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Atmospheric Measurement Techniques Discussions



# *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.

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The authors thank the reviewer for their constructive comments, which we feel have helped us to make significant improvements in our manuscript. We address each of the specific comments individually below.

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.

- We agree that the title could be improved (also suggested by Reviewer 1). However we do not feel that it is necessary to remove “novel” from the title, since, even though there have been some similar applications of Fast-GC, this is the first study to develop a dedicated technique for quantification of terpenes in ambient air, and so it is appropriate to describe this as a novel study. Furthermore, we feel that removing “in air” would remove too much information about the focus of the manuscript. In order to make the title more concise, we have replaced “..based technique” with “method” and we propose the new title as: “A novel Fast Gas Chromatography method for higher time resolution measurements of speciated monoterpenes in air”. We also agree that we should include a more broad discussion of relevant previous applications of Fast-GC. We have moved the brief discussion previously included on other Fast-GC studies from the methods section to the introduction, and we have expanded this discussion, as follows: “Previous studies have utilised Fast-GC based techniques for a variety of applications, including quantitative analysis of methanol and C2-C4 carbonyls in ambient air (Apel et al., 2003), analysis of monoaromatic VOC in gasoline (Hamilton and Lewis, 2003), to derive limonene emission rates within a plant chamber (Yassaa et al., 2010), and for qualitative analyses of the BVOC composition of essential oils (e.g. White et al., 2009), as well as for various forensic applications (Eckenrode, 2001). However, to our knowledge, this is the first study to apply Fast-GC separation to the quantitative analysis of terpenes in ambient air.”

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

- The sampling time varies depending upon whether the sample is plant chamber air



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or ambient air, and sample times for each application are outlined at the end of section 2.1. We have modified this sentence to make this clearer to the reader: “Following a fixed sampling time (for details see below), the trap is back-flushed with dry helium gas at 30 ml/min for 1-2 minutes in order to remove moisture. . .”.

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 cross calibrated with the PTR-MS?

- We thank the reviewer for this suggestion. The DSI calibration technique of Jardine et al (2010) looks very promising, although comparisons with permeation tube methods do show some discrepancies for some species, including alpha-pinene. However a dynamic calibration system is something we may investigate in future. In this study, the PTR-MS was independently calibrated, and was not cross-calibrated with the gas standard utilised for the Fast-GC calibration.

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 ratio? What standard was used to derive the sensitivities?

- We agree that it would be appropriate to include details of the PTR-MS instrument operation, and we have added the following section (Sect. 2.4 PTR-MS instrument de-



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tails): “A Proton Transfer Reaction - Quadrupole Mass Spectrometer (PTR-MS, Ionicon Analytik, Austria) was operated alongside the Fast-GC to provide a direct comparison of monoterpene quantification during various applications (see Sect. 3). The total monoterpene mixing ratio was determined by PTR-MS during plant chamber studies and ambient air monitoring, based on the sum of the m/z 81 and m/z 137 signals (with a dwell time of 1 s). The PTR-MS was independently calibrated for monterpenes via an $\alpha$-pinene permeation tube system and cross-calibration with a conventional GC-FID instrument (Agilent 6890). Drift tube conditions were 500 V, 45 °C and 1.97 mbar, giving rise to an E/N ratio of 117 Td. Air was sampled at a rate of 50 ml/min, and the instrument was supplied with zero air (model 111 Zero Air Supply, Thermo Scientific) for the first 15 min of every hour, and analysed sample air for the subsequent 45 min. The zero signal measured directly before and after each 45 min measurement period was averaged and subtracted from the intermediate ambient data. Under these operating conditions, the $2\sigma$ limit of detection for total monoterpene mixing ratio determined by PTR-MS was $\sim$60 ppt, with an associated measurement uncertainty of $\sim$16 %, for 1 minute averaged data.”

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?

- We would not anticipate any significant difference between calibrations achieved using standards of monoterpenes diluted in clean, dry air vs clean, dry nitrogen. However, this is not something that we have investigated directly. Rhoderick (2008) compared propane standards diluted in air and nitrogen, and found that the difference was <1%. This author subsequently used nitrogen to prepare gaseous monoterpene standards, which demonstrated good stability (Rhoderick and Lin, 2013).

