acp-2016-1178 : “Origin and variability of volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus)”

This manuscript presents the on-line measurements of 24 volatile organic compounds (VOCs) during a field campaign at a background site of Cyprus in March 2015. Based on the measurements, the temporal variability of VOCs was investigated. Six major sources and corresponding origins of VOCs were addressed by time series analysis, PMF receptor model, as well as CPF and CF. Furthermore, the influences of biogenic and anthropogenic sources on VOCs compositions were distinguished by a combined analysis of VOCs PMF factors with source apportioned OA. The work described in this manuscript would definitely provide a better understanding of the air pollution of VOCs as well as their sources and fate impacting the Eastern Mediterranean region.

Authors’ Responses to Referee #2

We would like to thank the Referee #2 for her/his general feedback and each of her/his useful comments/questions for improving the quality of this manuscript. All comments addressed by both reviewers have been taken into account in the preparation of the revised version of the manuscript. In this respect, several figures were notably modified and in the supplementary. Please note that figures numbers are now different in this new version.

In the present document, authors’ answers to the specific comments addressed by Referee #2 are mentioned in **blue**, while changes made to the revised manuscript are shown in *italic.*

The comments on the manuscript are listed as follows:

1/ Pages 2 - 3: It would be better to shorten the "Introduction" part. For example, the second, third and fourth paragraphs in this part on page 2-3 would be shortened by removing certain general information.

Following reviewer’s suggestions, we have made efforts to write a revised version of the introduction with conciseness. In the revised manuscript, it now reads (Pages 2 - 3):
“~~Ambient air is one of our vital natural resources. However, in addition to having direct or indirect impacts on the environment and climate, air pollution also has adverse health effects, most notably on the respiratory system (Nel, 2005). As a consequence, ambient air pollution has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC, 2013).~~

~~There are a myriad compounds found in ambient air.~~ Volatile Organic Compounds (VOCs) have been known as one of the principal trace constituents in the atmosphere and they include a large number of species having lifetimes ranging from minutes to months. Their distribution is the result of ~~three combined processes:~~ (1) the release of VOCs to the atmosphere by various natural and anthropogenic sources. Emission by vegetation is regarded as the largest natural source on a global scale (Finlayson-Pitts and Pitts, 2000; Guenther et al., 2000). ~~Anthropogenic VOCs are released into the atmosphere by various human activities, especially those related to vehicular exhausts, evaporation of gasoline, use of solvents, emissions of natural gas and industrial processes (Friedrich et al., 1999).~~ Although anthropogenic emissions are various (Friedrich et al., 1999) and are quantitatively smaller than biogenic ones at a global scale (Guenther et al., 2000), anthropogenic VOCs can be the most abundant found in urban areas. Once released in the atmosphere, the temporal and spatial variabilities of VOCs are influenced by (2) mixing processes, ~~closely related to meteorological conditions within the mixing boundary layer, which tend to redistribute air pollutants uniformly through advective and convective transport patterns on a regional or long-range scale, especially for long lifetime species (ethane, propane).~~ ~~During their transport, they undergo~~ and (3) removal processes or chemical transformations ~~due to atmospheric photo-oxidants~~ ~~such as ozone (O_3) during both night and day, nitrate radical (NO_3) at night and hydroxyl radical (OH) during daytime~~ (Atkinson, 2000; Atkinson and Arey, 2003). Therefore, in order to perform an exhaustive characterization of VOCs sources, it is important to know their chemical composition but also their potential intensity variations on different time scales.

A robust tool to identify emission sources i~~s~~ Positive Matrix Factorization (PMF - Paatero, 1997; Paatero and Tapper, 1994) ~~is one of the various tools developed to identify emission sources.~~ Over the last decade, this source-receptor approach has been intensively used in urban areas (e. g. Baudic et al., 2016; ~~Brown et al., 2007;~~ ~~Gaimoz et al., 2011; Latella et al., 2005;~~ Salameh et al., 2016; Yuan et al., 2012) but also in remote/rural environments (Lanz et al., 2008; Leuchner et al., 2015; Michoud et al., 2017; Sauvage et al., 2009). Other receptor models such as Principal Component Analysis/Absolute Principal Component Scores (PCA/APCS) (~~Chan and Mozurkewich, 2007;~~ Guo et al., 2007), UNMIX (Jorquera and Rappenglück, 2004~~; Olson et al., 2007~~) and Chemical Mass Balance (CMB) (Badol et al., 2008~~; Na and Pyo Kim, 2007~~) have been previously used in VOCs source apportionment. ~~Although both models have aims similar to that of PMF, they have different mechanisms and each approach has advantages and limitations as described in several comparison studies (e.g. Anderson et al., 2002; Miller et al., 2002; Song et al., 2008; Viana et al., 2008; Willis, 2000).~~ Studies show that PMF models are more efficient in identifying source profiles (Jorquera and Rappenglück, 2004~~; Miller et al., 2002~~). Yuan et al., 2012 stressed the importance of different reactivity of VOCs and the impact of photochemical aging on the interpretability of the resolved factors as source profiles that have not been considered in most of the studies applying PMF. Therefore, in remote/rural environments, despite the assumption of non-reactivity or mass conservation (Hopke, 2003), PMF can be either used to identify aged primary sources or to get insights about the sources and *processes involved in the evolution of measured VOCs (Michoud et al., 2017; Sauvage et al., 2009).*

