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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 have helped us to make significant improvements to our manuscript. We have addressed each of the specific comments individually below.

1. Are there concerns with the co-elution problem? Depending on the sample, this limitation might be substantial. If you used fast gas chromatography, but with a mass spectrometer detector, could you isolate the ions and thus still separate the co-eluted peaks? When some researchers are trying so hard to create more separation (e.g. 2D chromatography), it's surprising to see methods that are OK with less separation. There could be more instances, too, depending on the mixtures. The analyzed standards and field samples did not include every possible combination of BVOCs.

- We understand the reviewers concern, however we feel that the issue of whether co-elution is a problem very much depends upon the application. The Fast-GC methods outlined in this paper have been optimised for monoterpene quantification, and as such may be utilised to separate and quantify the 6 most common monoterpenes, as well as numerous less common monoterpenes (12 monoterpene isomers in total). In light of this, we believe that these Fast-GC methods are suitable for applications where the main objective is quantification of individual monoterpene structural isomers (and these methods are particularly advantageous in instances where high time resolution measurements are desirable). For OBVOCs, however, we acknowledge that the chromatographic separation is not as good, and thus in some scenarios co-elution of OBVOC may become more of a problem. In this case, a technique such as 2D GC would indeed be more appropriate, however, the 2D GC technique also has several drawbacks (see below). As such, the most suitable technique should be considered for each application. Since we agree that this is a very important consideration, we have now included the following discussion in the discussion and summary (section 4): "Due to the vast number of naturally occurring BVOC, co-elution of two or more species must be considered as a potential limitation of Fast-GC-FID terpene analysis. Other techniques with superior separation capability, such as two dimensional gas chromatography (2D GC), offer improved chromatographic resolution but have other limitations, such as relatively poor time resolution, lack of portability (making 2D GC unsuitable for short-term field deployments), and requiring a large amount of data processing (hence 2D GC is not an appropriate technique for long-term in situ monitoring). In this regard, the most suitable technique should be selected for each specific application. For applications where the main objective is high time resolution quantification of speciated monoterpenes, Fast-GC may arguably be the most suitable technique, whereas for quantification of very complex mixtures containing multiple OBVOCs (and where high time resolution is not required), a 2 dimensional GC technique may be more appropriate". Mass spectrometric detection of course has an advantage over the FID in that it can provide identification of GC analytes. This would be particularly useful in this type of study, and could be investigated in future. However, the relatively high carrier gas velocities (up to 90 cm/s) used in the Fast-GC methods presented here would be prohibitive to using MS detection. One feasible way to couple the Fast-GC with MS detection would be to split the outflow from the GC column between 2 detectors (e.g. one FID and one MS), in order to reduce the flow rate to the MS, however this would reduce the sensitivity of the instrument and result in a higher detection limit.

2. Measurements from this new technique are said to agree with PTR-MS data. Please quantify this relationship. The overlay of traces is a good visual clue, but correlation plots would be more affective to show the agreement. A correlation would show that the quality of the agreement may differ, depending on the sample source (and thus environmental factors, etc.). In addition, researchers allude to the impact from the typhoon on this instrument agreement, but more speculation should be made – humidity?

- We have added a new figure (Fig.7) to the manuscript, which shows correlation plots of monoterpene mixing ratios determined by PTR vs Fast GC for both the ambient measurements and plant chamber studies. In addition, we have separated the ambient data according to the "typhoon" and "non-typhoon" periods. This clearly demonstrates the reduced agreement between the two instruments during the typhoon event. We have given further consideration to potential explanations for the poorer agreement during the typhoon period, however any explanation we could offer would be purely speculative. Since the ambient measurements were conducted in Tokyo in late summer, the humidity was relatively high for the whole period (mean RH $\pm$ 1σ was 71 ± 11 %), and there was no notable change in average humidity during the typhoon period. Furthermore, Tani et al (2004) found that humidity had only a relatively minor influence on PTR-MS measurements of monoterpenes, and we have no reason to suspect a significant impact on the GC-FID. Therefore, we do not feel humidity changes can explain

the instrumental differences during the typhoon period.

3. The structure of the "chromatography methods" section is confusing. It jumps back and forth from the chamber method to the ambient; maybe isolate the two methods.

- Based on this comment, we have rearranged the chromatography methods section (2.2) and separated discussion of the plant chamber method (now section 2.2.1) and ambient air methods (section 2.2.2) into separate sub-sections.

4. Introduction: There are other studies that indirectly show unmeasured primary or secondary BVOC, for example Holzinger et al. 2005 in Atmos Chem. Phys.

- We have included the following sentence referencing this study: "Holzinger et al. (2005) observed large quantities of BVOC oxidation products within a Ponderosa pine forest, which implied significant unmeasured primary BVOC emissions within this region." (Page 10924 Line 4 of the AMTD manuscript).

5. Methods: Page 10926: BVOC standards are mentioned here, but not explained. How do you prepare the standards? If it is the same as what is explained in the calibration section, then this should be noted.

- This was the same standard explained in the calibration section. We have added a note to this effect for clarification. Details regarding preparation are also described in section 2.3.

