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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 are grateful to the reviewer for their comments, which have helped us to significantly improve our manuscript. We address each specific comment individually below.

1) p. 10923, l. 2: Please, define the abbreviation OBVOC when mentioning it for the first time in the abstract.

- We have modified the abstract so that the acronym "OBVOC" is now defined.

2) p. 10924, l. 10: Here is a typo in "monoterpenes".

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- We have corrected this mistake.

3) p. 10924, l. 9-20: In this paragraph characteristics of biogenic emissions are described. However, I found that no references were given to support the various statements.

- We have included references to the paper by Kesselmeier and Staudt (1999), and refer the reader to the references associated with Table 1, in order to address this.

4) p. 10928, l. 0-20: This part reads like an introductory part. The motivation is given for studying biogenic emissions in a plant chamber. Also typical constituents and concentration levels are discussed. I would like to propose to either include this part into the introduction or shorten it and highlight the key-points, such as characteristics in concentration, mixture and advantages of the Fast-GC method. Similarly, this could be done for p. 10930, l. 12-24. Possibly, a table could help to shorten but still provides all the information needed for the different methods.

- Section 2.2 has now been rearranged in line with this suggestion, and the suggestions from Anonymous Referee #1. As such, the first paragraph (10928 L3-14) now constitutes the introductory paragraph of Section 2.2.1 “Chromatography for plant chamber air analysis”, while the second paragraph (L15-20) is now used to introduce Section 2.2.2 “Chromatography for ambient air analysis”. This includes the key points for each type of measurement (ambient / plant chamber) in the relevant section, and breaks up the relatively long background information section presented in the original manuscript. We do not include motivation for plant or ambient air measurements in these sections, but we feel it is important to outline the key characteristics of both types of measurement that are relevant to the chromatography techniques presented. Regarding the background details given on Page 10930 - we agree that it would be more appropriate to include this information in the Introduction section, so we have moved the sentence “Recent studies suggest that BVOC potentially contribute a significant fraction of the boundary layer ozone formation within urban centres (particularly during summertime

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pollution episodes, e.g.; Lee et al., 2006; Curci et al., 2009), providing motivation for in situ observations of these trace gases in polluted atmospheres with biogenic influence (such as a city surrounded by forest land), as well as within the pristine forest boundary layer." to the introduction.

5) p. 10930, l. 2: The method GC_AMBIENT I was described and a chromatogram presented in Fig. 3. However, no data was shown in the application section. I understood that this method has a time resolution of 11 minutes, which is the highest of all presented methods (GC_CHAMBER – 14 min (p.10929, l.10) or 16.5 min (p.10929, l.21) or 17 min (p.10935, l.24), GC_AMBIENT II – 19 min (p.10930, l.28) or 22 min (p.10937, l. 28)). It is a pity that no data were presented for this method. Has this method been applied for either the plant chamber or atmospheric measurements? In Figure 3 a chromatogram was presented from measurements in unpolluted ambient air. Are there more data available? I think that in order to emphasize the improvements of the Fast-GC you would need to provide an example of data and the comparison to conventional instruments for this method as well. If there are no publishable data available, you could still describe the method GC_AMBIENT I as a suggestion. In this case, you would need to modify abstract and conclusions, and explicitly state that only GC_CHAMBER and GC_AMBIENT II have been applied and compared to the PTRMS.

- Unfortunately, we have not yet had an opportunity to deploy the Fast-GC instrument for an extended period of ambient air monitoring in a pristine forest environment. As such, the suitability of the GC_AMBIENT I method was tested by offline analysis of discrete air samples. 3L silcosteel canisters were filled with ambient air within a pine forest in Ibaraki prefecture, Japan, and Fast-GC analysis of these samples was subsequently performed in our laboratory using the AMBIENT I method. Since this method was tested and optimised using discrete offline air samples, we do not have a period of continuous ambient air data recorded using this method alongside simultaneous PTR-MS measurements to present in Section 3. However, we do not think that such a period continuous of monitoring should be regarded as a prerequisite to demon-