VOCs are also key players in photochemical processes leading to secondary pollutant formation, such as tropospheric O_3 *(Seinfeld and Pandis, 1998) and secondary Oxygenated (O)VOCs (~~Atkinson, 2000;~~ Goldstein and Galbally, 2007; Seco et al., 2007). ~~Undergoing multigenerational oxidation processes, these secondary OVOCs~~ These latter react with atmospheric oxidants leading to increasing functionalized products with sufficiently low volatility (Aumont et al., 2012; Jimenez et al., 2009; Kroll and Seinfeld, 2008) to take part in the formation of Secondary Organic Aerosols (SOA) by nucleation or condensation onto pre-existing particles (Fuzzi et al., 2006; Kanakidou et al., 2005). Furthermore, numerical simulation models ~~that take into account chemical transformations~~ suggest that the secondary OVOCs are still reactive and multi-functionalized several days after emission~~, allowing transport over long distances~~ and thus affecting the oxidant budget as well as the formation of ozone and SOA at remote locations (Aumont et al., 2005; Madronich, 2006). It is, therefore, essential to understand the sources and fate of VOCs in the atmosphere, and especially its evolution during long-range transport.*

~~Affected by important pollution sources,~~ The Mediterranean is a sensitive region affected by both particulate and gaseous pollutants. This air pollution is the combination of (1) long-range transported polluted air masses originating from 3 continents (Europe, Asia and Africa – e.g. Lelieveld et al., 2002; Pace et al., 2006; ~~Ziv et al., 2004~~) with (2) local emissions either of anthropogenic origin, associated to local human pressure from the surrounding industrial and densely populated coastal areas of the basin (Im and Kanakidou, 2012; Kanakidou et al., 2011) or of natural emissions (Kalogridis et al., 2014a; Liakakou et al., 2007; Owen et al., 2001) and forest fires ~~(Alves et al., 2010;~~ Bougiatioti et al., 2014)~~. Additional aggravating factors are among others: (3) climatic conditions favoring the development of photochemical processes (Fountoukis et al., 2011), (4) the scarcity of precipitation scavenging and (5) a tendency to accumulate pollution due to poor ventilation rates.~~ As a consequence, particulate or ozone concentrations are generally higher in the Mediterranean region than in most continental European regions especially during summertime (Doche et al., 2014; Menut et al., 2015; Nabat et al., 2013; Safieddine et al., 2014) ~~since climatic conditions favoring the development of photochemical processes (Fountoukis et al., 2011)~~. The Mediterranean region is also considered as a prominent climate change "hot spot", considering interactions between climate and air quality, and is expected to undergo marked warming and drying in the 21st century (Giorgi, 2006; Kopf, 2010; Lelieveld et al., 2014). However, air pollution in this region remains difficult to assess and characterize mostly because of a lack of atmospheric measurements. Additional information on the chemical composition of the air, including the speciation and the reactivity of VOCs, will further improve our current understanding of the complexity of the Mediterranean atmosphere."

2/ Page 8, lines 15 - 24: The "Off-line VOCs measurements" part on page 8 would be removed since data obtained by off-line measurement have not been used in this manuscript.

Off-line VOCs measurements were used in order to consolidate the robustness of the PMF dataset.

In the revised manuscript, and following a comment from reviewer #1, a short section has been added to give the results about the comparison between on- and off-line measurements.

Corrections applied in the revised manuscript:

Page 8, lines 1 - 4:"***Off-line VOCs measurements:***

[...] Here, VOCs measured off-line were used as independent parameters to consolidate the robustness of on-line measurements by inter-comparison of VOCs measured by different techniques. They will be further presented and investigated in another paper dedicated on biogenic and oxygenated VOCs."

