

The authors have satisfactorily responded to all my comments and questions and significantly modified the manuscript accordingly. However, I still have some major issues regarding the revised text.

We would like to thank the reviewer for taking the time to review the updated version of this manuscript. Our response to each of the comments and suggests are outlined below. **The reviewers comments are in bold and shaded grey.** The authors response is in plain black (reply to comments/original text) or red (updated) text.

1/ P7, lines 21-27. The toluene to benzene ratio cannot be used to “assess contribution of anthropogenic emissions”. This ratio only provides information regarding the photochemical age (or the integrated OH exposure) of the anthropogenic fraction of the whole VOC mixture. A T/B ratio of 1.54 do not indicate a significant anthropogenic contribution, but an integrated OH exposure of the anthropogenic inputs of about $16.106 \text{ molecules.cm}^3.\text{h}$ (i.e. a photochemical age of about 11h, considering an initial (T/B) of 2, which is a little bit low from my opinion, and an OH concentration of $1.5 \cdot 10^6 \text{ molecules cm}^{-3}$) and this whatever is the contribution of anthropogenic VOCs to the whole VOC/SVOC mixture.

In this study and considering the data shown in fig S6, benzene and toluene signals are very noisy (because very close to the dl of the instrument) which probably imply an important variability of the T/B ratio not directly related to the photochemical age of the potential anthropogenic inputs.

Also, with such low toluene concentrations and although monoterpenes concentrations are low, the interference from the monoterpenes fragmentation's in the drift tube ($m/z93$ representing classically about 5-10% of $m/z137$, depending on the E/N) could potentially be significant for the T/B ratio. While it's always interesting to have a look to this ratio, I'd put much less emphasis on it and, above all, I'd used it wisely.

The text has been updated accordingly

Despite not contributing large quantities to the total VOC measured, we cannot ignore the presence of the anthropogenic VOC species measured during all flights (Table 1 and Fig.2). During westerly flights (RF15 and RF21), air masses arrived from the north (Fig. S2), possibly transporting accumulated anthropogenic emissions from over mainland France. Easterly flights (RF20 and RF23) being principally influenced by local or southerly air masses, are likely impacted by anthropogenic activities over the Marseille and Fos Berre industrial area.

2/ P7, lines 27-30. An enrichment factor of a parameter X is classically defined as follows: $ER=X(t)/X(t_0)$. In the case of the ratio HCHO/CH₃CHO what is the reference (t_0)? Authors must also specify how HCHO has been measured in the experimental section. If measured by PTRMS, are the HCHO concentrations corrected by the RH? Although a throughout analysis of the VOCs is expected in a future paper, this section must be clarified to make it understandable and meaningful.

To summarize, the whole section 3.1 needs to be significantly improved and developed before publication.

Original text “Other evidence of anthropogenic influence is the low enhancement ratios of HCHO (Formaldehyde)/CH₃CHO (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). Full details of the VOC measurements aboard the aircraft will be provided in Waked et al. (in prep).”

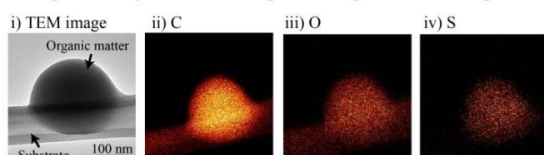
EF: We removed this sentence. The section has been updated as follows.

The principal VOC species measured by the PTR-MS during all flights were acetone (m/z 59) and methanol (m/z 33), followed by isoprene (m/z 69) and its oxidation products (MVK + MACR + ISOPOOH) (m/z 71) and then VOC species representative of monoterpenes emissions (m/z 137). Isoprene and its oxidation products showed a high temporal variation during flights suggesting a more local influence of these VOC species. Monoterpene VOCs, having a short atmospheric lifetime were measured in low concentration with little temporal evolution. 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, Fig. 2). Despite this, we cannot ignore the presence of the anthropogenic VOC species measured during all flights. During westerly flights (RF15 and RF21), air masses arrived from the north (Fig. S2), possibly transporting accumulated anthropogenic emissions from over mainland France. Easterly flights (RF20 and RF23) being principally influenced by local or southerly air masses, are likely impacted by anthropogenic activities over the Marseille and Fos Berre industrial area.