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strating the suitability of the AMBIENT I method for quantification of monoterpenes in clean air. Firstly, the instrument itself has shown good agreement with independent PTR-MS measurements under two different sampling scenarios (and using 2 different chromatography methods), which we feel validates both the sampling procedure and calibration of the Fast-GC instrument. So, the only potential cause for concern regarding the AMBIENT I method specifically would be if the chromatography method itself proved unsuitable for the application. The chromatographic trace presented in Figure 3c clearly demonstrates the good separation of multiple monoterpene structural isomers that may be achieved using the AMBIENT I method to analyse a discrete clean air sample. Furthermore, the initial temperature ramps and carrier gas velocities employed in the AMBIENT I and AMBIENT II methods are relatively similar, and the largest differences in the chromatography parameters occur after the monoterpene elution period. In light of this, although we do not have data from a period of continuous monitoring using the AMBIENT I chromatography method, we are confident that we have enough evidence to demonstrate the suitability of this method for the specified application. We do agree however that it is important to clearly state how the sample chromatograms for each method presented in Fig3 and Fig4 were obtained, so we have added the following statement to Section 2.2 (now Section 2.2.2 “Chromatography for ambient air samples”) to address this: “Figure 3 illustrates the chromatography parameters utilised in the GC_AMBIENT I method (Fig 3a), and shows typical chromatograms generated using this method for analysis of a monoterpene gas standard (Fig 3b), and to quantify monoterpenes in ambient air (Fig 3c). Figure 4 outlines the GC_AMBIENT II method parameters (Fig 4a), and shows chromatographic traces using this method for analysis of a terpene gas standard (Fig 4b), and to analyse ambient air within a suburban forest (Fig 4c). It should be noted that while the GC_AMBIENT II method has already been utilised for continuous in situ terpene monitoring (Fig 4c - see section 3.2.2 for details), to date the GC_AMBIENT I method has only been used to provide offline analysis of monoterpenes in discrete air samples. As such, the chromatogram presented in Fig 3c was not produced from an in situ measurement, but from analysis of a whole air

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sample that was collected within a pine forest in Ibaraki prefecture, Japan. For these measurements, air was sampled into 3 L silcosteel canisters and subsequently analysed in our laboratory using the GC_AMBIENT I method." Please also refer to our response to Anonymous Referee #1.

6) p. 10932, l. 20: Why did you not use the VOC gas standard mix (1 ppmV) and diluted it "online" to the needed concentrations? A small flow of the standard gas (e.g.5 sccm) diluted into a high flow (e.g. 5000 sccm) of e.g. synthetic air or nitrogen can provide concentration levels that are comparable to ambient (e.g. 1 ppbV).

- We did consider using this approach, and it is a calibration technique that we may explore in future. We have not investigated this method so far since the in-house standard showed good stability, and had the advantage of containing other monoterpenes as well as α-pinene and β-pinene, which was useful for peak identification purposes. The single 3 L gas canister is also more portable for performing routine calibrations in the field. Furthermore, the dilution required for this approach is considerable, and would likely introduce some uncertainties associated with accurately controlling the standard gas flow rate as low as 5 sccm.

7) p. 10934, l. 14-16: Did the uncertainty vary with the different methods (GC_CHAMBER, GC_AMBIENT I, GC_AMBIENT II)? What are the detection limits?

- For a few species the uncertainties did vary slightly between the various chromatography methods reported, as a result of slightly better peak separation in some methods compared with others, however the differences in the overall uncertainties between methods was very small ($\pm$ 1-2%), and the uncertainties for all methods were within the ranges reported here. The detection limits are provided in Table 1 - we have included a note to direct the reader to the Table as follows: "The 2σ limits of detection (LOD) for each terpene quantified via the Fast-GC methods outlined here are given in Table 1."

8) p. 10935, l. 5: More in-depth discussions of each study will be presented elsewhere.

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Is there already a reference that you could give?

- These manuscripts are currently in preparation, so unfortunately we are not able to provide any formal references at this stage.

