is impossible, we have performed a sensitivity study of our findings in terms of particle population size by, increasing five-fold the TEM analysis and comparing previous results. Indeed, the new statistics compare quite well (OA contribution ranging between 55 and 75% (compared to previously obtained values ranging between 35 and 52%), S contribution ranging between 10 and 43% (compared previously with ranges of 11 and 25 %), indicating that already the number of particles analysed here led to robust statistics, showing that OA clearly dominants the aerosol spectra. The results throughout the manuscript have been updated to reflect the larger statistics.

R3.2 P 1 line 32. "Externally mixed organic aerosols, were equally identified with S signals, which may suggest the presence of organo-sulphates" I really don't understand this sentence. (cf main

comment 4) The text has been modified to avoid confusion. Please refer to the response to general comment 4.

R3.3 P2 line 6 : "high mixing ratio of isoprene (2-4 ppbV) and oxidation products (0.6 and 1.2 ppbV)" These concentration ranges cannot be found in table 1 and figure 1. Please check carefully.
These values have been corrected.

R3.4 P3 line 5 : I suppose that the authors refer to airborne measurements. There is a significant amount of ground based studies in the literature which already identified and quantified SOA in the Mediterranean region.
This phrase has been removed.

R3.5 P3 line 30. Specify the lower cut off diameter of the aircraft aerosol inlet.
The upper cutoff diameter of the aerosol inlet is specified, the lower cutoff diameter has not been measured. 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).

R3.6 P4 line 2-4. Please specify the time resolution of both SMPS and OPC
The text has been modified to include this information.
Aerosol particle number concentrations were measured using a scanning mobility particle sizer (SMPS) with 162 size channels for particle diameters ranging from 20 nm up to 400 nm, with a time resolution of 84 secs. Larger particles size distributions were measured using a GRIMM optical particle counter with 16 size channels from 265 nm up to 3 microns, with a time resolution of 1 second

R3.7 P5 line 14-22 : The PMF analysis requires much more details and explanation (Q/Qexp vs number of factors, residuals, boostrap/fpeak etc..). This could be added in the SI.
Additional details are now included into the supplementary material, including figures S9 to S11 (Factor profiles, scaled residuals, Q/Qexp and fpeak analysis), as well as correlation with timeseries for 3 and 4 factor solutions.

R3.8 Also explain why adding inorganic ions (SO4 and NO3) allows a better separation of the factors. Why NH4 ions are not considered? I also suppose that the relative contributions of MOOA and LOOA reported in section 3.4.1 refer to the OA+SO4+NO3 mass concentration. Please clarify and discuss. Relative contributions to OA are from my point of view more relevant.

Additional text has been included to explain this.
Inorganic species SO_4 and NO_3 followed similar temporal profiles to the organic species and are suspected as coming from similar processes (Pearson R OA SO4 = 0.70, OA NO3 = 0.84). By combining these m/z values into the PMF matrix it allowed us to perform an apportionment of the main aerosol sources and not just those related to the organic molecules. Combining the organic mass spectral fragments with those of nitrate and sulphate, provided us with additional mass concentrations to perform a more robust analysis on this aerosol data. We omitted NH4 from the analysis since the signal was noisy.

They were relative contributions to OA.

R3.9 P5 line 24-31. Aerosol were apparently collected on TEM girds by means of a 2 stages impactor, but this information totally disappears in the discussion of the results. Is there any difference between the 2 particle size ranges? Also, what is the representativeness of the analyzed particles (at least 50 / gird) with respect to the whole particles population.

The text has been updated and is shown above in response to general comment 4. Only particles from the submicron stage were analysed for this study to be coherent with the cut off diameters measured by the other instruments (SMPS, AMS). Additional TEM analyses have been performed so that we now have >230 particles per sample. However, still the fraction of particles collected on the electron microscopy grid is so small when compared with the total particle population measured by the SMPS/CPC/OPC. Nevertheless, this technique is providing us with a qualititative snap shot into particle mixing state morphology and composition and we believe the comparison should provide useful information to readers to understand the mixing states of measured particles. The text has been modified (see response to Response to general comment 4.).