6. Page 10928 line 1-2: it is stated that this is the first application of fast GC of terpenes in air, but the previous line says that fast GC was used with plant emissions. Plant emissions are in air. Is this, instead, the first use of fast GC in ambient air?

- Yes. The discussion of previous applications of Fast-GC has now been expanded and moved to the introduction section, following suggestions from the other reviewers. This sentence has been amended and now reads as follows "However, to our knowledge, this is the first study to apply Fast-GC separation to the quantitative analysis of terpenes in ambient air."

7. Plant chambers give "cleaner" BVOC signals because there is no/low oxidation and there is one species being studied, but using an enclosure will also concentrate BVOCs due to the small mixing space. This is the most striking difference from an enclosurevs. ambient air around the plants.

- We attempted to get this point across in the original manuscript, but in case it wasn't clear, we have amended the 2nd paragraph on page 10928 as follows: "Furthermore, dilution of emitted BVOC within the enclosure is limited, and as such, single plant chamber emissions are relatively high concentration (∼ppb), low component BVOC mixtures, and thus are potentially well suited to fast gas chromatographic separation." Note that in the revised manuscript, this section is presented in section ".2.1 "Chromatography for plant chamber air analysis".

8. Page 10928, line 18: ": : : all at significant concentrations" – ambient VOCs are not very high, especially compared to that in an enclosure, because of the large space (the atmosphere) for diffusion and mixing.

- We have removed "all at significant concentrations" from this sentence.

9. Typically, when reporting GC column specs, film thickness is included.

- We have added details of the GC column film thickness alongside the other column specifications described in the "chromatography methods section".

10. Page 10929, lines 26-28: "peak identification and/or BVOC quantification was supported by independent offline GC-MS analysis" – explain. Is it the same sample? The same oven program?

- Concurrent with the Fast-GC analysis of plant chamber and ambient air, discrete air samples were collected into silcosteel canisters for offline analysis by GC-MS and/or a conventional GC-FID instrument. Thus it was the same sample, however the oven programme was different (offline instruments used conventional GC programmes). We have clarified this in the manuscript as follows: "It should be noted that during the initial

method development and testing period, BVOC-rich air (from single plant emissions and ambient air) was simultaneously analysed by Fast-GC and sampled into silcosteel canisters for independent offline analysis by conventional GC-FID and/or GC-MS, in order to support BVOC peak identification and/or quantification."

11. Page 10930, line 19: "typical fast chromatography" - what is "typical"? I thought this was new for ambient air?

- "Typical fast chromatography" refers to the very fast chromatography conditions typically used in other Fast-GC applications (i.e. not for analysis of atmospheric VOC). However we agree that this statement is somewhat ambiguous, so we have modified the sentence as follows: "Since GC analysis of BVOC in polluted air requires resolution of a vast number of closely eluting chromatographic peaks (numerous anthropogenic VOC, as well as multiple terpene isomers), we have found that very fast chromatography is not a viable technique for quantification of terpenes in air influenced by both biogenic and anthropogenic emissions."

12. Where gas standards made by injecting pure volumes into nitrogen? If they are diluted, then what is the solvent? There are a lot of statements about effective gas standards and significant degradation, etc. Are there citations of this work? Others have shown the stability of BVOC gas standards. Can you not dissolve the solid camphene to create a standard? Why is b-pinene used (vs. an average response of all monoterpenes, for example) for compounds without liquid standard?

- The terpene gas mixtures were prepared by injecting liquid standards of terpenes in isopropyl alcohol solvent into the nitrogen gas stream. We have modified this sentence so that it now states the solvent used, as follows "As such, independent terpene gas standards are prepared in-house, by injecting 1 μl volumes of a liquid standard (∼5 mmol dm-3 terpenes in isopropyl alcohol) into a nitrogen gas stream delivered to a 3 L silcosteel canister, which is subsequently pressurised to ∼35 psi." In our initial statement regarding concerns over monoterpene stability when stored in pressurised canisters, we reference Apel et al., 1999, since they reported relatively poor stability of α-pinene in high pressure cylinders and stainless steel canisters, in comparison with other VOC. We have now included an additional reference (Rhoderick and Lin, 2013). Whilst we feel that caution is still necessary in using pressurised monoterpene gas standards for absolute calibration, we agree that the recent advancements in this area should be mentioned, and we have modified the first paragraph of section 2.3 (calibration) as follows: “One of the major analytical challenges associated with accurate quantification of atmospheric terpenes is the implementation of a robust calibration technique. Compared with other non-methane hydrocarbons (NMHC), monoterpenes often demonstrate inferior stability when stored for prolonged periods in pressurised gas canisters (Apel et al., 1999; Rhoderick and Lin, 2013). Due at least in part to this apparent instability, certified gas standards containing multiple terpenes are not readily available, and hence calibration of these gases is generally less straightforward compared to that of other NMHC. A recent study by Rhoderick and Lin (2013) demonstrates that 20 l aluminium canisters with proprietary internal coatings are capable of containing gaseous monoterpenes in nitrogen without significant degradation for periods of >250 days, however further investigations are necessary to ensure consistency between canisters, and to test whether this level of stability may be achieved for gaseous mixtures containing both α-pinene and β-pinene”. We attempted to dissolve solid camphene in isopropyl alcohol solvent in order to directly determine the camphene FID response, however the reproducibility between individual samples of camphene solutions was poor in comparison with that of the other (liquid) monoterpenes. Using the average monoterpene response factor for camphene calibrations was not considered an appropriate approach, since some monoterpenes (e.g. myrcene) had response factors that were considerably lower than the theoretical values, which skewed the mean response factor. Instead, the β-pinene response factor was assumed for camphene, since these two isomers are structurally similar, and, although the solutions of solid camphene gave rise to FID responses with high uncertainty, the mean value was close to the β-pinene response.

