

Interactive comment on “Field measurements of biogenic volatile organic compounds in the atmosphere using solid-phase microextraction Arrow” by Luís Miguel Feijó Barreira et al.

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General comments (1) I would have liked to see a detailed characterization of the temperature effect as this C1 parameter is the main regulating force of monoterpene mixing ratios in a forested environment. The authors indicate considerable differences for α -pinene and D3-carene but I am still a bit confused on how one can deal with these effects under field conditions. I would assume that a reasonable approach would be to characterize the extraction efficiency along a wider range of temperatures and apply the respective correction under field conditions.

A: The proposed approach is one of the possibilities. However, the ideal solution would

C1

be to eliminate this effect. For that purpose, we would suggest the construction of a chamber that can be field portable and that is able to keep the temperature constant during both sampling and calibration. However, additional research is still needed to study both of these possibilities.

Text was modified on page 7, line 13: The effect of temperature on the amounts of analytes collected by SPME must consequently be assessed or avoided during quantitative field measurements.

(2) It would have been valuable if the authors could demonstrate the advantages of increased sampling capacity as a function of detection limits.

A: Indeed, it is important to develop a calibration method so that we can determine the detection limits for all used SPME systems. However, our results showed already the benefit of having increased capacity for both qualitative (e.g. we detected octanal with SPME Arrow but not with SPME fiber) and semi-quantitative measurements (e.g. errors related to the analysis of target compounds are usually higher when responses are closer to the baseline).

No modification was done to the manuscript.

(3) The amount of field data extremely low (15 points) and the assumptions on correlation (or not) with meteorological and environmental parameters should be more carefully approached and discussed. This is of particular importance especially when considering the title of the manuscript that at this stage could be misleading.

A: the whole section 3.4 has been rewritten and more carefully discussed.

Text was modified in page 10, line 5: The effects of meteorological parameters (Table S3) on the measured atmospheric levels of monoterpenes (Fig. 9) and aldehydes (Fig. 10) were also tentatively evaluated in this study, since some of these parameters can influence not only the VOC emissions/atmospheric mixing ratios but also the adsorption on the SPME sorbent materials. The ratios between the amounts of monoterpenes

C2

and aldehydes sampled with PDMS/Carbon WR and PDMS/DVB were also compared with the referred parameters, in order to understand if meteorological conditions affect differently the sampling with these materials (Fig. S8). Temperature has two opposing effects in field measurements performed at boreal forest sites. Increased temperature enhances VOC emissions from Scots pine (Tarvainen et al., 2005). In addition, it reduces the distribution constant of the analytes because adsorption is an exothermic process (de Fatima Alpendurada, 2000). During the sampling campaign, temperature remained almost constant, limiting the comparison between this parameter and the measured amounts of monoterpenes. The effect of temperature was then expected to be small when compared to other parameters, which was verified in our results. However, longer data sets encompassing periods of greater temperature variation are needed to perform this evaluation. Relative humidity (RH) and precipitation also have two opposing effects, since monoterpene emission rates not only increase at high humidity levels and during and after precipitation (Llusà and Peñuelas, 1999; Schade et al., 1999) but also causes a small decrease in the SPME extraction capacity (section 3.1.3). Oppositely to temperature, relative humidity varied considerably during the sampling campaign, which allowed to study the effect of this parameter in our results. An increase in monoterpene amounts was observed during a precipitation event when relative humidity was high, showing that the decreasing effect of these parameters on the sorbent collection is less significant when compared to their increasing effect on VOC emissions. A correlation was not found when considering the ratio between the amounts of monoterpenes sampled with PDMS/Carbon WR and PDMS/DVB, which is consistent with the small humidity dependence observed for the sampling with these materials under laboratory controlled conditions. Due to the constancy of temperature during the sampling campaign, ozone and PAR were also expected to affect significantly the measured amounts of monoterpenes. Indeed, some anti-correlation was found between the measured monoterpenes and these parameters. This result is likely to reflect the increased photooxidation during periods of the day when PAR is high, since the effects of temperature and/or light on monoterpene emissions have been