"At least 230 particles were analysed for size and composition for filters collected during each flight. The absolute number of particles analysed using offline electron microscopy is negligible in comparison to what is measured by online particle counters, however this technique provides us with a qualititative snap shot into particle mixing state, morphology and composition."

R3.10 P6 section 3.1. Please add a map (with the flight tracks) in this section instead of in the SI.
This has been added. Figure S5 is now Figure 1

R3.11 The authors state that one of the forest is a high isoprene emitter while the second is apparently more dominated by monoterpenes emissions. Considering the results presented in Tab1 and fig 1, isoprene and monoterpenes concentrations do not support this affirmation. Do you have any explanation?

The nature of the vegetation in the two forested areas is very different with principally isoprene emitting trees in the OHP forest (Quercus pubescens) and during the western flights the vegetation is evergreen oaks (Quercus ilex) and Alpine pines (halepensis). However, the lifetime of isoprene in the atmosphere is considerably longer than for monoterpene species and results in a high atmospheric background. In addition to this the meteorology experienced on the different flights were different enough that the quantity of relative emitted concentrations of each VOC species were different, and makes it difficult to compare the absolute concentrations of one flight with the other.

R3.12 P7 Section line 9-12. Even if the concentrations of aromatic VOC are low with respect to the total VOC concentrations measured here, they cannot be considered as negligible compared to isoprene and monoterpenes concentrations. They deserve more attention from the authors. For instance, what is B/T ratio. Does this ratio make sense with aged air masses? Are the concentrations of aromatics homogeneous all along the flight?

A figure has been added to the supplementary material showing the temporal evolution of toluene and benzene as a function of time as well as a plot of total OA against the Toluene Benzene ratio. Additional text is included in the main part of the manuscript.
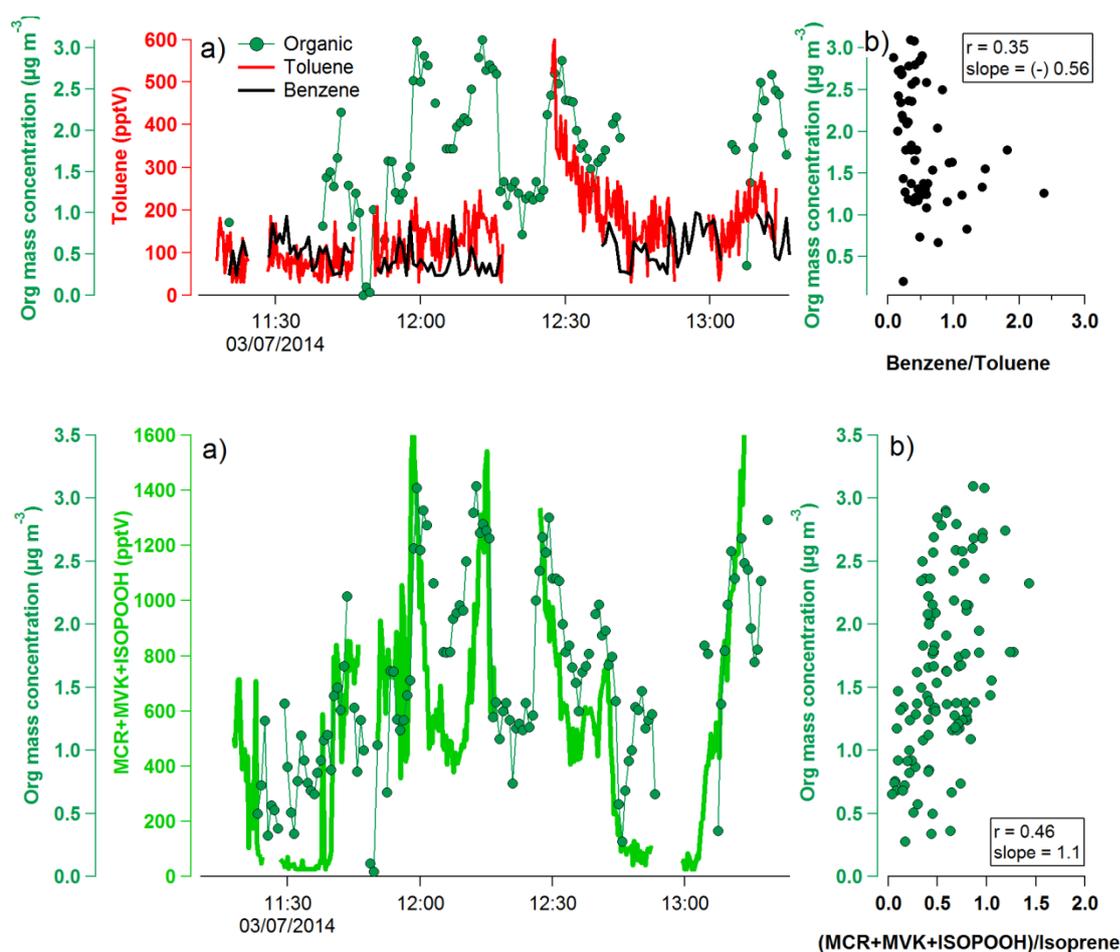
A time series plot of total organic aerosol (OA) with MCR+MVK+ISOPOOH shows a good relationship (Fig. S5a), and plotting the OA concentration against the ratio of (MCR+MVK+ISOPOOH)/isoprene provides us with a means to observe the evolution of the organic aerosol with the relative age of the air mass 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). We observe a reasonable correlation (r = 0.46) and positive slope (b = 1.1) with increasing OA as the relative air mass age increases, suggesting that SOA formation may have originated from biogenic precursors (Fig. S5b). Similar plots were prepared using anthropogenic precursor gases benzene and toluene (Fig. S6) showing a negative correlation with increasing organic mass concentration of r = 0.35 and a slope of -0.56. These trends suggest that the increases in OA concentrations are primarily related to biogenic emissions.

