

## ***Interactive comment on “Origin and variability of volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus)” by Cécile Debevec et al.***

**Anonymous Referee #1**

Received and published: 18 May 2017

General comments:

The article presents an extremely thorough and comprehensive overview of the field site on the Island of Cyprus. It details the analytical methods and instruments used; describes the chemical and broad aerosol composition; identifies the most likely sources of the pollutants observed; and describes the observations in the broader context of the “Mediterranean region”. It provides a very good description of the site for anyone wishing to make observations in this region. The article, however, is (inevitably) very long and I fear that some of the impact of the paper may be lost due to its length. That said, this is no reason to exclude the paper from publication and so I recommend that it be published subject to the authors addressing the following comments.

C1

Specific comments:

A wide range of VOCs are reported from the site and yet 1,3-butadiene a commonly reported anthropogenic compound which fits within the range of VOCs covered by the instruments used (and has important health and atmospheric chemistry impacts) does not appear to be reported. It would likely be of interest to many others in the field. Could this be included or were problems encountered for measurement of this compound?

Some of the VOCs reported here are unsaturated compounds which are known to be highly reactive to ozone. There are known potential interferences caused when measuring these compounds in the atmosphere with GC systems. Were any measures taken to remove the ozone from the samples? If not, were the additional uncertainties resulting from ozone reactions considered here? Perhaps inclusion of a short discussion of these issues could be added?

The PMF analyses show a couple of gaps in the time-series around the 10th and 21st March (Figures 8, 14, 17 and 19). I may have missed it in the text, but the authors should confirm that this due to a loss of data (assuming it is) rather than being unable to assign these periods to any of the 6 factors identified.

Some of the differences described when comparing the PMF analyses from different site in the region appear to be (possibly) explained by differences in how the compounds were apportioned. Early in the manuscript the authors describe how (paraphrasing) the PMF analysis was tuned to give optimal results for this site over this measurement period and presumably Michoud et al. have done similar for that study. Perhaps the only real way to make a valid comparison between the PMF results for the region would be to merge/re-assign the PMF factors to fit both sites? I can see that this may not be suitable for local pollution events, but would perhaps better describe the main factors affecting the “Mediterranean region”. I don’t expect the authors to actually do this here, but they could perhaps summarise the possible benefits and drawbacks of such a study.

C2

Technical comments/corrections:

Page 2, line 29: "A robust tool to identify emission sources is 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. . ."

Should read something like: "A robust tool to identify emission sources is Positive Matrix Factorization (PMF - Paatero, 1997; Paatero and Tapper, 1994) . Over the last decade. . ."

Page 3, line 22: ". . .and especially its evolution..."

Should read: ". . .and especially their evolution..."

Page 3, line 24: "Affected by important pollution sources, the Mediterranean is a sensitive region affected by both particulate and gaseous pollutants."

Should read something like: "The Mediterranean is a sensitive region affected by both particulate and gaseous pollutants."

Page 4, line 17: ". . .(geographical origin, fast/low transport)..."

Should read: ". . .(geographical origin, fast/slow transport)..."

Page 4, line 19: "It is ideally located, close from the coast"

Should read: "It is ideally located, close to the coast"

Page 4, line 23: "Our study performed in the Eastern Mediterranean will therefore offer a unique opportunity to provide a comprehensive characterization of VOCs for the entire Mediterranean."

This is a very grand statement and, I would suggest, is overstating the robustness of the study somewhat. Perhaps "detailed" rather than "comprehensive" would be more accurate?

Page 4, line 30: ". . .performed at an another background site of. . ."

C3

Should read: ". . .performed at another background site of. . ."

Page 5, line 12: ". . .European Research Infrastructure fir the observation of. . ."

Should read: ". . .European Research Infrastructure for the observation of. . ."

Page 5, line 17: ". . .more than 35 km of main Cypriot agglomerations, with very poor influences of these anthropogenic emission areas."

Do the authors mean "limited influences"?

Page 6, line 2: "AirmoVOC C6-C12, the measurement of C6-C10 hydrocarbons"

Why were measurements not made up to C12? Perhaps a statement could be made in the text for clarity here?

Page 13, line 21: "The most favorable conditions for high levels of VOCs (high temperatures, clear skies and low winds) were. . ."

I disagree with this statement as it is written. Warmer temperatures may lead to greater emissions from biogenic and also evaporative sources, however emissions from heating sources etc are normally observed to decrease. Warmer conditions are also commonly associated with greater boundary layer height leading to lower concentrations. Can the authors re-phrase this for improved clarity?

Page 13, line 62: ". . .and rainy periods may participate to a larger development of vegetation."

I suggest changing "participate" to "contribute"

Page 16, line 10: ". . .elevated during nighttime than during the daytime."

Should read: ". . .elevated during nighttime compared with daytime."

Page 16, line 14: ". . .low removal processes..."

Should this read: ". . .slow removal processes..." or ". . .limited removal processes..."?

C4

Page 17, line 26: "Note that, South-Southwest wind directions were mainly encountered during nighttime"

Could it be that the profile observed for this factor is simply dictated by the wind direction rather than a change in local emissions? Perhaps an added comment here would help to clarify?