C3

described previously (Aalto et al., 2014). Nonetheless, on-fiber oxidation might occur during SPME collection. For that reason, the effect of oxidants must be assessed further by performing complementary laboratory experiments under controlled conditions. Ozone and PAR did not affect distinctively the adsorption on the two different materials used in this study. PNC also seemed to increase with the amounts of monoterpenes present in the ambient air. This result is expected, since monoterpene oxidation in the atmosphere and consequent formation of low volatile compounds have been recognized to contribute to aerosol particle formation (Laaksonen et al., 2008). However, other factors can also contribute to the increase in PNC, such as long-range transport. With reference to aldehydes, the studied parameters seemed not to influence negatively the SPME collection. A similar trend between aldehyde amounts and temperature was observed during the most of the sampling period, showing that temperature did not affect the SPME sampling and suggesting the existence of a temperature-dependence on aldehyde emissions. However, as referred previously, temperature remained almost constant during the sampling campaign and additional studies under controlled conditions are required to confirm this evidence. Relative humidity and precipitation also coincided with a burst in aldehyde atmospheric amounts, excluding a negative effect of this parameter on the SPME sampling, but seemed to anti-correlate with these parameters when aldehyde amounts were low. This observation can be a consequence of the solubility of these compounds in water at low concentrations, but additional studies are also required to confirm this hypothesis. A correlation was not found between PAR and aldehydes. However, contrary to monoterpenes, some correlation with ozone was observed, which was expected since increased emissions have been reported in another study when vegetation was exposed to ozone (Wildt et al., 2003). On-fiber oxidation studies are also still required for aldehydes. The effect of aldehyde amounts on PNC was not very clear, which might be a consequence of the lower atmospheric reactivity of these compounds. No correlation was observed between atmospheric parameters and the ratio between the amounts collected on PDMS/Carbon WR and PDMS/DVB, which agrees with the non-dependences on temperature and relative humidity verified

C4

in laboratory studies. Even though the effects of atmospheric parameters on the SPME sampling were preliminarily evaluated with our method under atmospheric relevant conditions, longer data sets and quantitative data are needed to estimate accurately the correlation of these parameters with BVOC mixing ratios.

Specific comments

(4) P1L19. If there is a technical possibility to additionally evaluate the effects of ozone under relevant atmospheric conditions it would have been a valuable addition to this study.

A: A technical possibility to evaluate the effects of ozone under relevant atmospheric conditions would be to generate different oxidants in a chamber/flow tube and perform measurements, maintaining all other conditions constant. This approach would be very challenging, since adding oxidants to the chamber will also decrease the analytes concentration. There are also some possibilities that could possibly be used with our method to avoid the effect of ozone and other oxidants on the measured amounts of VOCs (e.g. the use of an ozone scrubber or a heated stainless steel tube connected to our sampling device). These studies must be performed further.

Text was modified on page 10, line 31: Nonetheless, on-fiber oxidation might occur during SPME collection. For that reason, the effect of oxidants must be assessed further by performing complementary laboratory experiments under controlled conditions. Text was modified on page 11, line 14: On-fiber oxidation studies are also still required for aldehydes.

(5) P2L26-L27. I don't think that the conventional GC-MS techniques are "laborious, expensive and prone to contamination". GC-MS is the most widely used technique for quantification of ambient monoterpenes, with no interferences on temperature or wind speed as demonstrated for SPME. Therefore, I would suggest removing this sentence completely.

C5

A: The sentence was removed and the main advantage of SPME compared to TD-GC-MS was referred.

Text was modified on page 2, line 24: Alternatively, monoterpenes have been successfully sampled on tubes packed with an adsorbent material (such as Tenax TA/Carbopack-B), and subsequently desorbed into a thermal desorption-gas chromatograph-mass spectrometer for off-line or on-line analysis (e.g. Haapanala et al., 2012; Hakola et al., 2012; Wong et al., 2013). The main limitation of this method is the requirement of sophisticated instrumentation that is less convenient for field measurements (e.g. thermal desorption unit and cryofocusing). Solid-phase microextraction (SPME) has also been used for the collection of monoterpenes (e.g. Yassaa et al., 2010; Zini et al., 2001). This technique combines sampling and pre-concentration of analytes in a single step and allows for direct thermal desorption into a heated gas chromatograph injection port (Koziel et al., 1999).

(6) P4L16. I was wondering if the sampling time could be reduced and if you could explain the reasons that you have chosen this approach. 45minutes is long time for sampling ambient mixing ratios that can dramatically change in such time frame.

A: The sampling time could likely be reduced, especially when using SPME Arrow. The main reasons for using a 45 minutes sampling time were to sample detectable amounts of target analytes with all SPME systems and to reduce the significance of errors associated with the time lag between sampling and injection (even though sample modification was not expected to be significant due to the retraction of extraction materials under the SPME needle and the fact that SPME syringes were closed with a cap).

Text was modified on page 4, line 19: Samples were collected in static mode for 45 minutes, to sample detectable amounts of target analytes with all SPME systems and to reduce the significance of errors associated with the time lag between sampling and injection.

C6

(7) P4L27. Have you tried to develop a method under SIM mode? It is commonly known that the sensitivity is much reduced when using a mass scan.

A: A SIM mode increases the sensitivity of the method. However, at this stage of development, we would like to know what type of compounds can be identified and a scan mode was then chosen for that purpose. This approach allowed to study compounds that were not considered during the laboratory tests (limonene and nonanal).

Any modification was done in the manuscript.

