Interactive comment on “Atmospheric mixing ratios of methyl ethyl ketone (2-butanone) in tropical, boreal, temperate and marine environments” by A. M. Yañez-Serrano et al.

Anonymous Referee #1

Received and published: 31 May 2016

The manuscript presents a valuable and solid contribution to the literature on oxygenated VOCs in the atmosphere. I have a number of mostly minor comments that I hope can help further improving the manuscript.

1. Introduction, line 71/72: I think it is unfair to characterize all biomass burning as anthropogenic since a substantial fraction of it is not man-made; naturally occurring fires can be caused by triggers such as lightning.

line 93: I fail to see how MEK can be produced by cis-2-butene or cis-2-pentene. I also did not find that in the cited literature. Please elaborate or drop.

line 121: MEK is of rather low toxicity; it is widely used as a solvent in the US, both in the chemical industry, and commercially. It is known as “paint-thinner”, and available over the counter in home improvement stores such as “Lowes”. Aside from its contents in paints and varnishes, it is also used in other household products, such as glues. As the result of such uses, its major fate is evaporation to the atmosphere. Here are some useful sources:

https://www.americanchemistry.com/ProductsTechnology/Ketones/Methyl-Ethyl-Ketone-MEK.html

https://www3.epa.gov/ttn/astw/hlthef/methylet.html

MEK manufacturing and use have been increasing in the last ten years, such that emissions very likely have as well.

2. Results section, line 262f.: While the interpretation that higher MEK mixing ratios near the canopy stem from direct canopy emissions is attractive, a chemical production through fast chemical reactions of emitted terpenes with ozone cannot strictly be excluded. A similar situation was presented by Holzinger et al. (ACP 5, 67-75, 2005). While it would be unusual that MEK, not acetone, is produced from certain terpene structures, the possibility cannot be excluded using the evidence presented. Of course, this origin discussion makes no difference with respect to MEK entering the lower atmosphere. With respect to deposition (and mixing ratios where given), the authors may want to cite Karl et al. (ACP 5, 3015-3031, 2005) and Schade et al. (Biogeochemistry, 106, 337-355, 2011).

line 356: the HYSPLIT citation is incorrect; it should be NOAA not NASA. In fact, the HYSPLIT webpages give concrete instructions on how to cite the model use, which should obviously be followed. The model’s use in this case also appears incomplete: several back trajectories for each case should be shown if the preferred ensemble is not used, trajectory heights need to be given, and weather maps should be consulted as a sanity check. This is a major shortcoming in the manuscript.
This is a poor analysis. It should either be dropped or expanded properly. Simple correlations are not always meaningful, especially in the given setting. Instead, a multi-variate analysis such as a factor analysis (see citation used in line 449) could be performed to evaluate sources, but even in that case, their interpretation may be difficult unless well-defined tracers are available and separated into different factors. In the author's case, the interpretation of acetone, acetaldehyde, and methanol as "biogenic" is questionable since all three compounds, especially acetone and acetaldehyde, have substantial anthropogenic sources. In the case of acetone, its sources are likely very similar to MEK, which makes the exploitation of the MEK to acetone correlation a potentially much more useful variable to explore. The authors barely touch on that in line 375 and 384/385.

3. Discussion section, line 463: "mechanical stress" is undefined. In the particular use here it actually means "cutting", i.e. physically injuring, the plant, which, in nature, is either due to herbivores (common) or infrequent events such as strong storms or heavy snow/frost load (less common). In this respect, I question the formulation of "close agreement" (line 479), since branches or leaves were not cut to enable "the installation of the branch enclosure", or were they? (see also line 546) Anthropogenically cause "wounding" (e.g. deGouw et al. papers) is typically related to crop harvesting.

line 515: lowest MEK abundance at CYPHEX? According to your Figure 5, MEK in "clean" air masses was lower at the T2 site at night. Did you mean averages or medians were lowest at CYPHEX? Also, revise the following section (lines 517f.) after reviewing air mass origins and "correlations".

line 528: What are "night-time anthropogenic activities"? The Guha paper does not list those, but rather links MEK abundances dominantly to soil and agricultural sources.

line 538: It seems the Le Calvé reference is outdated, see above.

5. It would be useful to present a comparison of the MEK data listed in this manuscript and published measurements, such as in Jordan et al and McKinney et al, which the authors already cite.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-317, 2016.