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Atmospheric Measurement Techniques
Discussions

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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(1) Page 6, Lines 16−17: What is the sampling time? 10-min?

A: The sampling time was indeed 10 minutes. The information was added to the text.

Text was modified on page 6, line 23: Static and dynamic collections were performed during 10 minutes.

(2) Page 7, Line 2: Does it lead to only "underestimation"? Doesn't it happen to overestimate?

A: In the particular case of α-pinene, an underestimation will be observed in comparison with the other studied monoterpenes that are less volatile. However, it is true that an overestimation will be most likely observed if other monoterpenes with higher volatility than α-pinene are measured.

Text was modified on page 7, line 10: An underestimation of the measured amounts of a compound with higher volatility or an overestimation relatively to the most volatile compounds are then expected when quantifying monoterpenes under field conditions where temperature changes can be significant.

(3) Page 7, Lines 15−24: What is the sampling time and the temperature in the calibration? And which type of SPME was calibrated? In Table S1, the calibration carves for only one type of SPME are listed. Later, field data obtained from all types of SPME were quantified. Therefore, calibration carves for all types of SPME should be shown.

A: The calibration of the instrument response during field measurements was performed by using liquid standard solutions at different concentrations. The SPME systems were not calibrated to allow their comparison.

Text was modified on page 7, line 30: The calibration of instrument response was performed for the field measurement of monoterpenes (α-pinene, Δ3-carene and limonene) and aldehydes (octanal, nonanal and decanal), to estimate the mass adsorbed on the coating materials of the different SPME-based systems (Table S1). Liquid standard solutions at different concentrations were used for this purpose. Text was modified in page 8, line 16: However, when the calibration of analytes response was performed with standard solutions (but not the calibration of SPME collection), Δ3-carene and limonene levels increased relatively to α-pinene (Fig. 6A).

(4) Page 9, Line 4: Is it "the ratio between nonanal and decanal"? I think that the authors did not show the results of nonanal in the laboratory experiments.

A: The first mentioned ratio is the one obtained during field measurements between decanal and nonanal. Octanal was not measured with SPME fiber. However, during laboratory experiments, the tests were performed for octanal and decanal and the second mentioned ratio is the one obtained between decanal and octanal. Even though these ratios could probably still be compared because analytes belong to the same homologous series, the sentence was eliminated since additional tests would be required to confirm this possibility.

The sentence was removed.

(5) Page 9, Line 17−Page 11, Line 5: I felt that the discussions here were vague and subjective, and were not based on statics. What is the reason of the difference between SPME Arrow (PDMS/DVB) and SPME Arrow (PDMS/Carbon WR) in Figs. 6 and 7?

A: the whole section 3.4 was completely rewritten to emphasize that the purpose of the section was to evaluate preliminarily the effect of atmospheric parameters on 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).

Text was modified on 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 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 (Llusià 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 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 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.

(6) Page 10, Lines 6−7: What is the reason of the anti-correlation between the measured monoterpenes and PAR?

A: At summer time, the main factor determining monoterpene emissions at the boreal forest is temperature due to the temperature-dependent residence in specific storage structures located internal or external to the leaf. However, a PAR effect on monoterpene emissions was also found to be important (e.g. at spring-time when temperature is still low). In our study, the anti-correlation between PAR and monoterpenes is most likely not related with lower emissions from vegetation. Higher PAR is usually observed in the beginning of afternoon, which usually coincides with the period of the day with higher atmospheric reactivity. This reactivity is most likely the main reason why a correlation between PAR and monoterpenes is not observed. A discussion was added to the text.

Text was modified in page 10, line 27: 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 described previously (Aalto et al., 2014).

(7) Page 10, Lines 13−14: This sentence is inconsistent with the previous two sentences. Explain the reason more carefully.

A: The sentence was revised.

Text was modified in 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.

(8) Page 10, Lines 21−22: Is negative effect of RH and precipitation on the amount of

aldehydes surely “evident”? Discuss more carefully.

A: A more careful discussion was added to the text.

Text was modified in page 11, line 8: 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.

(9) Page 10, Line 26: Insert “not”: . . ..any correlation was “not” observed. . . Am I right?

A: The sentence was corrected.

Text was modified in 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. 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 in laboratory studies.

(10) Page 14, Figs. 1 and 2: In the results of SPME Arrow (PDMS/DVB), the values of peak area of _-pinene are larger than those of _3-carene. According to kinetic data shown in Figs. S2 and S3, the values of peak area of _-pinene are smaller than those of _3-carene. Are they consistent? How were the error bars calculated? Define them.

A: The concentrations of analytes were not changed during all experiments and it is true that α-pinene was expected to be slightly higher during SPME Arrow (PDMS/DVB) kinetic studies and during comparison between extraction efficiencies. However, considering the error bars, the amounts of α-pinene and Δ3-carene were quite similar when using a PDMS/DVB sorbent and results are still consistent with the SPME fiber

coated with the same extraction material (Figs. S2, S4 and S7). The error bars in Figs. 1 and 2 are the standard deviations from 3 repetitions. In Figs. S2-S3, three repetitions were performed at 10 minutes and the obtained RSD was used for all the calibration. The RSD will be likely higher at lower sampling times and lower for the longer sampling times. However, because most of the laboratory tests were performed at 10 minutes (except for temperature and RH studies that were performed at 20 minutes) and field measurements were performed at longer sampling times (45 minutes), the used RSD is representing a worst-case scenario in the kinetic studies.

Text was modified in page 5, line 24: For an estimation of standard deviations during kinetic studies, 3 repetitions were performed at 10 minutes, corresponding to the minimum sampling time used during all other experiments and consequently to the higher expected variation. Text was modified in page 6, line 32: Three replicates were performed for each temperature and relative humidity studied.

(11) Figs. S2−S7: How were the error bars calculated? Define them.

A: The error bars in Figs. S2-S3 were calculated as described in the previous question. In Figs S4-S7, three repetitions were performed and the obtained standard deviations were used as error bars.

Text was modified on page 5, line 24: For an estimation of standard deviations during kinetic studies, 3 repetitions were performed at 10 minutes, corresponding to the minimum sampling time used during all other experiments and consequently to the higher expected variation. Text was modified on page 6, line 15: Three repetitions were performed with each SPME system. Text was modified on page 6, line 32: Three replicates were performed for each temperature and relative humidity studied.

(12) Fig. S11: The data of meteorological parameters seems to be different from those in Figs. 6 and 7. Is it just a careless mistake? The title of the left axis should be “ratio”. It should not be “mass adsorbed (ng)”..

A: There was a mistake in the x-axis (date) that was corrected. The title of the y-axis was modified to Carbon WR/DVB (ng/ng).

Text was modified on page 6, line 1 (supplement)

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2017-329/amt-2017-329-AC1-supplement.pdf

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