Page 8, lines 15 - 26: "***VOCs intercomparison:***

[...] The sum of pinenes measured by the GC-FID was compared to the (non speciated) monoterpenes measured by PTR-MS, yielding the same variability and consistent ranges of concentrations (r: 0.92 and slope: 0.96). The same conclusion was obtained for α-pinene, measured by GC-FID and off-line technique, and acetaldehyde, measured by PTR-MS and off-line technique. Correlation between on-line and off-line measurements of α-pinene and acetaldehyde concentrations displayed good determination coefficients (r: 0.83 and 0.90 for α-pinene and acetaldehyde, respectively). The slope is also close to one for both compounds (1.10 and 1.16 for α-pinene and acetaldehyde, respectively). Note that, no ozone scrubber was applied on GC systems to prevent any ozonolysis of the measured compounds. However, different ozone scrubbers were used during the sampling of off-line measurements as recommended by Detournay et al. (2011). The consistency of on-line measurements of α-pinene and acetaldehyde with off-line ones, in term of levels range and variation, ensured a limited interference of VOCs reaction with ozone on results derived from GC measurements.

As a result, recovery of the different techniques, regular quality checks and uncertainty determination approach have allowed to provide a good robustness of the dataset."

3/ Page 8, lines 27 - 30: The comparison of measurements between PTR-MS and GC-FID shows low intercept of 0.10 µg.m-3 for benzene and 0.13 µg.m-3 for toluene, as stated in the manuscript. However, the intercepts would not be low enough when the mean concentrations observed at the CAO in this campaign (0.37 µg.m-3 for benzene and 0.19 µg.m-3 for toluene) are considered.

We agree with the reviewer that the intercepts are relatively high in comparison with the mean concentrations. Note that, the two instruments had different time resolution: for PTR-MS, signals of every masses were acquired every 10 min with a dwell time of 5 s

per mass and, for AirmoVOC, each measurement of 30 min started with an analysis period of 22.5 min. Additionally, the lowest concentrations were generally entailed by higher relative uncertainties than the mean/high concentrations.
In order to nuance that point, we have decided to replace "low" by "acceptable" in the revised manuscript (Page 8, line 10).

4/ Page 14, line 3: It is stated that the CAO was affected by air mass originating from "West of Turkey" (Page 14, line 3). But in the most part of the manuscript, it is stated that the CAO was affected by air mass originating from "South of Turkey". And in Figure 18, the factor contributions to VOCs were similar when air masses were originated from West of Turkey (C5) compared to from Marine (C2). Does this indicate that the "West of Turkey" is clean area?
On one hand, in the manuscript, "West of Turkey" refers to a source region (i. e. cluster 5) of the classification of air-mass origins (Fig. 2 of the revised manuscript) based on the analysis of the retroplumes. "South of Turkey" refers to potential origin of regional contribution observed at CAO when air masses were originated from both the Southwest Asia and the Northwest Asia (i. e. clusters 7 and 4, respectively). Potential emissions areas were pinpointed by concentration field (CF) results of anthropogenic factors. CF method consists in redistributing concentrations of a variable observed at a receptor site along the back-trajectories, ending at this site, inside a gridded map. The CAO station was mostly influenced by continental air masses originating from "Southwest Asia" (cluster 7 – 31 %) and "Northwest Asia" (cluster 4 – 28 %) while it was only influenced 10 % of the field campaign by "West of Turkey" air masses (cluster 5). These findings explain why it is stated that the CAO was affected by air mass originating from West of Asia. These air masses have transported toward the site regional contribution of potential emission from the South coasts of Turkey area.

On the other hand, a higher continental influence was noticed on anthropogenic factors when the site received air masses coming from the West of Asia than the West of Turkey (Fig. 16 of the revised manuscript). Potential emissions areas associated to air masses originating from the West of Turkey were the Southwest coasts of Turkey (as depicted by CF results of factor 6 plotted in Fig. 14 of the revised manuscript– note that, potential emissions areas were the same for factors 3 to 6). Additional more distant emissions areas of the West of Turkey were not observed by CF plots, such as the Istanbul region, which corresponds to the most densely populated areas of Turkey, with expected high anthropogenic emissions. Istanbul is far from CAO station of 700 km while the South coasts of Turkey are much closer from the site (100 km - 250 km from CAO). As a consequence, the shorter distance of potential emissions areas, associated to the South coasts of Turkey, could lead to an injection of fresher anthropogenic sources in air masses observed at the receptor site. Furthermore, the Southwest coasts of Turkey correspond to less densely populated areas compared to the Southeast coasts of Turkey (potential emissions area associated to air masses originating from the West of Asia – Fig. 14 of the revised manuscript). These findings only indicate that CAO is not influenced by important anthropogenic emissions areas when air masses were originated from the West of Turkey and cannot suggest that the "West of Turkey" is a clean area.

