

# ***Interactive comment on “Development of a thermal desorption-gas chromatography-mass spectrometry method for the analysis of monoterpenoids, sesquiterpenoids and diterpenoids” by Aku Helin et al.***

**Anonymous Referee #2**

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The study by Helin et al. describes in depth the analytical method of a thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) to quantify a series of Biogenic Volatile Organic Compounds (BVOC). While the core analytical method has been previously used extensively, such a detailed description of the processes and parameters affecting the sampling collection is a valuable addition. The authors focus their investigations to diterpenes, a highly understudied class of compounds that exhibits difficulties in quantification due to their volatility, low abundance, sticky nature and experimental artefacts. The paper reads well but few critical points deserve more

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attention. Therefore, the paper is suitable for AMT and I could recommend publication but only after addressing the following comments/concerns.

#### General comments

1. There seems to be a confusion on the terminology that starts from the title itself and extends to various points of the text. Terpenes are a class of compounds that include monoterpenes, sesquiterpenes and diterpenes. However, it's true that in the literature terpenes and terpenoids are frequently used in the same bases. But monoterpenoids, sesquiterpenoids and diterpenoids are actually modified terpenes, with different chemical formulas (eg. Chan et al., 2016). I would recommend changing the title to the more general "Biogenic Volatile Organic Compounds" or "Terpenoids". Consequently, individual corrections on the text over case-based referral to the individual species is needed.
2. My most serious concern has to do with the striking claim that there is no need for heating the Teflon lines in field applications, in contrast to almost all experimental approaches in the field to date. That conclusion was derived performing sampling recovery tests over which a second sample was taken subsequent to the original (L159: "Inlet line recovery was calculated simply by the relationship of analytes found in the second tube divided by the amounts in the first tube.") One would naturally expect that when the line is kept at the same temperature, artifacts cannot be evaluated properly. The losses on the line could be better illustrated if after the first sample, a subsequent "blank" sample over a now heated line is taken. In this approach, the amount of VOCs stuck in the tube could be quantified and the proper temperature for heating up the lines could be ascertained.
3. Similar to the previous comment, the authors describe in S1.5 the problems that arise with the replacement of the Teflon line. It seems that a new line is causing more artefacts comparing to a used one, indicating some saturation over the line surfaces. In general, the inlet line experiments should be explained in greater detail. The claim

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that Teflon lines should remain unheated for field applications has the potential to mislead future research and therefore it cannot become acceptable unless strong and well described proof of concept is presented.

4. There is a lot of useful information, results and discussion in the supplementary information. Sometimes, it becomes challenging to follow the text while browsing through Figures, Supplementary Figures, additional discussion and references. I would recommend to bring forward the supplementary discussion, including several of the figures.

5. In order to derive some quantitative emissions of diterpenes from needles, the experiments (both in lab and field) were performed under unrealistically high temperatures. While this is acceptable for validating the method, it should be further noted that these are stored compounds coming for the pools of the plant material and further highlight the reasons for this approach. Some investigations between the vapor pressure and measured emissions would be nice addition to the paper, if possible.

#### Specific comments

L34-40. The authors probably refer to the comparative reactivity method. If so, the reference of Kovacs and Brune is misplaced. Instead the study by Sinha et al (2008) should be cited.

L93. Please make a comment on how the commercial adsorbent tubes compare with the custom-made ones.

L154-155. Zero air generators and carbon cartridges have frequently shown that are not completely scrubbing the VOCs. Have you tested the efficiency of these methods? How do they compare between them?

L182 & L239. Please use equations in separate lines so they are clearly distinguishable from the rest of the text.

L375. O<sub>3</sub> removal. Have you tested other scrubbers? Why the heated stainless steel in the optimal solution of ozone removal and not e.g. KI scrubbers or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> infused



quartz filters? Please refrain from strong claims that are not supported by experiments.

L386. Please make a comment on the saturated peaks of Sup. Fig. 19-20.

L463. Similar to my major comments, it has not been sufficiently demonstrated that the ambient sampling DTs does not require heating lines. One potential experiment to help towards this direction would be to sample through a long inlet line the analyte mixture at different temperatures and present a plot of inlet temperature vs signal.

## References

Chan, A. W. H., Kreisberg, N. M., Hohaus, T., Campuzano-Jost, P., Zhao, Y., Day, D. A., Kaser, L., Karl, T., Hansel, A., Teng, A. P., Ruehl, C. R., Sueper, D. T., Jayne, J. T., Worsnop, D. R., Jimenez, J. L., Hering, S. V., and Goldstein, A. H.: Speciated measurements of semivolatile and intermediate volatility organic compounds (S/IVOCs) in a pine forest during BEACHON-RoMBAS 2011, *Atmos. Chem. Phys.*, 16, 1187–1205, <https://doi.org/10.5194/acp-16-1187-2016>, 2016.

Sinha, V., Williams, J., Crowley, J. N., and Lelieveld, J.: The Comparative Reactivity Method – a new tool to measure total OH Reactivity in ambient air, *Atmos. Chem. Phys.*, 8, 2213–2227, <https://doi.org/10.5194/acp-8-2213-2008>, 2008.

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