R3.13 P7 line 13-20. I'm puzzled by the OH reactivity section. Either provide more details (Atkinson and Arey 2003 is a 40 pages review, and no reference are provided for Waked et al), either this section can be removed from the paper.

This section has been removed

R3.14 P7 line 23-24. I suppose that the uncertainties provided here (and throughout the whole manuscript/tables/figures) correspond to the standard deviation associated to the average values. This must be specified clearly as well as which part of the flights have been averaged.

Yes, these uncertainties correspond to standard deviations. This is now clearly specified throughout the manuscript.

R3.15 P7 line 29-31 : see main comment 4

EM imaging..

We have added more explanation, updated the figures and clarified the text in order to respond to the reviewers comments. Details of these changes are outlined above.

R3.16 P7 line 31-32 : "The high contribution of externally mixed particles indicates that most of aerosol particles were recently emitted from their source" sounds contradictory with the sentence p7 line 27 "The organic aerosol measured during all flights was well oxidised, . . ., with little evidence of fresh primary organic aerosol."

The text in this section has been updated. Changes are included above in response to previous comments.

R3.17 P8 line 3 : direct comparison between TEM analysis and AMS results are not relevant without a thoughtful analysis of representativeness of the particles analyzed by TEM with respect to the whole particles population.

We agree with the reviewer and have modified the text of this section accordingly. These modifications have been included above in response to other comments.

R3.18 P8 line 15. In order to support the assumption of the presence of organo-sulfates, did the authors check the ionic mass balance (SO4, NO3, NH4) from the AMS results? In other words, did they observe a deficit of NH4?