Corrections applied in the revised manuscript (Page 23, lines 28 - 33):

"Additionally, a higher continental influence was noticed on anthropogenic factors when the site received air masses coming from the West of Asia than the West of Turkey. Potential emissions areas associated to air masses originating from the West of Turkey were the Southwest coasts of Turkey (as depicted by CF results plotted in Fig. 14), corresponding to less densely populated areas compared to the Southeast coasts of Turkey. Note that, additional more distant emissions areas of the West of Turkey, such as the Istanbul region with expected high anthropogenic emissions, were not observed by CF plots that could explain why CAO was not influenced by important anthropogenic emissions areas when air masses were originated from the West of Turkey."

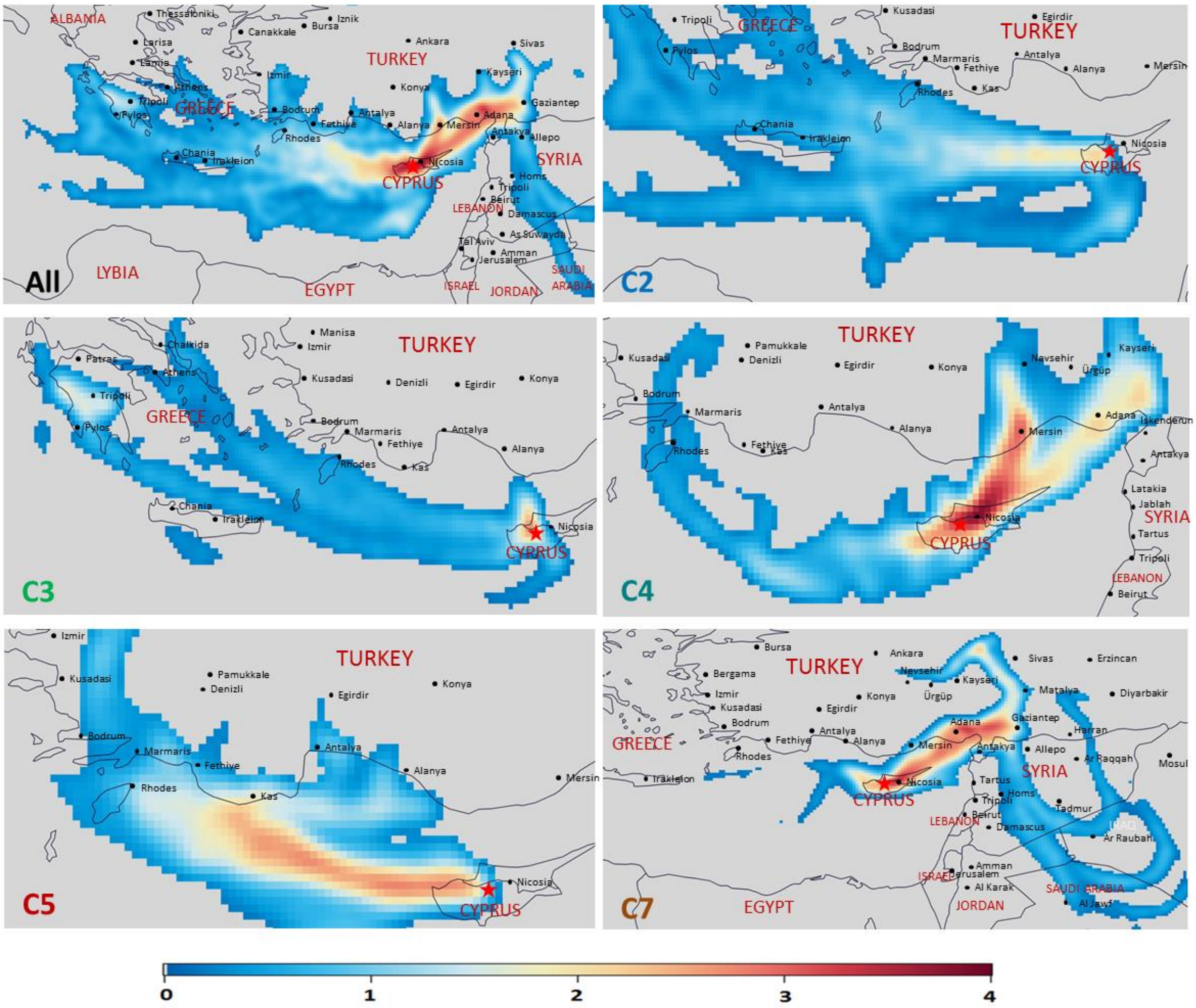