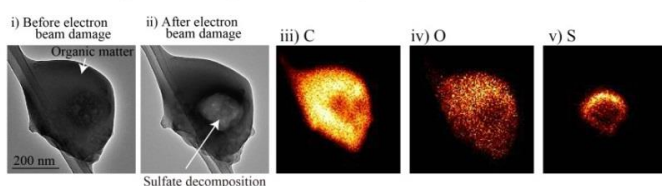
3/P8, line 11-21. This is now much clearer. I'd change the title of fig 4a accordingly: “homogeneously mixed amorphous organic aerosol particle”

These changes have been made.

a) Homogeneously mixed amorphous organic aerosol particle



b) Internally mixed organic aerosol particle with sulfate



4/P10 lines 6-9. I agree with this conclusion, but the caveats developed above must be considered here.

The text has been updated: 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. Similar plots were prepared using anthropogenic precursor gases toluene and benzene (Fig. S6) showing a negative correlation with increasing organic mass concentration of $r = 0.35$ and a slope of -0.56 . However, as the toluene and benzene concentrations are both close to the detection limit, care needs to be taken when interpreting these ratios. Generally,

although anthropogenic precursor's species are present, the VOC concentrations and trends measured suggest that the increases in OA concentrations are primarily related to biogenic emissions.

5/ P10 lines 25-30. “plotting the two species as a function of..”. Be more accurate. In fig S10, Delta MOOA and Delta LOOA are reported without defining what the delta stands for.

We have chosen to isolate the increases in organic aerosol above the background concentrations in order to clearly represent the formation of SOA from local VOC precursors species. The background values are determined from measurements made between the airport and the valley area. During these transects, little temporal variation was observed in either the aerosol particles or in the gas phase species. The particle size distribution measured by the SMPS showed a single mode at 100 nm, concentrations of short lived VOC species such as isoprene was high, concentrations of longer lived species such as MACR+MVK were low. A full list of background values versus those in the high concentration area are listed in Table S2.

The text has been updated as follows:

During the flights, as the valley area is approached, the sampled air masses become gradually more oxidized with respect to biogenic emissions, providing us with a well-defined sample area to evaluate the contribution of biogenic SOA on background/regional air masses. In order to isolate the formation of OA resulting from the oxidation of VOC species, the change in the OA concentrations above the background was calculated (ΔOrg). The background values were determined based on measurements during transects of the flight between the valley area and the airport. During this time, aerosol concentrations were low with little temporal variation. Particle size measurements display a single mode at 100 nm with average particle concentrations of 3000 cm^{-3} . Measurements of VOC species during this background period result in average concentrations of Isoprene of $1544 \text{ pptV} \pm 696 \text{ pptV}$, and lower concentrations of longer lived species MACR+MVK of $661 \text{ pptV} \pm 239 \text{ pptV}$ (Table S2).

For the resolved PMF factors, LOOA and MOOA, background values were determined to be 0.27 and $0.41 \mu\text{g m}^{-3}$ respectively (Table S2). Organic concentrations corrected for background concentrations are referred to as $\Delta\text{-LOOA}$ and $\Delta\text{-MOOA}$. Plotting these two factors against the ratio of MACR+MVK+ISOPOOH/isoprene (relative air mass age) (Fig. 7 and S10), we observe a significant increase of the $\Delta\text{-LOOA}$ species with air mass age until a maximum is reached at ratios of 0.65.