13. There is a long discussion in the ambient air section about ozone scrubbing and then a paragraph on the BVOC losses on the sodium thiosulfate filter – separate these “method” parameters from the data obtained in the ambient application (which is the title of the section).

- We have rearranged section 3.2 (“Ambient air monitoring”) in line with this suggestion. This section is now separated into two sub-sections - 3.2.1 “ozone removal” and 3.2.2 “Ambient terpene measurements in a suburban forest”.

14. Since the ambient samples are the only ones with the addition of a filter, is there any chance that other studies sampled particulate matter in addition to gas-phase BVOCs.

- Only ambient air was sampled via the chemical filter to remove ozone, however all air analysed (both ambient air and from plant chamber) was sampled via a series of porous PTFE filters integrated within the Markes Unity thermal desorber, in order to remove any particulate material.

15. Page 10937, line 2: “tentatively identify” – can you confirm?

- Unfortunately at this stage we cannot confirm that the peak we observe is pinonaldehyde. This is something that we are continuing to investigate, however since at this stage it is speculation, we feel that the following re-wording to describe this observation would be more appropriate: “Furthermore, a new unidentified chromatographic peak was observed when sampling α-pinene in the presence of ozone. This unidentified peak eluted in the retention window corresponding to C9-C10 oxygenated terpenes, which suggests that it may be an α-pinene oxidation product.”

16. Page 10938, line 11: how can linalool be light and/or temperature dependent? Studies have shown that linalool is likely temperature and light dependent (like isoprene), but not temperature dependent only. Sole temperature dependence has a different diurnal profile, with significant ambient mixing ratios at night (like what was observed for apinene).

- We have modified this sentence as follows, in order to be clear that we are not implying sole temperature dependence of the linalool emission rate “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, giving rise to a diurnal profile characteristic of primary BVOC with a light and temperature dependent emission rate”.

17. Fig 3: Define “unpolluted” ambient air. Was this an experiment? If so, where are the experimental details? There is no application of fast GC using the Ambient I method. Are the traces in Figs 2 and 4 not from the application of each in the field?

- For the purposes of this study, “unpolluted” ambient air refers to air where the majority of anthropogenic VOC are below the instrument detection limit, and thus will not interfere with BVOC chromatographic analysis. We have added a note to this effect in the Fig 3 caption. The traces in Figs 2(c) and 4(c) are from the plant chamber air and ambient air applications detailed in Section 3. The trace shown in Fig 3(c) is also from a real air sample, however we have not yet had opportunity to deploy this instrument for ambient air monitoring in a pristine forest environment. So, in order to test the suitability of the AMBIENT_I method, we performed offline analysis of discrete canister samples containing clean air from within a pine forest in Ibaraki prefecture, Japan. Since this method was tested, optimised and validated using discrete offline samples, we do not have a period of continuous ambient air data recorded using this method to present in section 3. To make this clearer, we have stated the origin of the samples analysed to produce the chromatographic traces 2(c), 3(c), and 4(c) within the text (sections 2.2.1 and 2.2.2), as follows: “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 via an in situ measurement, but from analysis of a whole air 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.” We have also added a note to provide information regarding the source of Fig 2c, 3c and 4c in the relevant figure captions. Please also see our answer to a similar question from Referee #2.

18. The title is awkward. “Chromatography-based” technique would be better, but it seems as if the authors want to name the instrument “Fast Gas Chromatography”. Maybe reconsider the title.

- In light of this comment and a similar suggestion from Anonymous Referee #3, we have revised the title slightly, in an attempt to make it more concise. However, we do feel that is important to clearly state that it is a Fast-GC technique in the title. We propose replacing “..based technique” with “method” as follows: “A novel Fast Gas Chromatography method for higher time resolution measurements of speciated monoterpenes in air”

19. The abstract mentions “OBVOC” without defining this acronym

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

20. Page 10928, line 8: “typically relatively” very awkward phrasing

- We have deleted “typically” from this sentence.

21. Page 10933, line 12: “to each species” or “of each species”

- We have changed the wording to “for each species”.

22. Page 10934, line 4: cut “a study by”, thus leave “Faiola et al. (2012) demonstrate: : :

- We have modified this sentence to begin “Faiola et al. (2012) demonstrate..”

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 10921, 2013.