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?



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What was the humidity in the chamber?

- We have provided some further details regarding the plant chamber study in the manuscript, as follows: “During these experiments, a young white spruce plant (∼50 cm tall) potted in soil was enclosed in a ∼5 L teflon chamber and supplied with ∼3 L/min continuous flow of dry air (including ambient CO2 levels) from a zero air generator (Model 111, Thermo Scientific). The humidity of the chamber air was not controlled, and as such it gradually increased during the course of the experiment, as a result of transpiration.” We can only provide a very crude approximation of the plant volume / chamber volume ratio, but we estimate that this was of the order of ∼0.6.

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

- We understand the reason for this suggestion, however we believe that this level of analysis would go beyond the scope of this paper. Results from this plant chamber study will be presented elsewhere at a later date. However, for information, we have added the temperature data to Fig 5 (see response to point 8).

8. FastGC-PTRMS intercomparison. The PTR-MS signals in the figures are shown probably at their original frenquencies (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



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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.

- We have produced an updated version of Fig 5, to include PTR-MS data averaged over each 6 min Fast-GC sampling period, as well as to show the temperature of the chamber throughout the experiment. We have also created a new figure (Fig 7) to show the scatter plot, with regression slope and correlation coefficient, for Fast-GC vs PTR-MS derived monoterpene mixing ratios during this plant chamber study (and also for ambient measurement data). Although the peak concentrations shown in Fig 5 are slightly higher in Fast-GC compared to PTR-MS, the addition of the 6 min averaged PTR-MS data and error bars to indicate measurement uncertainty indicates that these values were in fact equivalent, within uncertainties. The values at ∼100 min are also equivalent within the measurement uncertainty.

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 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?

- The new figure (Fig 7) shows scatter plots of PTR-MS vs Fast-GC monoterpene mixing ratios for the ambient data shown in Fig 6, and indicates that there is indeed an offset between the Fast-GC and PTR-MS monoterpene measurements, with the GC values, on average, 38% lower than the PTR-MS values. However, this is similar to the findings of other studies, and we cannot be certain of the reason for this offset. We have included a reference to the paper by de Gouw and Warneke (2007) (see comment 8), which provides a useful context for interpreting/understanding our observations, in Sect. 3.2.2 as follows: “Several other studies have also reported offsets between PTR-MS and GC derived ambient monoterpene mixing ratios, with GC instruments typically reporting lower monoterpene concentrations compared to PTR-MS, by ∼20-50 % (de



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Gouw and Warnecke, 2007 and references therein)." In light of this comment, we have also acknowledged other potential causes of the offset between Fast-GC and PTR-MS derived monoterpene concentrations, as follows: "A similar offset was reported in the monoterpene fluxes derived by conventional GC-MS and PTR-MS instruments above a Californian ponderosa pine plantation (Lee et al., 2005), and indicates the presence of additional monoterpenes below the GC detection limit, and/or some interference from other compounds to the PTR-MS signal (m/z 81 and 137), although inaccuracies in the zero air subtraction for the PTR-MS signal, or systematic discrepancies resulting from the use of different calibration techniques should also be considered." While plots to show diurnal trends in this data would undoubtedly provide an interesting insight into the discrepancy between PTR and GC monoterpene measurements, we feel that this would go beyond the scope of this paper. The focus of this manuscript is to demonstrate the capability of the Fast-GC methods for quantification of monoterpenes in air, and providing comparisons with PTR-MS data is a useful tool for this purpose. The manuscript is not intended to provide an in depth comparison of PTR-MS vs GC observations (and instrument comparison studies for this purpose are published elsewhere).

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.

- We have mentioned suitability for REA measurements in the summary section, as follows: "In future, the Fast-GC methods presented in this study could potentially be utilised for indirect monoterpene flux measurement techniques, such as relaxed eddy accumulation (REA). The shorter measurement cycles offered by Fast-GC would be particularly advantageous in this application, where measurement frequency is often limited by sample analysis time, and there may be concerns related to sample degra-



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dation in the interval between sampling and analysis."

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