Table S2. Background and study area concentrations measured for the main species during RF20

	Background	valley area
Organic ($\mu\text{g m}^{-3}$)	1.05 ± 0.39	2.80 ± 0.52
MOOA	0.41 ± 0.23	1.12 ± 0.30
LOOA	0.27 ± 0.22	1.39 ± 0.21
Sulphate ($\mu\text{g m}^{-3}$)	0.04 ± 0.02	0.15 ± 0.04
Nitrate ($\mu\text{g m}^{-3}$)	0.33 ± 0.06	0.69 ± 0.14
Ammonia ($\mu\text{g m}^{-3}$)	0.11 ± 0.11	0.50 ± 0.13
Isoprene (pptV)	1544 ± 696	962 ± 540
MACR+MVK (pptV)	661 ± 239	901 ± 358
Toluene (pptV)	84 ± 34	131 ± 27
Benzene (pptV)	83 ± 28	75 ± 37
Monoterpenes (pptV)	201 ± 20	234 ± 34

Original text: “we observe a significant increase of the LOOA species with air mass age until a maximum is reached at ratios of 0.65.”

Here the question is what happen for higher m/z71 to m/z 69 ratio?

Text has been added: A slower increase in concentrations of LOOA at higher ratios suggests that as the relative photochemical age of the air mass increases, LOOA becomes more oxidized and is converted to MOOA, as has recently been illustrated in chamber experiments by Palm et al., (2018). Plotting these two factors as a function of air mass age relative to anthropogenic VOC species (ratio of toluene/benzene), we observe a relatively flat and decreasing trend (Fig. S10a).

“MOOA remains relatively stable, indicating an independent source.” That’s a little bit short.

As MOOA is associated to SO₄, one can suspect that MOOA is related to long range transport episodes or regional pollution impacted by anthropogenic emissions.

Additional text has been included.

Given that MOOA does not change with the relative air mass age in the measured area, and that it is associated with SO₄ and NO₃ species, it is reasonable to suggest that the MOOA is associated with long-range transported aerosol.

Considering the modelling results (fig 9) it seems that anthropogenic SOA cannot be neglected (17-28% of OA, fig 9).

Additional text has been added.

In the model, these high O:C ratios arise because of organic compounds from isoprene oxidation, which all have O:C ratio greater than 0.8, as well as some ELVOCs compounds (monomers) from monoterpenes oxidation. We can conclude from these observations that the low volatility products (ELVOCs) from monoterpenes oxidation as well as isoprene oxidation products may therefore correspond to the measured LOOA concentrations. Although the SOA contribution of anthropogenic VOC precursors is low (Couvidat et al, 2013; Sartelet et al. 2018), the results of the model show a high contribution of anthropogenic compounds (up to 30%). These anthropogenic compounds could correspond to the regionally transported SOA, potentially identified as MOOA.

6/ P11, line15 : “we do not believe that isoprene derived SOA contributed significant amounts to the OA measured during these flights”. Replace by : “we assume that..... do not...”

but 15-35% (fig9) is not totally insignificant.

Yes, we meant that the contribution of isoprene-derived SOA formed via the IEPOX route is assumed to be low. The text has been updated:

“Since the measured aerosol particles are neutralized (Fig. S11) and the measured NO concentrations are still reasonable high (0.30 ppbV), we assume that isoprene derived SOA, following the IEPOX formation route, do not contribute significant amounts to the OA measured during these flights.”

7/ P12, lines 25-28: “Although isoprene emissions are much higher than those of monoterpenes and sesquiterpenes over that region”

**Please be more quantitative
Additional information has been included.**

“Isoprene derived SOA represent only about 15 to 35%”

**15-35% is a high contribution, from my perspective, considering isoprene-SOA.
“4% to 7% are from semi-volatile organic compounds (pinic acid, norpinic acid and pinonaldehyde)” Please be homogenous with the legend of fig 9 :”Monoterpene products”
“17% to 23% from organic nitrate”**

We agree, 15-35 % is a substantial contribution. In our sentence, the word “only” was just to emphasize that this contribution was low compared to the contribution of monoterpene-derived SOA.

We understand the confusion for the reader and modified the text accordingly.

Although isoprene emissions are 2.5 times higher than those of monoterpenes and 11.6 times higher than those of sesquiterpenes over that region during the period of simulation, isoprene-derived SOA represent about 15 to 35% of the simulated OA, which is lower than the monoterpenes-derived SOA that represent 35% to 40%. Sesquiterpenes-derived SOA represents about 10%. Amongst the monoterpenes-derived SOA, 4% to 7% are monoterpene products (first generation semi-volatile organic compounds: pinic acid, norpinic acid and pinonaldehyde), 9% to 14% are ELVOCs/HOMS, and 17% to 23% are organic nitrate. In total, biogenic-derived OA represents about 66% to 80% of OA. The rest is made up by aromatics derived OA (2% to 3%) and anthropogenic intermediate and semi volatile organic compounds (17% to 31%).