9) p. 10935, l. 10: Was the zero air, which was introduced into the chamber, humid?

- The zero air introduced to the chamber was supplied via a zero air generator (Thermo Scientific) and was dry. We have modified this sentence 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).

10) p. 10935, l.27: Good agreement between the sum of monoterpenes has been observed between Fast-GC and PTR-MS measurements. This is presented in Figure 5. Could you please quantify how good was this agreement (e.g. via a correlation plot, Pearson coefficient)? Could you comment on the occasions for which the two instruments differ from each other (_ 50 min, _ 350 min)? Is the difference significant or within the uncertainties of the measurements? Were all the measurements above the detection limit?

- We have added an additional figure to the manuscript (Fig. 7), which contains correlation plots of Fast-GC vs PTR-MS derived monoterpene mixing ratios in both ambient air and plant emissions, and the corresponding R2 values are reported to indicate the strength of correlation. We have included the following paragraph in Section 3.1 to discuss the correlation based on Figure 7: "The correlation between the Fast-GC and PTR-MS derived total monoterpene mixing ratios measured during this experiment is presented in Figure 7. It should be noted that the final Fast-GC measurement was classed as an outlier (since all but one of the individual monoterpenes were below the instrument detection limit) and was thus excluded from this plot. Figure 7 demonstrates the close agreement between the two instruments for quantification of monoterpenes in single plant emission studies (R2 coefficient = 0.82), and indicates that the total

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monoterpene mixing ratio reported by Fast-GC was on average ∼4% higher than the corresponding PTR-MS value. As such, the total monoterpene mixing ratios reported by the two instruments may be considered equivalent, within the experimental uncertainties." The differences between PTR-MS and Fast-GC derived monoterpene values shown in Fig. 5 during the 2 periods highlighted by the reviewer are significant (outside of instrument detection limits). However, these periods correspond to the start and end of the experiment, where the chamber temperature was low and monoterpene concentrations were at a minimum. As a result, several of the individual monoterpenes quantified by Fast-GC were close to or below the detection limit. In light of this, we feel that these data do not provide a fair comparison between Fast-GC and PTR-MS total monoterpene concentrations. We have added the following sentence to the end of section 3.1 to highlight this: "It should be noted that measurements at the start and end of the experiment correspond to the lowest chamber temperatures (<25 °C) and therefore minimum monoterpene mixing ratios. As a result, some of the individual monoterpenes quantified by Fast-GC were close to (or below) the instrument detection limit at these times, and the agreement between Fast-GC and PTR-MS derived monoterpene mixing ratios was reduced in comparison with data from other periods." We have also produced an updated version of Figure 5 to include the PTR-MS signal averaged over the 4 min sampling period of the Fast-GC, as well as error bars to demonstrate the uncertainties associated with the averaged PTR-MS and Fast-GC derived total monoterpene concentrations.

11) p. 10936, l. 4-6: Here you point out that the Fast-GC is smaller, lighter and consumes less power than conventional systems. These are great advantages of your system and you should specify precisely how small and light it is (as well in comparison to the PTR-MS). Why don't you include a picture of your equipment?

- We have included information regarding size and weight of the GC used in this study in the "Chromatography methods" section (section 2.2) as follows: "Resistively heating the column also negates the need for a conventional GC oven, and as a result the 300

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Series GC is smaller and lighter than standard GC systems (instrument footprint = 320 mm x 370 mm; weight = 7.5 kg)." We also refer the reader back to this section when we reference the benefit of these specifications in section 3.2. We are not sure that there would be much value in including a photograph, since we reference the manufacturer, and photographs are readily accessible from their website.

12) p. 10936, l. 22: Please give a description of your inlet lines. How long was the inlet, was a filter used for particles, was the line heated and insolated? I think Figure 1 presents as well some details about the sampling flows and position of the ozone scrubber. Maybe, just refer to Fig 1 and give some more details about the sampling strategy.

