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**Atmospheric Measurement Techniques Discussions**

# *Interactive comment on* "Quantitative and enantioselective analysis of monoterpenes from plant chambers and in ambient air using SPME" *by* N. Yassaa et al.

**Anonymous Referee #3**

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The article presents an interesting investigation in to the potential for SPME to sample monoterpenes in the atmosphere and from plant chambers. The approach has been used in only a very limited way in atmospheric science, and the paper will be of interest to a wide range of scientists interested in VOCs. There are however a number of areas where further technical details are required in the manuscript, or a reorganisation of material that is already available. Should these change be made then the publication should be appropriate for AMT.

Minor issue: Why does the abstract refer to HS-SPME; HS is never defined or used,



but is presumably referring to headspace.

Ozone is one of the major interferences in sampling of monoterpenes for analysis by GC, however the systems used to remove ozone in this paper are not described in any detail (only a link to a reference). Can a short description of this key element be provided.

Similarly humidity may have an important role in determining the amount of substance that can be adsorbed on the SPME element. For adsorbent tube methods humidity is well established to often lower breakthrough volumes. Further details are needed in the manuscript to identify any evidence for the impacts of water vapour on the SPME adsorption process.

Figure 3 and associated text requires some clarification. The description of this providing a measure of monoterpene adsorption efficiency is somewhat misleading. Not all monoterpenes in the figure give the same ion/MS response and so some form of normalisation on the y axis would be better (e.g ng C). Without this it is difficult to know whether the low pinene values are because of adsorption effects / displacement or simply a lower MS response when compared to limonene. Better description of the conditions for this experiment, eg monoterpene mixing ratio, sampling time, are needed such that it can be placed in the context of Figure 5?

In more general terms I find the description of 'extraction efficiency', used in a number places in the manuscript, a little confusing. On first reading this seemed to me to refer to efficiency of desorption from the SPME fibre. The authors mean this in the sense of extraction efficiency from air, but it is an unusual use of the phrase. This is really analyte accumulation, rather than efficiency, in that the efficiency of organic uptake is presumably constant, until saturation of the fibre occurs.

P3351. Normally limit of detection for this type of measurement is determined on a statistical basis extrapolated from higher mixing ratio standards, but the text implies that that it has been directly determined through dilution of NPL cylinder standards to

as low as 2 ppt. This is some achievement - please give the conditions which have allowed this and give the associated uncertainty. Can an example chromatogram at this exceptionally low level be shown, in conjunction with a blank fibre example? A statistical definition of the reported detection limit should be provided, 3:1s/n for example. For a paper concerned with quantitative assessment of monoterpenes the limit of quantification (LOQ) should also be given.

P3355. GC injection from the SPME fibre is given as 5 mins – is there any preconcentration step prior to injection?

P3358. Why would a high SPME adsorption efficiency necessarily result in poor separation? The two processes are in principle completely decoupled? Does this rather refer to difficultly in desorption from the fibre under the given injector conditions?

Similarly in a number of other places the text makes reference to optimising the system for resolution of enantiometric pairs. This needs some further clarification, since resolution is a function of the GC column, not the SPME collection step. Since the column type is fixed in this study one would expect R to be a constant. Fig. 4 indicates that R is approximately 1.5 for all fibres, but with varying peak tailing, and this some needs explanation. One assumes this is down to ease of injection from the different fibre types. Any discussion of resolution requires quantitative information in the text, e.g on peak-to-valley separation and skew, not simply an eyeball inspection of the chromatogram.

Fig 5. shows the accumulation of material on the fibres as a function of time exposed, although the conditions in the chamber (T, humidity, mixing ratio) are not given. As the authors identify this approach is only quantitative when sampling is not influenced by competitive adsorption, and so it needs to be placed in the context of the information in Table 3. I found it difficult to make the links between the two data sets since one is a graph and the other in tabular form. Can these be brought together in a single figure?

Line 20 p 3359 – comment on 100ppb not being exceeded – needs a better demon-



stration using the data/experiments that shows this to be the critical concentration.

Why not calibrate the zNose instrument with either compressed gas or diffusion gas standards and turn peak area in to real numbers?

Spelling. Fig 4 ‘monoterpenes’, and clarify whether this is a standard and at what mixing ratio.

Spelling . Fig 5 ‘efficiencies’. As outlined earlier this should really be described as monoterpene accumulation, or similar, rather than efficiency. This also applied to Fig. 6

Figure 9 did not reproduce on my version of the pdf, but I didn’t notice this until the end of the paper. Hence one might question whether this figure is really needed.

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