Considering this potential very high contribution of organic nitrates, they should be evidenced by the ratio $\text{NO}^+/\text{NO}_2^+$

There is little variation in the measured $\text{NO}^+/\text{NO}_2^+$ ratio. The ratio was calculated to be approximately 0.2 and was always lower than the ratio calculated during the calibration exercise (0.34).

Using the method described in Keidler-Scharr et al., (2016), we estimate the contribution of organic nitrate to be approximately 32% (of the total nitrate) for RF20 and up to 40% for RF23. However it should be noted that nitrate aerosol particles did not contribute more than 5% to the total aerosol mass. Therefore the model estimate of 17 to 23% of organic nitrate is largely overestimated. We assume that this is because hydrolysis is not taken into account in the model. Hydrolysis is said to be responsible for the elimination of the organic nitrate functionality leading to the evaporation of nitric acid from the particles (Rindelaub et al., 2016).

The text has been modified accordingly:

“The contribution of organic nitrate modeled is not reflected in the measurements, where only 5% of the total measured aerosol mass contained nitrate aerosol. This difference is likely due to hydrolysis not being accounted for in the model. However, under ambient conditions hydrolysis could eliminate the organic nitrate functionality, allowing nitric acid to evaporate from the particles (Rindelaub et al., 2016).

8/P13, line 19 : again, 15-35% of isoprene SOA is significant.

Original text “A lack of direct evidence of IEPOX SOA (m/z 82 $C_5H_6O^+$) in the cToF-AMS measurements leads us to conclude that the formation of SOA, from isoprene precursor species was not important during this measurement period. This was confirmed through the use of the Polyphemus model, which shows that although the contribution of monoterpene and aromatic species is low compared to that of isoprene and its oxidation products, the yield of SOA formation from these precursor species is much more important.”

The text has been updated.

A lack of direct evidence of IEPOX SOA (m/z 82 $C_5H_6O^+$) in the cToF-AMS measurements leads us to conclude that the formation of SOA, **following an IEPOX formation route** from isoprene precursor species was not **dominant** during this measurement period. The Polyphemus model, determines a contribution of Isoprene SOA, **formed through alternative pathways, of the order of 15 to 35%. Therefore, although not possible to accurately identify the formation pathway of the measured SOA, we can assume that it is at least partly associated with biogenic isoprene VOC species.** The model also illustrates that although the emission of monoterpene and sesquiterpene species is low compared to that of isoprene, the yield of SOA formation from these precursor species **is more important. This is in agreement with recent observations by Zhang et al., (2018), who showed that SOA is dominantly formed from monoterpene emissions in southern USA.**

Zhang, H, Yee, L.D, Lee, B; H., Curtis, M.P, Worton, D.R, Isaacman-VanWertz, G., Offenberg, J. H. , Lewandowski, M., Kleindienst, T.E, Beaver, M.E, Holder, A.L., Lonneman, W.A., Docherty, K.S. , Jaoui, M, Pye, H.O.T, Hu, W, Day, D.D, Campuzano-Jost, P, Jimenez, J., Guo, H, Weber, R.J, de Gouw, J, Koss, A.R, Edgerton, E.S, Brune, W, Mohr, C, Lopez-Hilfiker, F.D, Lutz, A, Kreisberg, N.M, Spielman, S.R., Hering, S, Wilson, K.R, Thornton, J.A, Goldstein, A. H. Monoterpene SOA dominate atmospheric fine aerosol Proc.Nat Acad Sci Feb 2018, 115 (9) 2038-2043; DOI: 10.1073/pnas.1717513115

.9/ P17 line 29. Lee et al (2016) was added in the reference list, but never cited in the text. As well, f91 is not discussed. Such discussions could bring valuable insights on the Biogenic SOA importance and origin.