Yes, we did check but there was no significant deficit of NH4, the neutralization graph is included in the supplementary materials, and additional information has been included in the text. The plot is coloured by SO4 concentrations to show that sulphate concentrations were not associated with periods when the NH4pred/NH4meas ratio were low.
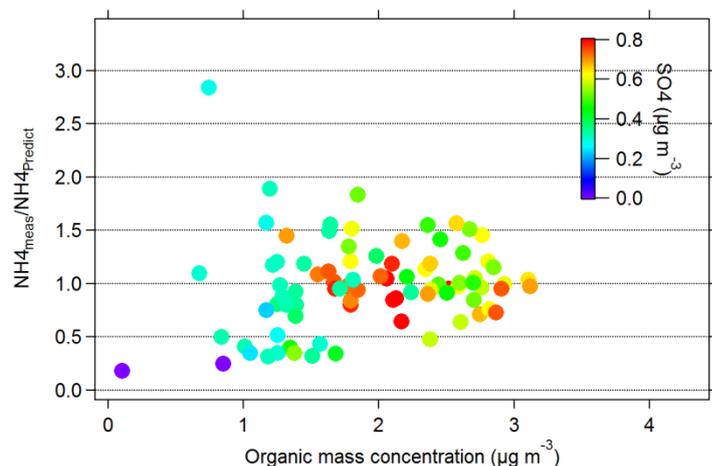

Figure S11: Average surface concentrations (in $\mu g\ m^{-3}$) of submicron organic matter (OA_1) simulated during the a) RF20 03/07. and b) RF23 07/07 flights. The flight path is shown with bold black lines.

Updated text P11, L7: "Aerosol concentrations measured by the cToFAMS appear to be fully neutralised with little evidence of acidity (Fig. S11), and the NO_W concentrations measured during these flights varied from 6 up to 10 ppbV, however the average concentrations of NO are 0.30 ± 0.2 ppbV, suggesting that the real contributions of NO_X (See section 2.3) is also likely to be low. There have been some reports of isoprene-derived SOA formation (hereafter isoprene SOA) in high-NO regions but the contribution of this pathway is considered to be much smaller (Jacobs et al., 2014).

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-Halel et al., 2015). 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."

R3.19 P8 line 30 : The authors should also mention and discuss the potential influence of industrial activities (Fos-Berre area) on the ultrafine mode observed during the easterly flights.
The contribution of anthropogenic sources and specifically the Fos-Berre area are now included in the text

"This *m/z* 91 was present in all OA mass spectra and was significantly higher for the LOOA (f91 = 0.007) than for the MOOA (f91 = 0.003). The contribution of f91 to biogenic organic aerosol over coniferous forests (mainly monoterpenes emitters), varied from 0.005 up to 0.019, and has been shown to be due to the $C_7H_7^+$ fragment (Lee et al., 2016). Our contribution of f91 falls into background OA levels (Lee et al., 2016), showing that the contribution of monoterpene or other pathways to m/z 91 are not important. It should be noted that *m/z* 91 can also be associated with fragments of primary OA and the contribution of anthropogenic aerosols from the industrial zone (Fos-sur-Mer) south of the flight area cannot be ruled out."

R3.20 P9 line 6-7: 'with lowest values corresponding to highest fractions of fine particle concentrations (Fig. 5). These observations are in agreement with previous field studies'

Considering fig 5 and the error bars, it's impossible to conclude.

The figure now uses the difference between a condensation particle counter (CPC) having a particle cut off diameter of 5 nm and the SMPS having a particle cut off of 17 nm, the difference in the total number measured by these two instruments represents nucleation mode particles in the range from 5 nm to 17 nm. The error bars are still relatively high, however the overall trend in these measurements illustrate that the highest concentrations of fine particles are associated with lowest isoprene concentrations. The text has been changed accordingly

P9, Line 13: "Using the measurements available during these four flights, we investigated this relationship between biogenic VOC species and nucleation mode particles; we calculated the ratio of isopreneC/monoterpeneC (Carbon associated with Isoprene/Monoterpene) and compared it to the number concentration of nucleation mode particles. As a result of the low time resolution of the SMPS, we were limited to a small number of points per flight. Data was combined for all flights, giving average ratios of isopreneC/monoterpeneC varying between 0.05 and 8 (average 3 ± 1), with lowest values corresponding to highest fractions of fine particle concentrations (Fig. 6). Although the variation among points is high, the general trend of these observations is in agreement with previous field studies over mixed deciduous forests (Kanawade et al., 2011) and with laboratory studies in