Page 18, line 13-29: This section is should be re-written for clarity.

I think the main point of this paragraph is that for two specific periods (when the air mass was originating from the southwest) factors 3, 4 and 5 (and other combustion tracers) were all well-correlated. The reason for this was the sizeable distance travelled from the source region and so would adversely affect the PMF analysis results. Hence, these periods were omitted from the subsequent analyses.

Page 18, line 33: "Factor 3 displays faire correlation with ethylene ( $r = 0.94$ ). Factor 3 seems to correlate. . ."

Should read: "Factor 3 displays fair correlation with ethylene ( $r = 0.94$ ) and seems to correlate. . ."

Page 19, line 2: ". . .increase in midmorning. . ."

Should this read: ". . .increase in mid-morning. . ."

Page 19, line 13-14: ". . .this source exhibits higher contributions during the day with peaks at 5 h - 6 h, 10 h, 12 h, 15 h LT corresponding to. . ."

The diel variation in figure 12 doesn't seem to agree with this statement. Can the authors please clarify what they are referring to here?

Page 19, line 17-23: When discussing the contributions to factors 4 and 5. Gasoline evaporation is included in both. More clarification is needed to explain why these factors are distinct from one another.

C5

Page 20, line 25-26: "Hence, the high abundance of long-lived species in combination with the lack of shorter-lived compounds suggests here aged air masses transported towards the sampling site."

Should perhaps read: "Hence, the high abundance of long-lived species, in combination with the lack of shorter-lived compounds, suggests that aged air masses are being transported towards the sampling site."

Page 21, line 27-28: ". . .acetone ( $2.72 \mu\text{g. m}^{-3}$ ) with either biogenic origins (biogenic source 2) and primary/secondary anthropogenic origins. . ."

Should perhaps read: ". . .acetone ( $2.72 \mu\text{g. m}^{-3}$ ) with both biogenic origins (biogenic source 2) and primary/secondary anthropogenic origins. . ."

Page 22, line 5-6: ". . .to provide a comprehensive characterization of VOCs for the entire Mediterranean."

Not convinced that this can be described as comprehensive? I'd prefer this to be dropped to just read: ". . .to provide a characterization of VOCs for the entire Mediterranean."

Page 22, line 8: "On both sampling site, primary anthropogenic. . ."

Should read "At both sampling sites, primary anthropogenic. . ."

Page 22, line 9: "Similarly to our regional. . ."

Should read "Similar to our regional. . ."

Page 22, 4.1.2 Comparison with another PMF study performed at a remote site of the Mediterranean region:

Some of the differences described here appear to be (possibly) explained by differences in how the compounds were apportioned. Early in the manuscript the authors describe how (paraphrasing) the PMF analysis was tuned to give optimal results for this

C6

site over this measurement period and presumably Michoud et al. have done similar for that study. Perhaps the only real way to make a valid comparison between the PMF results for the region would be to merge/re-assign the PMF factors to fit both sites? I can see that this may not be suitable for local pollution events, but would perhaps better describe the main factors affecting the “Mediterranean region”. I don’t expect the authors to actually do this here, but they could perhaps summarise the possible benefits and drawbacks of such a study.

Page 23, line 27: “. . .contributions were twice higher when. . .”

Should perhaps read “. . .contributions were twice as high when. . .”

Page 23, line 26-28: “The average OA contributions were twice higher when the station was under continental influence comparing to the one under marine influence.”

I think this statement needs clarifying. From the look of the figure it depends which continent you refer to (Africa, Europe or Asia). Perhaps I am reading this incorrectly, but some clarity in the text would help here I think.

Tables, Figures and captions:

Table 1, caption: “Details of technics and measurements. . .”

Should read: “Details of techniques and measurements. . .”

Figure2: Can the resolution of the figure be improved? The axes and figure caption look slightly blurred to me.

Figure3: In the bottom right hand corner of the figure it states “calm = 0%”

The authors should clarify what this means and its significance, or remove it from the figure altogether.

Figure 5, caption: “Time series of a selection of anthropogenic VOCs (isoprene and  $\alpha$ -pinene – green lines)”

C7

Should this be “biogenic”?

Figure7: Certain masses are reported and shown in the figure which presumably relate to the PTRMS protonated masses. It would be useful to the reader to have the compound name(s) (accepting the uncertainty in exactly which compounds are being reported by the PTRMS), also listed in the figure.

Figure 8: Could a fifth panel be included in this figure for a stacked-area plot showing a time-series of the percentage contribution of each factor to the total? This would show very neatly which are the dominant sources factors at each point along the timeseries.

Figure 9, 12, 13, 18 and 19: A very minor point: Individual panes/plots are labelled as “a, b, c and d”, but are described in the caption as “A, B, C, and D”

Please change these for consistency/clarity

Figure 10: Could this figure be moved into the Supplementary information section?

Figure 11: Perhaps it shows my lack of knowledge of the geography of the Mediterranean region, but this figure is difficult for me to read. Is it possible to include some major country names as markers?

Could this figure be moved into the Supplementary information section? It is only rarely referred to in the text.

Supplementary Information

No 1,3 butadiene data is given in table SI-5 – was it measured? If so, it would be of interest.

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Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1178, 2017.

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