The section is updated (Page 11).

Other sources of biogenic SOA can originate from the oxidation of monoterpene and sesquiterpene VOC species, or additionally from isoprene SOA, that do not follow the IEPOX route. In all cases, the contribution of m/z 91 in the cToF-AMS mass spectra, often identified as being the $C_7H_7^+$ fragment (Lee et al. 2016; Riva et al., 2016) would be enhanced. This m/z 91 was present in all OA mass spectra and was higher for the LOOA ($f_{91} = 0.007$). However, in previous studies these f_{91} values are considered as background (Hu et al., 2015; Lee et al., 2016), hence making it difficult to associate the measured SOA with these formation routes. It should be noted that m/z 91 can also be associated with fragments of primary anthropogenic OA, and the contribution of anthropogenic aerosols from the industrial zone (Fos sur Mer) south of the flight area cannot be ruled out”.

Non-exhaustive list of technical corrections (figures/legends, mostly)

P2, line 4. The acronym of methacrolein is defined as MACR, but MCR is used all throughout the manuscript and in the figures (except in table 1).

This has been changed throughout the manuscript to MACR.

Figure 1 : add the flight numbers in the legend.

Figure 1. Typical flight track traveling a) west (RF 15 and RF 21) and b) east (RF 20 and RF 23) of Avignon (black circle). Points of the flight track are coloured by organic aerosol concentrations.

Figure 4 a) change the legend (see comment 3)

This figure has been updated, please refer to our response to comment 3.

Figure 5 : Y axis label. What is the lower cut off diameter of the SMPS 15 or 17 nm?

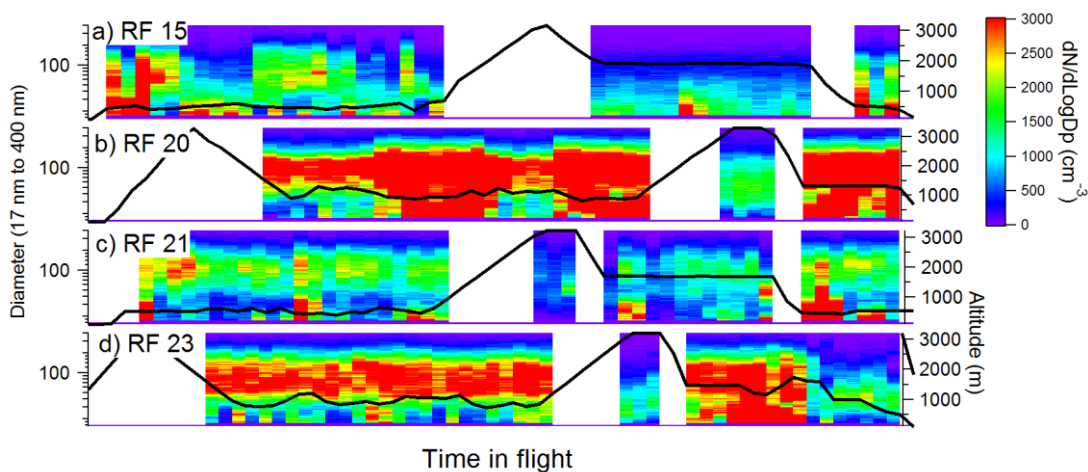


Figure 5. Aerosol size distribution measured by the SMPS for a) RF15 b) RF20, c) RF21, d) RF23 from 17 nm up to 400 nm. The colour scale indicates aerosol concentration $dN/d\log D_p$. Altitude is illustrated as the black line and is represented on the right hand axis.