Figure 14 (of the revised manuscript): Potential source areas contributing to the VOCs factor 6 in function of air mass origins. Contributions are in units of µg.m^{-3}. All – without distinction of air mass origins; C2 – marine air masses; C3 – Europe; C4 – NW Asia; C5 – West of Turkey; C7 – SW Asia. Low numbers of samples associated to clusters 0 and 1 (Local and N. Africa, respectively – figure 2) don't allow to apply CPF analysis only considering these air masses origin.

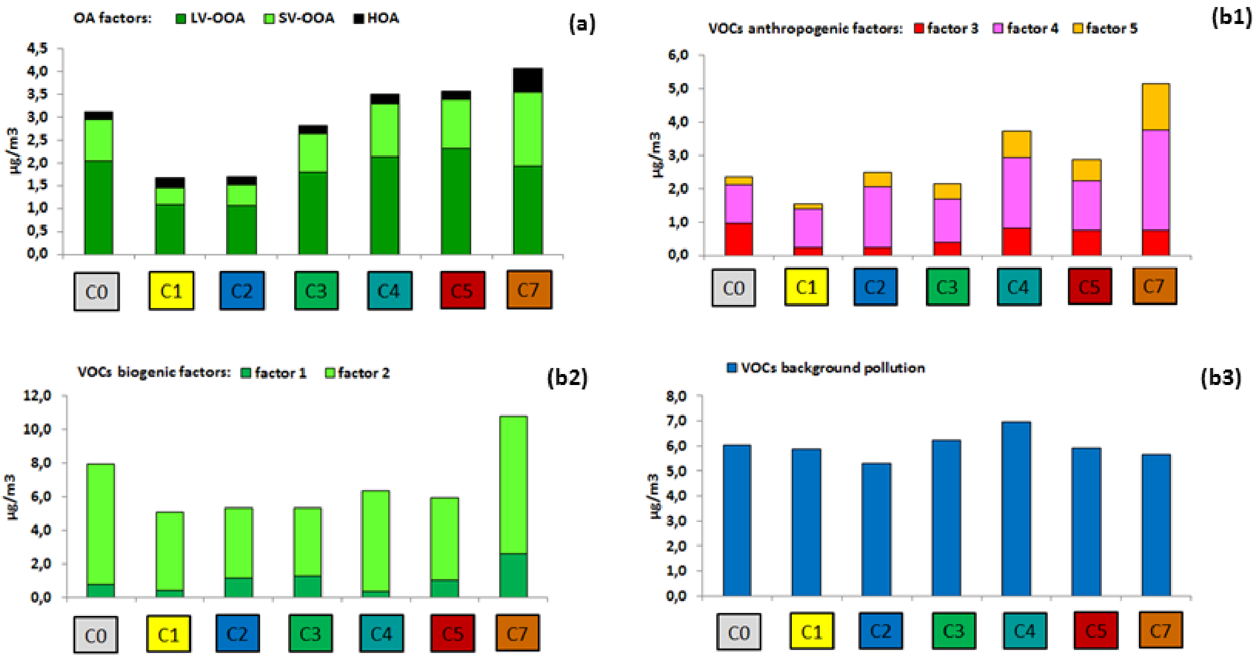

Figure 16 (of the revised manuscript): Accumulated average contributions of the OA and VOCs factors (figures a and b, respectively) in function of air mass origins. Classification of air masses: C0 - Local; C1 - N. Africa; C2 - Marine; C3 - Europe; C4 - NW. Asia; C5 - W. of Turkey and C7 - SW. Asia. VOCs factors: factor 1 - biogenic source 1; factor 2 - biogenic source 2; factor 3 – short-lived combustion source; factor 4 – evaporative sources; factor 5 – industrial and evaporative sources; factor 6 – regional background. OA factors: HOA - hydrogen-like OA; SV-OOA – semi-volatile oxygen-like OA; LV-OOA – low-volatile oxygen-like OA.

