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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile organic compounds (VOCs) in photochemically aged air from the Eastern and Western Mediterranean" *by* Bettina Derstroff et al.

Anonymous Referee #1

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The paper "Volatile organic compounds (VOCs) in photochemically aged air from the Eastern and Western Mediterranean" presents VOC measurements during the summertime CYprus PHotochemical EXperiment 2014 in western Cyprus. The manuscript described the VOC measurements in great details. It also attempted to use two different models to interpret field data. The conclusions are not quite clear and don't seem to be important or contribute to any new knowledge. However, I think the community would appreciate the valuable data for this location provided by the CYPHEX campaign. I would suggest the authors could carry out some kind of photochemical aging analysis, source attribution analysis, or make more useful of the FLEXPART transport to improve the quality of the manuscript.

Several concerns and specific suggestions of the paper are:

1. Local anthropogenic emissions: for a population of 1.15 million, it might be worth to explore the importance of local emissions on the VOC levels. Could the high correlations of VOC vs CO (and aromatics) give some insights?

2. The title doesn't reflect what is told from the manuscript. It stated 'photochemically aged air' but the manuscript doesn't provide any analysis on this matter.

3. Abstract: loss rates: significant digits should be consistent for all reported numbers. These numbers all seem very small. Are they important?

4. Introduction (and its references) should be updated to reflect some newest developments on their global budgets particularly for methanol and acetone. More regional studies for this area should be cited otherwise I don't really see the motivations of this study.

5. Humidity dependent instrument sensitivity: a. Only two calibrations were performed: beginning and end of the campaign, but the humidity seems to vary a lot during the campaign. It is unclear how humidity was accounted for the measurements. Given some conclusions are related to the variability of ambient humidity, authors should be very careful on their observation's dependence on RH. b. The paper also commented that instrument sensitivity for methanol and isoprene didn't show any humidity dependency. Why is that? It seems PTR methanol sensitivity has a strong dependence on RH. c. One simple check on the RH effect is to examine if the background signal changed a lot during the campaign.

6. Page 6. Acetic acid measurements: It seems PAA measurements were not subtracted from the PTR 61.0284 amu. Would the main conclusion change if such subtraction were attempted?

7. Section 2.2.2: So I assume the GC-MS reports speciated monoterpene measurments? Has any attempt done to compare the GC-MS measured vs. PTR measured

monoterpene? Are they consistent? Also, more details should be reported for the GC-MS system.

8. Page 8 Line 253: again here it seems the PTR monoterpene is reported, but later GC-MS data is reported. It is very confusing which dataset is used for the monoterpene analysis.

9. Page 8 line 254: Any particular reasons that the tropical forest region is used to compare the data in Cyprus? The location of the site is 34 degree N, which is at mid-latitude.

10. Section 3.1: I would suggest the authors also take a look at MVK+MACR, since their lifetime is longer than isoprene so they could give a relatively regional perspective on the biogenic emission for Cyprus.

11. Page 9 lines 280-295: discussion on Fig.5. How does RH change your results? How does RH impact the observations here? It is stated that "But as soon as the wind came from a region where the distance between ocean and site was shorter, isoprene levels decreased rapidly", which is awkward written and need to be improved by the way. However, from Fig.5., it seems the opposite. Isoprene level is clearly higher after $\sim$9:30AM than before it, so does DMS.

12. Page 10 line 335-337: 'the measured production... the loss rate ...' I don't think they are ever mentioned in the method part. Are they measured or calculated?

13. Page 11 Line 344-346: a) the authors state that secondary production is expected to be minor in a remote site due to a lack of precursors. However, this is only true if the sample is fresh. Are there any evidence suggesting the air is mostly fresh? Use some photochemical clocks could easily tell that (Isoprene/MVK+MACR, Benzene/Toluene, etc) b) I don't see evidence to support the conclusion that in-mixing from free troposphere contributed to the enhancement of acetic acid. It seems to be purely speculation here.

14. I am not convinced the usefulness of diel variability analysis for the whole campaign given there are clearly several meteorological/transport conditions during the period, while the paper still spend much effort to discuss the overall diurnal pattern, median vs mean values, etc. How about discuss those main transport conditions in more details?

15. Ozone seems to be a good indication for fresh/aged air too. And the observed ozone is high. Are they coming from free troposphere, or are they from aged air? These could give insights on the VOC analysis particularly for acetic acid, but are lacking in the current version.

16. Section 3.2.2: It is not clear how useful the box model is. Are the conclusions already well known? Given the boxing model is not constrained at the local scale, it seems to be not necessary to this paper.

17. Page 14, Line 447-451: a) Photolysis rate cannot be neglected for acetone given it is 1/3 -1/2 of its loss terms. B) How is OH measured? It is not mentioned in the method.

18. Page 14, line 459: a few place mentioned PBL height 500m. Is this a good assumption for this region?

19. Page 15, Line 484: again, the role of free troposphere should be clarified, and ozone could be helpful.

20. Page 15 Line 495: Ocean's role for OVOCs: Could correlations with DMS be more helpful?

21. Section 3.2.4: I don't get too much information from this section. What is the main point? The lower CO emission for this region is interesting, but so do anthropogenic VOCs. An analysis based on transport pattern or aging would be more interesting.

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