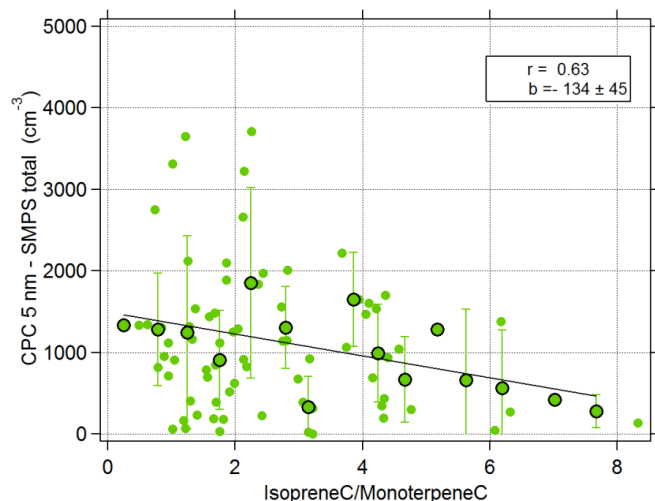
Figure 6 : Y axis label : add units ; figure legend : 17 or 15 nm?

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 calculated over a number of IsopreneC/MonoterpeneC ratios (size bins of 0.5), Error bars represent $\pm 1 \sigma$ of the average CPC5nm – SMPS values. . The black line represents the linear correlation fit.

Figure 7 : explicit the Delta

In response to comment no.5 text explaining the delta value has been included.

The text has been updated as follows:

During the flights, as the valley area is approached, we observe the sampled air masses become gradually more oxidized with respect to biogenic emissions, providing us with a well-defined sample area to evaluate the contribution of biogenic SOA on background/regional air masses. In order to isolate the formation of OA resulting from the oxidation of VOC species, the change in the OA concentrations above the background was calculated (ΔOrg). The background values were determined based on measurements during transects of the flight between the valley area and the airport. During this time, aerosol concentrations were low with little temporal variation. Particle size measurements display a single mode at 100 nm with average particle concentrations of 3000 cm^{-3} . Measurements of VOC species during this background period result in average concentrations of Isoprene of $1544 \text{ pptV} \pm 696 \text{ pptV}$, and lower concentrations of longer lived species MACR+MVK of $661 \text{ pptV} \pm 239 \text{ pptV}$ (Table S2).

For the resolved PMF factors, LOOA and MOOA, the background values were 0.27 and $0.41 \mu\text{g m}^{-3}$ respectively (Table S2). Organic factors corrected for background concentrations are referred to as $\Delta\text{-LOOA}$ and $\Delta\text{-MOOA}$. Plotting these two factors against the ratio of MACR+MVK+ISOPOOH/isoprene (relative air mass age) (Fig. 7 and S10), we observe a significant increase of the $\Delta\text{-LOOA}$ species with air mass age until a maximum is reached at ratios of 0.65.

Figure 7. 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 as a

proxy for photochemical age of airmass). The delta value (Δ) are calculated from the increases in OA above background concentrations (Table S10).

Figure 9 : Put side by side all the monoterpenes derived SOA components.

Changes have been made to the figure.

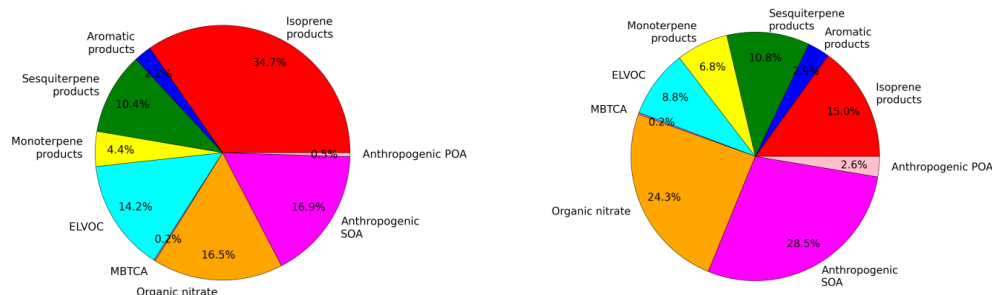


Figure S3 : X axis : wrong units ! , MCR+Isoprene? / Legend : ISOPOOH is missing

This figure has been modified and updated.