5/ **Page 16, lines 10 - 11:** The interpretation of low concentration of α-pinene in daytime would not be convincing. Both α-pinene and isoprene can react with daytime oxidants with lifetime of 1.4h and 2.3h respectively (please see "3.5.1" part). But high concentration was observed for isoprene in daytime, while low concentration was observed for α-pinene in daytime. Please provide more interpretation

We have decided to remove the phrase “A possible interpretation could be that α-pinene was rapidly consumed by daytime oxidants due to its high reactivity.” In the revised manuscript, the interpretation of monoterpenes variability is explained by nocturnal monoterpenes emissions, as other studies, since some additional elements were given in Sect. 3.5.1, when the variation of biogenic source 1 was discussed. Furthermore, a second paper is under preparation and is dedicated to drivers of BVOCs emissions at CAO.

Correction applied in the revised manuscript (Page 15, lines 27 - 31): *“Surprisingly, α-pinene concentrations were elevated during nighttime than during the daytime. A similar nocturnal pattern has been observed elsewhere (Harrison et al., 2001; Kalabokas et al., 1997; Kalogridis et al., 2014) and was attributed to nocturnal emissions from monoterpenes storing plants from the understorey vegetation. These nocturnal maxima were also enhanced by the slow removal processes (i.e. low concentrations of oxidizing species) and the shallow nocturnal boundary layer.”*

6/ Page 20, "3.5.3 Regional background (factor 6)": It would be suggested to add a clear definition of "regional background". The definition would be helpful to understand the factor 6, since the source areas associated with factor 4, 5 and 6 are all South of Turkey or Southwest/Southeast of Turkey.

As noticed by reviewer #2, CF plots highlighted similar potential source areas associated with factor 4, 5 and 6. However, contributions of these factors were different in function of air masses origin as depicted in Fig. 16 of the revised manuscript.

Contributions of factor 6 were rather stable whatever the air mass origin (from 5.2 µg.m^{-3} to 6.6 µg.m^{-3}) that underlines the background character of this factor. This factor was mainly composed of ethane, propane and some OVOCs, species with high atmospheric residence times. Because of their low reactivity, species of this factor tend to accumulate in the atmosphere and show significant background levels. Factor 6 can be interpreted as a regional contribution of various remote sources of the Mediterranean region transported towards the receptor site by aged air masses which have not been recently in contact with relatively significant anthropogenic sources.

Contrarily, factor 4 and 5 were more influenced by regional contributions. Factors 4 and 5 contributions were twice as high when the station was under continental influence comparing to the one under marine influence (Fig. 16 of the revised manuscript). Furthermore, the authors noticed a higher continental influence on VOC anthropogenic factors contribution when air masses were originated from the Eastern Mediterranean (clusters 4, 5 and 7 associated to air masses originating from West Asia) compared to the Western Mediterranean (cluster 3 associated to air masses originating from Europe) as expected with the distance of respective potential emission areas. The strongest continental influence was when air masses originated from the Eastern Mediterranean region. As a result, factors 4 and 5 were of local/regional origins but were not representative of the continental regional background as factor 6.

As suggested by reviewer #2, a definition of "regional background" was added in the revised manuscript (Pages 20 - 21, lines 29 - 2): *"As a conclusion, factor 6 can be interpreted as a regional contribution of various remote sources of the Mediterranean region, showing hence the continental regional background (Hellén et al., 2003; Leuchner et al., 2015; Sauvage et al., 2009). These sources were transported towards the receptor site by aged air masses which have not been recently in contact with additional anthropogenic sources. Within the time of transport of emissions from distant sources, atmospheric oxidation removes the reactive species and the remaining fraction contains mostly the less-reactive species, such as ethane, propane and some OVOCs. Finally, it is reported here as "regional background"."*

7/ Pages 23 – 25, "4.2.2 Relationship between VOCs and OA": It would be suggested to add p value associated with correlation coefficient (r). With the p value, it would be more convincing to state that the correlation is statistically significant.

As suggested by reviewer #2, p-values associated to each Pearson correlation coefficients of the Section 4.2.2 (Pages 24 - 25) were calculated and indicated in the revised version of the manuscript. The authors stated that Pearson correlations discussed in this section were statically significant since all p-value were below 1.3 10^{-14}.

8/ Page 46, figure 5: the word "anthropogenic" in the caption of Figure 5 would be "biogenic”; the word "m69" in the fourth drawing would be "isoprene".
The word "anthropogenic" in the caption of figure 5 was replaced by "biogenic" and the word "m69" in the fourth drawing was replaced by "isoprene".