Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-957-RC1, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "A mechanism for biogenic production and emission of MEK from MVK decoupled from isoprene biosynthesis" *by* Luca Cappellin et al.

Anonymous Referee #1

Received and published: 3 December 2018

General comments:

Cappellin et al. describe a possible mechanism for the biogenic production of methyl ethyl ketone (MEK) from both exogenous and endogenous methyl vinyl ketone (MVK), which is decoupled from the plant's isoprene synthesis.

Earlier studies (even by one of the co-authors of this study) attributed isoprene an anti-oxidative role in plants, which was explained with its capability to capture reactive oxygen species (and thereby being oxidized to MVK/MACR). Over the last years, different studies have questioned this assumption. Cappellin et al. unequivocally show here that MVK production within plants under heat stress is not necessarily linked to the

plant's capability to synthesize isoprene. Therefore, the manuscript has the potential to become an important contribution to the controversial discussion, whether isoprene exerts an antioxidant role in plants.

In general, the manuscript is very well written, in a clear and concise way. However, I'm struggling a bit with the experimental design and the data interpretation. The Methods part misses details on peak assignment in PTR/SRI-ToF-MS, and CO2 measurements/calibrations (see comments below). The number of replicates (3) in each experiment is borderline. This is also reflected in the large error bars in Figure 2.

It is pretty brave to make statements on interconversion of in part isomeric compound using solely PTR-MS. Even when using NO+ ions for chemical ionization in the PTR/SRI-ToF-MS you have a lot of interfering ions from the compounds you were investigating. Moreover, natural isotopes of some of the investigated compounds could interfere with the parent ions of other compounds. The description of the data analysis in the methods section does not reveal if this effect was taken into account, nor does it explain satisfactorily how the ions signals were attributed to the different compounds. Especially in the case of the various alcohols a proper identification seems almost impossible with the instrumentation you used. I would expect to have a table containing all the different compounds and the associated ions in the two measurement modes of the PTR/SRI-ToF-MS. This would allow the reader to better judge whether the peak assignment is justified.

To my mind, such an experiment would have strongly benefited from additional analyses capable to distinguish isomeric compounds, such as GC-MS or similar.

Although I know it is a lot of work, I would recommend to perform additional experiments and to trap VOCs for GC-MS analyses in order to eliminate any doubt in the interpretation of the data.

The quality of some of the original figures was very bad (the updated ones submitted as Author Comment are OK).

Specific comments:

p. 2, line 18: was there really formed any 3-buten-2-ol? In Figure 1a, the 3-buten-2-ol seems to be zero throughout the whole experiment.

p. 2, lines 21-22: you disregard here that there is no possible direct conversion of 3-buten-2-ol to MEK. How sure are you about these data? I guess it is really tricky to properly distinguish 3-buten-2-ol from MEK using solely PTR-MS.

p. 4, lines 13-15: The calculated assimilation rate is very low. I've never seen assimilation rates in a comparable range as the dark respiration values in a light (!) experiment. What was the PAR you used in these experiments? Apparently, you used the PTR-ToF-MS to measure CO2 levels: have you considered different humidities in dark/light experiments when calibrating the PTR-ToF-MS for CO2? Can you comment on the accuracy of this method to measure CO2?

p. 5, lines 20-23: These reaction yield calculations require further explanations, either here or in the Methods section. Where do you "SHOW" that 73% of MVK is converted into MEK?

p. 8, line 16: is there a reason why you heated your sample line to 110°C? At such high temperatures you may encounter surface assisted reactions and thermal decomposition of larger compounds, possibly interfering with the ion signals of interest. The compounds you were interested in should all be fairly volatile, excessive line heating is therefore counter-productive in this case.

p. 8, line 27: I guess this is 10ul/min of liquid standard. What is the actual volume mixing ratio of the compound in the VOC-bag inlet air?

p. 9, line 3: what were the CO2 concentrations at the outlet of your VOC-bag? Depending on the enclosed leaf area, during light conditions at this modest flow rates you might have run into CO2 deficit conditions for your plant. This could have affected your measured VOC signals.

Figure 1: are these data of a single experiment or the mean over several experiments? This should be indicated in the figure caption. Since you have a possible interconversion of the measured compounds as well as emission and re-uptake, the y-axes should be labeled "Net VOC flux".

Figure 2: The overall quality of this figure is very bad! The resolution is indisputably low. The error bars and asterisks are almost not visible. I assume the compound grouping here is based on the different ion signals when using H3O+ ions for chemical ionization in PTR-MS, yielding the same ion for the different groups. This should be stated somewhere. As you are focusing on endogenously formed compounds here, it would make sense to normalize the signals measured in the different conditions to the stomatal conductance of the leaves. This way you might get an idea on the actual concentration of these compounds within the leaves.

Figure 5: you completely neglect the conversion of 3-buten-2-ol to MEK here, although, considering Figure 1, this seems its major conversion pathway. Again, the resolution of the background image could be improved.

Technical corrections:

p. 2, line 3: remove "plenty of". How can you claim there is plenty of evidence for the heat dissipating and thylakoid membranes stabilizing properties of isoprene, when you cite only two publications? Btw: how large can the heat dissipating effect of isoprene be when you compare the isoprene emission fluxes (nmol/(m^2*s)) with leaf transpiration (mmol/(m^2*s))?

p. 2, lines 19-20: remove this sentence. Why would the plant produce isoprene to scavenge ROS, if the isoprene oxidation products are similarly cytotoxic and in turn need to be scavenged themselves?

p. 3, lines 2: "..., though the full mechanism was not described.": nor is it described here. What are the enzymes involved in the detoxification reactions? Just saying.

p. 4, line 14: this is no proper sentence. You compare assimilation and isoprene emission values with a light intensity.

p. 5, line 18: Fig. 5 is a possible pathway for the biogenic formation and emission of MEK, but does not really explain it. A proper explanation would require the investigation of the enzymatic pathways involved in the MEK production.

p. 5, line 19: The results suggest that WITHIN PLANT isoprene oxidation is not the source of these VOCs IN YOUR EXPERIMENT! Atmospheric oxidation of isoprene is undoubtedly the main source of MVK in the atmosphere.

p. 10, lines 4-5: the cited reference does not contain any information on the spectral peaks to monitor!

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