- We have added the following details to section 3.2.2 (Ambient terpene measurements in a suburban forest - previously section 2.2) regarding the configuration of the inlet lines: "Air was drawn from an inlet on the roof of the two storey measurement station via an 8 m ($\frac{1}{2}$" id) PFA manifold at a rate of $\sim$5 L min-1, and sub-sampled from this manifold through a Na2S2O3 ozone filter and $\sim$1 m x 1/8" PFA line at 75 ml min-1 to the Fast-GC (see Fig 1)." The lines were not heated and insulated, but the relatively short sample lines and the high flow rate through the main manifold led to a residence time of <30 seconds. The Na2S2O3 ozone scrubber removed particles $\geq$1 μm, and the Unity thermal desorber contains a series of integrated porous PTFE filters in order to remove particulate material, so a separate particle filter was not deemed necessary during this study.

13) p. 10936, l. 25: How did you decide on the position of the ozone scrubber? Why was it placed directly before the instrument and not at the beginning of the sampling line?

- The main sample manifold supplied several other instruments in addition to the Fast-GC (including PTR-MS and LIF), some of which required ozone to be present in the air supply, so it was not possible to site the ozone scrubber at the inlet. A further con-

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sideration was due to the higher flow rate through the main manifold (∼5 L min-1 vs 75 ml min-1 through the sub-sample line), and the limited capacity of the ozone filters, it would have been necessary to change the filters (thus briefly interrupting measurements) much more frequently (every few hours) if it had been sited at the main inlet. However, as air was drawn through this line at a relatively high flow rate (∼ 5L min-1), this resulted in a residence time of <30 s within the main manifold, and as such it was not considered necessary to position the ozone scrubber at the main inlet. We have added the following test to the manuscript, to clarify this: "The Na2S2O3 filter was positioned within the sub-sample line rather than at the inlet, since the main manifold also supplied air to several other instruments, some of which required ozone to be present in the air supply. However, the relatively high flow rate through the main manifold resulted in a residence time of <30 s, and as such significant ozone destruction was not anticipated to occur within this sample line. Furthermore, given the high flow rate through the main manifold and the limited capacity of the Na2S2O3 filters, positioning the filter at the inlet would have necessitated a filter change every few hours."

14) p. 10937, l. 20: Were all terpenes lost in the ozone scrubber with the same rate?

- No, the percentage losses of all monoterpenes were similar (3±2%), but there was some small variation between the individual isomers. We found the largest loss rate (4.9%) for Δ-3-carene, while loss of limonene was only 0.7%. We have added a sentence to this effect in Sect. 3.2.1 ("Ozone removal"): "Of the monoterpenes, the largest percentage loss was observed for Δ-3-carene (4.9%), while the limonene mixing ratio demonstrated the smallest decrease (0.7%) when sampling via the filter."

15) p. 10938, l. 10: What was your instruments detection limit?

- Limits of detection are provided for each method in Table 1, but for convenience we have added the linalool LoD in brackets here: "In contrast, the maximum linalool mixing ratio at FM Tama was observed during early afternoon, while night time concentrations were often close to the instrument detection limit (4 ppt),. . .".

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16) p. 10938, l.12-13: Similar to comment 10). Please give numbers of how good is the agreement between PTR-MS and Fast-GC measurements. In order to compare and judge on the two instruments performances a list of uncertainties, detection limits, time resolution, slopes of correlation plots and correlation coefficients would be great.

