

Interactive comment on “Volatilizable biogenic organic compounds (VBOCs) with two dimensional gas chromatography-time of flight mass spectrometry (GC × GC-TOFMS): sampling methods, VBOC complexity, and chromatographic retention data” by J. F. Pankow et al.

Anonymous Referee #1

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The manuscript describes the use of solid phase micro extraction fibers (SPME) and adsorption/thermal desorption (ATD) cartridges coupled to GCxGC-ToF/MS for the analysis of volatilizable biogenic organic compounds (VBOCs). The authors describe the collection, identification and chromatographic characterisation of VBOCs in complex samples using GCxGC-ToF/MS. While the use of SPME and ATD to biogenic hydrocarbon analysis and application of GCxGC-ToF/MS to these compounds are not com-

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pletely novel the authors do present a coupled analytical methodology that is very sensitive and selective and that will provide an improved understanding of the complexity of biogenic hydrocarbon emissions. The authors also present the beginning of a VBOC retention index database that will prove to be useful for future work and raise a key point about the lack of available standard material for the vast array of observable VBOC. In general, the manuscript is well written and well organised and I would recommend publication after the following comments are addressed:

Specific Comments

1. Page 3651, line 7 "...loss can occur because of mechanical/herbivore wounding." needs citations.
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.
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?
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.
5. On page 3661, lines 1 and 3, the authors refer to "zero split", I am assuming this is

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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?

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

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

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".

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 10. 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.

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

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would not be too much work to do this and I would encourage the authors to go back and determine the secondary retention indices.

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?

Technical Corrections

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

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 3647, 2011.

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