**Atmospheric
Measurement
Techniques
Discussions**

Interactive
Comment

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

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Received and published: 7 November 2010

For clarity we transcribe each referee comment/suggestion, and then follow this with our answer.

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

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material that is already available. Should these change be made then the publication should be appropriate for AMT.

We would like to thank the anonymous referee # 3 for the comments, suggestions and appreciations. Below are the responses to each single comment:

Minor issue: Why does the abstract refer to HS-SPME; HS is never defined or used, but is presumably referring to headspace.

This has been corrected in the text of the manuscript.

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.

The following description has now been given in the text of the manuscript: The ozone scrubbers were prepared by flowing 10 mL of a 10% [w/w] aqueous solution of $Na_2S_2O_3$ through 47 mm diameter glass fiber filter disks and subsequent drying under a nitrogen purge flow of 80 mL min-1 at 50 °C for 4 h (Pollman et al., 2005).

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.

Previous reported investigations have shown only a minor effect of water vapour on the adsorption process through the SPME fibre coating (Akdeniz et al., 2009). N. Akdeniz, J. A. Koziel, H.-K. Ahn, T.D. Glanville, B.P. Crawford, D.R. Raman, Air sampling and analysis method for volatile organic compounds (VOCs) related to Field-scale mortality composting operations. J. Agric. Food Chem. 2009, 57, 5658-5664.

Figure 3 and associated text requires some clarification. The description of this pro-

viding 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.

If the referee refers to Figure 3 as it is stated in the comment report, then this later shows the comparison of extraction efficiency of a single monoterpene with three different fiber coatings. Since each individual monoterpene has the same MS response factor regardless the nature of the SPME fibre coating and therefore the comparison does not need further normalization. However if the referee refers to Figure 5, then I do agree with the referee that this figure cannot provide comparison of the extraction efficiencies, or according to the referee the analyte accumulation, on PDMS-DVB fiber coating because the analytes present obviously different MS responses and also different partition coefficients between air and the SPME fibre. Nevertheless the purpose of Figure 5 is to show the kinetic of adsorption of different monoterpenes on PDMS-DVB fiber. Regardless of MS response or partition coefficient of a single monoterpene, Figure 5 does show that some monoterpene (i.e. a-pinene, around 20 mins) reaches equilibrium quite earlier than other (i.e. limonene, latter than 60 mins). This is certainly not related to MS response nor to partition coefficient but rather to competitive adsorption.

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.

Since the mixing ratios of each monoterpene in the NPL cylinder standard is around 2 ppb, determination of limit of detection for each monoterpene has been achieved by making the appropriate dilution using filtered compressed air. For instance 2 ppt has been obtained by introducing to the dilution system 1 mL of NPL standard and 1000 mL of filtered compressed air. The system is controlled with a MPI custom built control/regulator (V 25) containing accurate calibrated mass flow controllers. While the limit of detection is determined considering a signal-to-noise ratio of 3, the limit of quantification is obtained using a signal-to-noise ratio of 10.

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

Among the advantages of SPME is that, thanks to the very small size of the fiber, it does not need any preconcentartion procedure prior to injection in contrast to the sorbent tube. In fact the preconcentration occurs in the GC column.

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 resolu-

tion 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.

We do agree with the referee # 2 that the varying peak tailing observed in Fig. 4 is obviously not related to the GC column separation conditions as a series of optimisation analyses were completed in order to minimize the analysis time and maximize resolution of the enantiomers. These analyses focused on adjustment of the initial temperature of the column and the temperature program, since these two parameters have been previously found to be critical for the beta-cyclodextrin columns (Yassaa et al., 2001). Since these optimum separation conditions have been used to test the three SPME fibre coatings, we suggest that this is rather related to the difference in the recovery of adsorbed components which seems to depend on the nature SPME fiber coating materials. The worst case was obtained when SPME fibre coating was a mixture of carboxen and divinylbenzene.

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?

While Fig. 5 shows the adsorption kinetic of a single monoterpene at a fixed mixing ratio, Table 3 reports the calibration curves at a fixed exposure (ca, 20 min). Fig. 5 allowed the determination of the exposure time that can be quantitatively used without affecting any a single monoterpene with a competitive adsorption. Table 3 enables determination of the mixing ratio limit, at which the adsorption of a single monoterpene

is still linear at a given sampling time (20 min).

Line 20 p 3359 – comment on 100ppb not being exceeded – needs a better demonstration using the data/experiments that shows this to be the critical concentration.

This has been explained in the section (3.3 Calibration curves and detection limits)and therefore the sentence has been modified to:

Such competition on DVB-PDMS can be avoided by limiting sampling to 20 min.

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

We have attempted to calibrate the zNose instrument with gas standards but that was successful only for limonene.

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

It has now been modified to:

Fig. 4. Reconstructed mass chromatographic profiles (m/z 93) of monotrpenes (50 ppb of diluted CDs standard gas) sampled with three different SPME fibre . . . .

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

The titles of Fig. 5 and Fig. 6 now modified to : Extraction kinetics. . .

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.

Fig. 9 serves for validating the SPME method as it indicates that both SPME (Table 5) and VOC analysis by GC-FID (Fig. 9) showed b-myrcene as the most prominent chemical emitted, followed by limonene. These two chemicals made up more than

95% of the total monoterpene emissions.

A better resolution of Fig. 9 is now provided.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 3345, 2010.