- As we mention in our response to comment 10 - we have added an additional figure to the manuscript (Fig. 7), which contains correlation plots for Fast-GC vs PTR-MS derived monoterpene mixing ratios in both ambient air and during a plant emission study, and contains corresponding slopes and R2 values to indicate the strength of correlation. We have also modified the manuscript to include discussion of the correlation plots for ambient air measurements in section 3.2.2 ("Ambient terpene measurements in a suburban forest") as follows: "Figure 7 shows correlation plots for PTR-MS vs Fast-GC derived monoterpene mixing ratios during the AQUAS TAMA campaign (using PTR-MS values averaged over each 10 min Fast-GC sampling period). Data recorded during the typhoon event (classified according to in situ atmospheric pressure measurements at the FM Tama field station) were analysed separately; for these purposes, measurements corresponding to atmospheric pressures of 965-985 hPa were classed as "typhoon" observations. Excluding the typhoon data, Figure 7 demonstrates reasonable agreement between the PTR-MS and Fast-GC monoterpene measurements (R2 coefficient = 0.73) while the slope indicates that the Fast-GC derived monoterpene mixing ratio was, on average, 38% lower than the corresponding PTR-MS value. This is a significant offset, outside of instrumental uncertainties (10% for the total monoterpene mixing ratio quantified by Fast-GC and 16% for PTR-MS)". The Fast-GC detection limits are detailed in Table 1, while the PTR-MS detection limit is given in section 2.4 "PTR-MS Instrument details".

17) p. 10938, l. 25: Your summary seems more like a brief discussion.

- We agree that section 4 contains some further discussion, as well as a summary, so we have re-named this section "Discussion and summary".

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18) Table 2: In this table and in the main text, you present the total analysis time of each method. Please, could you double-check these times and try to be consistent. It would be good to present the methods that were used for determining the chromatograms as presented in Fig. 2-4, and Fig. 5-6. Were the same methods used?

- The methods outlined in Table 2 are the same methods used to generate the chromatographic traces presented in Figures 2, 3, and 4. However, we found a mistake in the flow velocity plotted in Fig 2, which may have caused some confusion. We also suspect there may be some confusion as a result of the times reported for each method. In some cases we refer to the "cycle time" (the time between the start of 2 consecutive samples - which includes the time taken for the GC to cool to the start temperature following first sample analysis) while in other places we refer to the "analysis time" (the time for taken for the chromatographic separation only). To address this, we have modified Table 2 so that it gives both the analysis time and cycle time for each GC method. We have also noted that on occasions we used approximate times (e.g "$\sim$13 min") rather than quoting exact times, which may also prove confusing. As a result, we now use the exact analysis and cycle times throughout the manuscript.

19) Figure 2-4 are very good graphs. Just, in order to help the reader, it might be useful to shade or draw lines throughout all graphs (a-c) when parameters in the program (a) were changed.

- We have modified figures 2-4 as suggested, to highlight changes in the points where changes in chromatography conditions take place.

20) Figure 5: Could you please include error bars?

- We have updated Figure 5 and included error bars for values of the total monoterpene mixing ratio (for both the total monoterpenes determined by Fast-GC and the 6 minute averaged PTR-MS derived value).

21) Figure 5: In Figure 6, GC method and cycle time are given in the caption. Could

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you please include these here as well?

- We have added the following information to the Fig 5 caption: “The GC_CHAMBER chromatography method was used to determine the monoterpene composition, at a sample frequency of 1 measurement every ∼17 minutes.”

22) Figure 6: Were the concentrations of monoterpenes measured at the detection limits of the instruments? A comparison between PTR-MS and Fast-GC detection limits would be interesting.

- The total monoterpene mixing ratio was above the PTR-MS limit of detection for the entire measurement period. The dominant monoterpenes, α-pinene and β-pinene, were above the Fast-GC detection limit for the majority of the observation period, although there were a few occasions were ambient concentrations were very close to or below the LOD. Other monoterpene isomers were close to the Fast-GC LOD for substantial periods of the campaign. The Fast-GC detection limits are given in Table 1 (4-5 ppt for individual isomers), and the PTR-MS detection limit (∼60 ppt for total monoterpene signal) is now reported in a new section - Section 2.4 “PTR-MS instrument details”.

23) Figure 6: Please add labels to the x-axis.

- We have updated Fig 6 to include an x-axis label.

24) Figure 6: Please include instrumental uncertainties.

- Due to the large number of data points for multiple species / instruments presented in Fig 6, we feel that there is some loss of clarity when error bars are added to this data. As an alternative to displaying the uncertainties visually, we quote the values in the figure caption, as follows: “The corresponding instrumental uncertainties were 8-12% for monoterpenes, and 20% for linalool."

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