

Interactive comment on “A novel Fast Gas Chromatography based technique for higher time resolution measurements of speciated monoterpenes in air” by C. E. Jones et al.

Anonymous Referee #3

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The paper by Jones et al. presents useful developments, characterization and application of a fast GC technique which is demonstrated to enable measurements of speciated monoterpenes at a time resolution higher by at least a factor of two relative to conventional GC instruments. This is a crucial advantage for field measurement applications, because biogenic emissions of monoterpenes can be highly variable in response to rapid environmental triggers such as meteorological, or stress-related (e.g. herbivore or wounding stress). Another advantage is that the instrument is reported to be more compact and thus more portable, which makes it convenient for in-situ field measurements. The paper seems suitable for publication, subject to minor improvements.

Further to other referees' comments I would just have a few suggestions/questions that hopefully can be addressed by the authors:

1. The title seems a bit too long and may have a potential for enhancement. Although no doubt the study is original and novel, portable fast GC measurements have been reported previously (e.g. Hamilton and Lewis, 2003; Apel et al., 2003; Eckenrode, 2001) and a fast portable GC-MS is commercially available (Inficon, East Syracuse, NY, USA). I think these references can be mentioned and/or discussed in the introduction. However, it is probably true that no fast GC technique has been so extensively focused on monoterpenes. Is the word "novel" necessary for the title or could it be omitted? If it was omitted I do not think it would affect in any way the extreme usefulness of the authors' work for the BVOC community. Removing the words "technique " and "in air" could also help shortening the title.

2. P10926 L10. Can you provide the value for the fixed sampling time?

3. Calibration methods are critical for achieving the acceptable accuracy and it is nice that the authors compare the gas standard and direct injection methods and give them some critical evaluation. Another method that could be considered, perhaps in the future study, is a Dynamic Solution Injection (DSI) technique (e.g. Jardine et al., 2010). Was the gas standard that was used for calibrating GC also crosscalibrated with the PTR-MS?

4. Because the results are compared to PTR-MS measurements, I was expecting at least a brief Section on "PTRMS methods" following Sect. 2.2 "Chromatography methods". I think it could help the reader to interpret the comparisons better. In particular, it would be relevant to mention how the zero-air was measured, what was its source and how it was subtracted from the signal. For example, potential interferences to the PTR-MS signal (m/z 81+137) are mentioned in the discussion, but it is not clear if the signals presented were derived on either m/z 81, 137 or both and whether the count rates were normalized for water clusters? What were the drift-tube conditions and E/N

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ratio? What standard was used to derive the sensitivities?

5. A simple question: the study seems focused on quantification of monoterpenes in air, but the gas standard for the GC is a mixture of monoterpenes in nitrogen. Does it matter?

6. P.10935 Sect. 3.1: It is unclear how big and what phenological stage the plant was. Was it a seedling? A potted plant with soil? How was the VOC-free air generated to supply the chamber? What was the ratio of the plant's volume to the chamber volume? What was the humidity in the chamber?

7. P.10935 L.24 "the chamber was exposed to constant light conditions ($\sim 900 \mu\text{mol m}^{-2} \text{ s}^{-1}$) and a variable temperature ($23\text{--}31^\circ\text{C}$).". Would it be useful to show concentrations of the monoterpenes vs temperature for both the GC and PTR-MS data?

8. FastGC-PTRMS intercomparison. The PTR-MS signals in the figures are shown probably at their original frequencies (state the dwell times in the methods) which is good. Fig 5 corresponding to chamber results shows extremely good correspondence of the total monoterpenes from the two instruments. It might be interesting to show in addition the PTR-MS signal that is averaged to the equivalent GC sampling time (5min?). The two datasets averaged to the corresponding frequencies could also be shown on a scatter plot with uncertainties, and summary regression statistics, as was also suggested by the other referees. The quantitative comparison between GC and PTR-MS was the subject of many papers (e.g. de Gouw and Warneke, 2007) which might serve some guidance in this respect. Despite visually excellent agreement in Figure 5, it seems that the peak concentrations (at 150-200 min elapsed time) are slightly higher in GC than PTR-MS and the opposite is true around the 100 min. It might be further useful to show the temperature trace on that graph.

9. Regarding Fig. 6. see the comment above. In addition it might be useful to show the diurnal trends on a separate panel. In the upper panel PTR-MS saw higher concentrations which is typically the case encountered in field measurements. However, I

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wonder why the minima seem also higher. Could it be because of the inaccuracy in the zero air subtraction in PTR-MS, was there a systematic offset in the GC, or what could be the other reason?

10. Although the higher frequency is not suitable yet for direct eddy covariance flux measurements, it might be interesting to point out that the fast-GC technique could offer advantages for indirect flux measurements such as relaxed eddy accumulation which would benefit from more replicates. This potential could be briefly suggested in the discussion or conclusions.

References:

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