controlled environments showing that high concentrations of monoterpenes, relative to isoprene, can favor new particle formation (Kiendler-Scharr et al., 2009)."
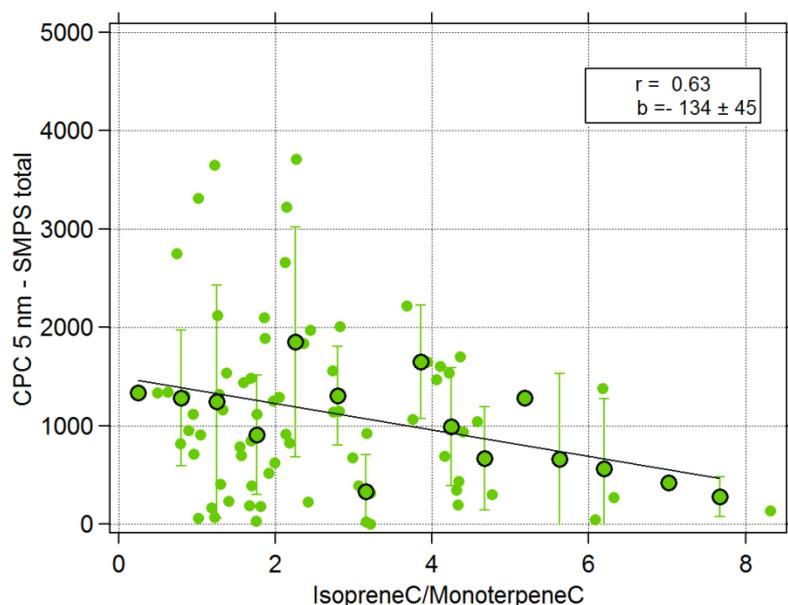

Figure 6. Difference between the CPC (cut off 5 nm) and the SMPS (cut off 17 nm) as a function of the IsopreneC/MonoterpeneC ratio. Values for the four biogenic flights are included, as well as average values over IsopreneC/MonoterpeneC ratios. Error barsrepresent ± 1 σ of the average CPC5nm – SMPS values. .The black line represents the linear correlation fit.

R 3.21 P9 line 24-26. I don't understand why fig S8 is in the supporting information. From my point of view one of the main results from this study.

This has been moved to the main part of the manuscript, Fig 7.

R3.22 P9 line 30 : "MOOA, contributing 55%" of OA or OA+SO4+NO3? What are the O:C ratio for MOOA and LOOA?
The percentages here refer to the contribution of each of the identified factors to the total resolved factors (which would include concentrations of OA+SO4+NO3).
The text has been updated to clarify this.

The O:C ratios are now included in the text.
The MOOA component is associated with inorganics species and had higher O:C ratios than the LOOA factor (0.83 and 0.76, respectively).
**
The two resolved factors include (i) a more oxidised organic aerosol (MOOA, contributing 55% to the resolved factors), containing high contributions from m/z 44 and associated with inorganic peaks (m/z 30, 46 (NO_3), and 48, 64, 80 (SO_4)) and (ii) a less oxidised organic aerosol species (LOOA, contributing 45%) with little contribution from inorganic m/z (Fig. 6 a)).

R3.23 P10 line 16 : "This m/z 91 was present in all OA mass spectra and was significantly higher for the LOOA than for the MOOA." Be more quantitative.
The values of mz 91 for the two types of spectra are now included in the text, as well as comparison to prevous studies.
"This m/z 91 was present in all OA mass spectra and was significantly higher for the LOOA (f91 = 0.007) than for the MOOA (f91 = 0.003). 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."

R3.24 P11 section 3.4.2. Not really convinced by the relevance of this section within the scope of this paper. Anyway. Why modelling results are only compared with measurements during the vertical profiles? How model and measurements compare during the low altitude legs?

Modeling results are compared to measurements during the whole flight.
We have added text to clarify this:
Line 22, p11: Modeling results are compared to measurements by averaging the measured and modelled concentrations during the whole flight, along the flight path.

R3.25 P12 line 11-12. "The model estimates a significant contribution of isoprene SOA (approximately 15 to 35% to the total SOA). This cannot be confirmed by measurements due to the lack in a significant contribution of m/z 82 in the AMS spectra" This sentence makes no real sense.

