

The authors would like to thank the referees for their thoughtful comments and reviews. Responses to the referee comments are provided below.

Responses to Referee 1:

1. Page 3651, line 7 "...loss can occur because of mechanical/herbivore wounding." needs citations.

Response: The Heiden et al., 2003 paper describes VBOC emissions due to mechanical/herbivore wounding and stress. This reference has now been cited on page 3651.

2. It would be good to be consistent with the format of the split ratios which are described several times in the text, sometimes as 10:1 and other times as 1 in 10, e.g., page 3655, line 9 and as "1 in 10 and 1 in 5" and Table 3 as "20:1 and 15:1". See also page 3661, lines 5 and 6.

Response: Agreed. All of the split ratios in the text now appear as "x:1", consistent with Table 3.

3. The authors use an internal standard, presumably to correct for extraction efficiency although its use is not defined, please clarify how the internal standard was used for at least the 21 components that there were standards for, i.e., if it was used to correct for extraction efficiency during thermal desorption how was it applied, was an average value used for all components or were specific compounds corrected to a particular internal standard component. What's the reason for the choice of the four internal standard components? They are chemically very different to the analytes of interest, would deuterated analogues not be more appropriate?

Response: The following text has been added to the paper on page 3658: "The IS compounds were used: 1) to monitor the overall effectiveness of the thermal transfer from each sampling cartridge to the primary GC column; 2) as clearly identifiable (e.g., non biogenic) retention time markers; and 3) a source of constant reference signals during the determination of the MDL values reported here as based on analyses carried out at varying on-cartridge levels of isoprene and the other target analytes. Isotopically-labelled IS compounds were not necessary in this study."

Isotopically-labelled IS compounds could also have been used, but were not required here since the goals of this study were limited to initial estimation of method detection limits and measurement of relative retention times.

4. In section 2.2, the various approaches used to remove ozone from the sample stream prior to collection are discussed but it is not clear what method was used when the ATD cartridges were collected as described on page 3658, line 26.

Response: KI impregnated filters were used. This information has now been added on page 3658.

5. On page 3661, lines 1 and 3, the authors refer to "zero split", I am assuming this is synonymous with splitless, if it is then to be consistent in the manuscript these occurrences should be replaced with splitless and if not please clarify what this is?

Response: Zero split is synonymous with splitless, however the former is used more often with ATD while the latter with GC. On page 3661 line 1, we now say: "zero split (splitless)" to clarify.

6. Table 4 presents the MDLs for 21 target compounds - how were these determined? From calibration curves? It is not obvious to me.

Response: The following text has been added to the paper on page 3661: "No blank problems were experienced for any of the target compounds. As such, all MDL values were assessed by varying the on-cartridge mass amounts of the target analytes, and determining which values yielded an instrument signal to noise ratio of 10:1. MDL values were then calculated as equaling the mass amounts at 10:1 signal-to-noise divided by the sample volume of 5 l."

7. Table S1 - I think it would be useful to show the forward and reverse matching statistics along with the tentatively identified compounds.

Response: Spectral match statistics are highly dependent on signal strength and background signal, and so are imprecise measures of compound identification. Nevertheless, the following text has been added to the paper on page 3665: "Of the 417 tentative identifications in Table S1, six resulted from search similarity values in the range 680-699, while 56 resulted from values in the range 700-799, and 355 resulted from values in the range 800-990."

8. Page 3662, lines 13 - 14 - the authors say that they used the "initial" set of chromatographic conditions. Why use the initial chromatographic conditions if there had been improvements? Presumably this sample was collected and analysed before improvements were made. Since it appears that this is the only data that is discussed it might read better if the references to which chromatographic conditions were used are removed from each of the discussions about the figures and move to the beginning of section 4.2, where the authors could state that "the improved chromatographic conditions were used for all analysis unless otherwise stated".

Response: Agreed. References to the chromatographic conditions for Figures 2 and 4-6 have been removed and the following text has been added on page 3661: "Figures 2-6 show chromatograms for samples run using the improved set of chromatographic conditions (Table 3) unless stated otherwise."

9. Page 3662, line 22, the authors say "moderately larger than blank levels", please clarify what this means in what quantitative terms, ie., twice the blank values etc.

Response: On page 3662 the word "moderately" has been replaced with "two to five times".

In section 4.2, I got a little confused between where the samples were from, that were being discussed. It might make sense to subdivide that section into one referring to the field branch

enclosure measurement and another for the laboratory study. It might also make sense to add an additional panel to Fig 1 showing the sampling setup for the branch enclosure experiment.

Response: In Section 4.2, a brief description of each sample (e.g., *Cedrus*, *ATD*, *laboratory*) is now provided at the start of each relevant paragraph.

11. In section 4.3.1 the authors describe how retention indices were determined. To calculate the first dimension retention index the authors use the same basic approach as reported by Arey et al. (2005; *Analytical Chemistry*, 77, 7172 - 7182). For the secondary retention time the authors determine a ratio and not an index, in contrast to the work of Arey et al., who did calculate a retention index. Reporting an index is much more useful, so can the authors explain why they chose to report a ratio? Perhaps it would not be too much work to do this and I would encourage the authors to go back and determine the secondary retention indices.

Response: An examination of the retention index introduced by Arey et al. (2005) shows that it is considerably more difficult to put into practice than GC first dimension retention indexes. As such, it seems unlikely that practitioners in the atmospheric measurements field would soon adopt the Arey et al. (2005) second dimension retention index. In contrast, the retention ratio proposed in our work is simultaneously simple to understand, simple to use, and effective.

12. Page 3663, line 10 - the authors say they have tentatively identified methacrolein, methyl vinyl ketone and hexenal. Standards are available for these components would it not be relatively easier to confirm their identifications?

Response: First, if any of these three tentatively identifications were incorrect, the actual and tentative structures will have been similar, so failure to confirm these identifications does not substantively detract from our demonstration of the wide chromatographic range and power of GC×GC for VBOCs. Second, all three of these compounds are known to be emitted by plants, and so actually confirming their presence in our particular samples would have added little to the field.

Technical Corrections

1. Page 3662, Line 7 - use of wrong tense, should replace "are" with "were".

Response: Done.