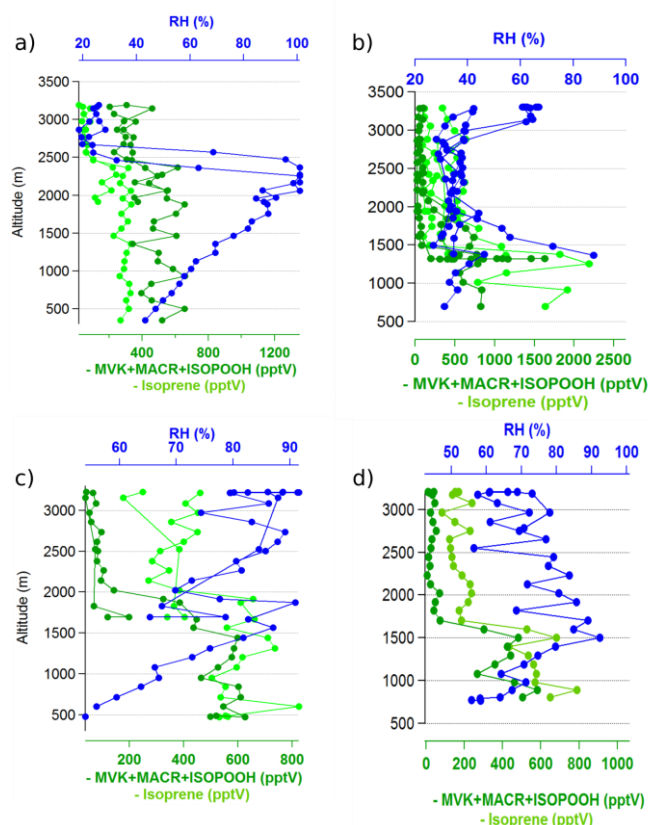


Figure S3. Vertical profiles of RH, isoprene and its oxidation products (MVK+MACR+ISOPOOH) for: a) RF15, b) RF20, c) RF21, d) RF23.

Figure S6 : No identified Y axis for benzene, X axis : I suppose it's Toluene/Benzene and not Benzene/Toluene

This figure has been corrected and updated.

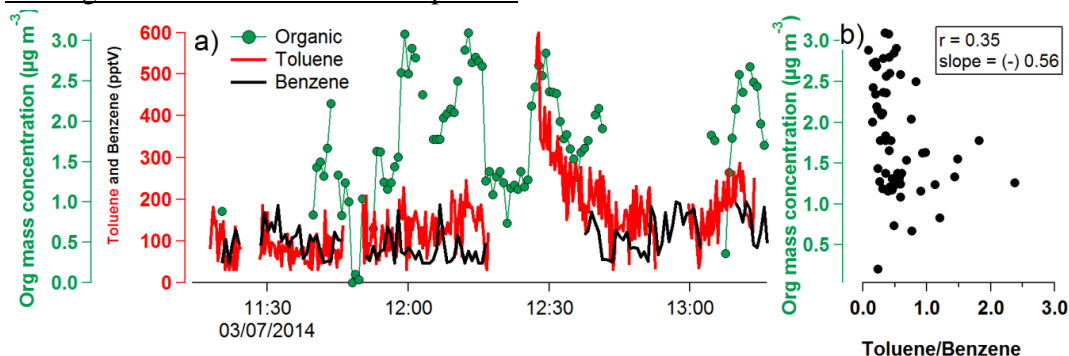


Figure S6. Comparison of total organic matter ($\mu\text{g m}^{-3}$) measured by the C-ToF-AMS with a) Toluene and Benzene concentrations, as a function of time, and b) against the ratio of the Toluene/Benzene.

Figure S7 : Develop and modify the legend (you didn't calculate air mass age, just used proxies). Define Delta, flight numbers

Figure S10 Variations of these two PMF factors with the relative air mass age calculated using either a) anthropogenic VOC or b) using MCR+MVK+ISOPOOH to calculate the relative air mass age. Δ LOOA and Δ -MOOA represent organic concentrations above the determined background (0.2 and 0.4, respectively)

Figure S11 : Wrong legend

This error has been corrected.

Figure S11. NH_4 measured to NH_4 predicted plotted against organic aerosol during flight RF20. The points are coloured by SO_4 concentrations.