A very low contribution of m/z 82 means
1/ that there is a very little influence of isoprene SOA ; in that case the model is wrong or
2/ the isoprene SOA formation is formed through non-IEPOX pathways and in that case the question is how isoprene SOA is modelled?

The modelling of SOA formation is based on chamber experiments. The formation pathway used to represent the observed SOA in chamber experiments in low NOx environments is a non-IEPOX pathway, and the isoprene SOA surrogate is assumed to be a methylmethyl dihydroxy dihydroperoxide, as specified line 13 page 11.

For clarity on how the model was made, line 12 page 11, we have added text. The modelling of SOA formation is based on smog chamber experiments, which provide information on SOA yield as a function of organic mass concentration for each precursor, and uses an Odum approach (Odum et al., 1996). Stoechiometric coefficients of SOA surrogates and their saturation vapor pressures are selected to fit data from smog chambers. Candidates for SOA surrogates are estimated from the literature (Couvidat et al., 2012).

R3.26 Table 1 : please check the values and unit. Concentrations averaged during the whole flight or only low altitude legs? How the uncertainties are calculated (same for table 2)? Why C8 and C9 aromatics are not reported in the table?
The units and values are corrected in Table 1. The concentrations are averaged during low and constant altitude parts of the flight. The uncertainties are calculated from the standard deviations of the averaged values. The C8:C9 aromatics (combined) are now included in table 1

The table caption has been updated to clarify this.
Table 1. Mean concentrations of the different gas phase species measured during low and constant altitude parts of each flight. The error represents ± 1σ on all the measurements.
**R3.27 Table 3 : What do you mean by "Pr"?**
Pr reprents the Pearsons r correlation coefficient. The Table caption has been changed to include the necessary information.

R3.28 Figure 1 : Check values, add error bars, add % in the pie charts and add the flight codes (RF15 3006 etc..) in each panel in addition to a/, b/, (same for all figures)

These figures have been updated as requested by the reviewer.

Figure 2. Contribution of the different measured gas phase species aboard the ATR-42: a) RF15, b) RF20, c) RF21, d) RF23. The pie charts illustrated in each figure represent the contribution of all VOC species *except those of methanol and acetone*.
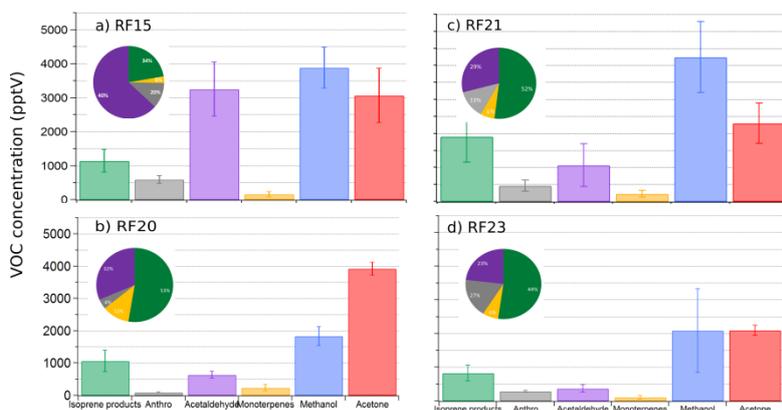
R3.29 Figure 5 : why no x error bars?
The Y error bars are calculated by averaging the number concentration as a function of fixed size bins for the MCR+MVK/ISOPRENE. The error bars are standard deviations based on the mean variation of measurements within the fixed bins of the MCR+MVK/Isoprene values.

R3.30 Figure 6 b : Why only 7 points represented here while _100 are represented in fig S8?
The points were averaged over bins of 0.1 (MCR+MVK+ISOPOOH/ISOPRENE). This allowed us to have a clearer representation of the trends in the data. This is clarified in the figure legend.

R3.31 Figure S6 : 11 RF represented, only 4 discuss in the manuscript. C8 aromatics are not only m-xylene.

This figure is now changed to only include the 4 flights in the manuscript rather than the whole CHARMEX campaign. The legend is changed to include C8, C9 aromatics and not only m-xylene.