(8) P5 and P6. I would suggest bringing supplementary figures S2, S3 and S4 into the main paper.

A: The figures were brought to the main paper.

Text was modified on page 17, line 1: Figs. S2, S3 and S4 modified to Figs. 1, 2 and 3.

(9) P7L13-14. If the extraction efficiency is reduced at higher temperatures (where we expect higher emissions) the final results will be heavily influenced. Please elaborate in detail.

A: The sentence was corrected.

Text was modified on page 7, line 13: The effect of temperature on the amounts of analytes collected by SPME must consequently be assessed or avoided during quantitative field measurements. Text was modified on page 7, line 25: Even though the effect of relative humidity was negligible in our study, this parameter might greatly influence the SPME collection when using other sorbents or when sampling other analytes.

(10) P7L16. A plot (rather than a table) would have been more useful.

A: In order to compact the information obtained during calibration studies, results were presented as a table. All relevant parameters were carefully provided in the table and in the text.

C7

No modification was done to the manuscript.

(11) Fig. 4. How many samples were used? Please add errorbars.

A: The results are the average amounts measured during all the campaign. This information was added to the caption. Repetitions were not performed during field measurements, since a satisfactory repeatability was obtained during laboratory measurements and 4 different systems were compared simultaneously in the field (which would require 12 systems for 3 repetitions and a long time to finalize the measurements of each experiment). For that reason, error bars were only added to the laboratory experiments. The detailed results during all sampling campaign are represented in Fig. S8 (Fig. S5 in the new version of the manuscript) and Table S2, which show the consistent improvement in extraction efficiency when using SPME Arrow comparatively to SPME fiber during all sampling period.

Text was modified on page 23, line 4: Figure 7: Comparison between the average mass of identified monoterpenes (α -pinene, Δ 3-carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with different PDMS/DVB SPME devices (fiber and Arrow) from ambient air and measured by GC-MS.

(12) Section 3.4: The effects of meteorological parameters should be addressed in a more comprehensive and detailed manner. Some conclusions (e.g. P9L29-31, P10L3-4, P10L7-15) are drawn very easily and without strong evidence driven by data. I would suggest to completely re-write this section, using softer language and presenting the available data in a different manner. Maybe xy plots (where x is the SPME arrow PDMS/DVB and y the PDMS/Carbon WR) colored by a 3rd dimension which would be the respective meteorological parameter, would depict better both the differences between the materials and the impact of the parameters. It is however understandable that eg. temperature did not vary significantly during the sampling period but I would have liked to understand why the two materials match on the 12.8 and have 100% difference on the 14.08.

C8

A: All section 3.4 was completely rewritten to emphasize that the main purpose of the section was to evaluate preliminarily the effect of atmospheric parameters on the SPME sampling. In Figs 6 and 7, the trends between SPME Arrow (PDMS/DVB) and SPME Arrow (PDMS/Carbon WR) were similar. The differences in the extracted masses are likely related with a combination of several factors, including the distinct extraction efficiencies, competitive adsorption and different effects of atmospheric parameters (e.g. temperature and relative humidity).

Corrected as described above.

(13) P10L11. While this may be true, no real evidence is provided that PNC was increased due to a particle formation event or not due to some transport. Please provide some evidence or revise the text accordingly. P10L25-26. As above.

A: The sentences were revised.

Text was modified on page 10, line 33: PNC also seemed to increase with the amounts of monoterpenes present in the ambient air. This result is expected, since monoterpene oxidation in the atmosphere and consequent formation of low volatile compounds have been recognized to contribute to aerosol particle formation (Laaksonen et al., 2008). However, other factors can also contribute to the increase in PNC, such as long-range transport. Text was modified on page 11, line 15: The effect of aldehyde amounts on PNC was not very clear, which might be a consequence of the lower atmospheric reactivity of these compounds.

(14) P10L31. The authors correctly recognize but only briefly discuss the limitations of their dataset.

A: The limitations of our data set were clarified.

Text was modified on page 11, line 19: Even though the effects of atmospheric parameters on the SPME sampling were preliminarily evaluated with our method under atmospheric relevant conditions, longer data sets and quantitative data are needed to

C9

estimate accurately the correlation of these parameters with BVOC mixing ratios. Text was modified on page 13, line 26: Longer data sets are also required to study in more detail the effects of atmospheric parameters on the SPME sampling under atmospheric relevant conditions.

(15) P11L20. It is a bit strange to see a technical paper entitled "Field measurements. . ." to use as final statement the fact that "more studies are needed to develop a proper calibration method for field measurements". It denotes that the current manuscript did not sufficiently fulfill its purpose. Please revise.

A: The sentence was revised.

Text was modified on page 13, line 25: More studies under controlled conditions are needed to understand the influence of co-adsorbed species and oxidants on the SPME sampling and to develop a proper calibration method for quantitative field measurements.

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