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Quantifying sesquiterpene and oxygenated terpene emissions from live vegetation using solid-phase microextraction fibers

Nicole C. Bouvier-Brown [a,*], Rupert Holzinger [a,1], Katrin Palitzsch [b], Allen H. Goldstein [a]

[a] *University of California, Berkeley, CA, USA*
[b] *J.W. Goethe-Universitaet, Frankfurt am Main, Germany*

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Abstract

Biogenic terpenes play important roles in ecosystem functioning and atmospheric chemistry. Some of these compounds are semi-volatile and highly reactive, such as sesquiterpenes and oxygenated terpenes, and are thus difficult to quantify using traditional air sampling and analysis methods. We developed an alternative approach to quantify emissions from live branches using a flow through enclosure and sample collection on solid-phase microextraction (SPME) fibers. This method allows for collection and analysis of analytes with minimal sample transfer through tubing to reduce the potential for losses. We characterized performance characteristics for 65 μm polydimethylsiloxane–divinylbenzene (PDMS/DVB) fibers using gas chromatography followed by mass spectrometry and optimized experimental conditions and procedures for field collections followed by laboratory analysis. Using 10–45 min sampling times and linear calibration curves created from mixtures of terpenes, emissions of methyl chavicol, an oxygenated terpene, and an array of sesquiterpenes were quantified from a Ponderosa pine branch. The detection limit was 4.36 pmol/mol (ppt) for methyl chavicol and 16.6 ppt for β-caryophyllene. Concentrations determined with SPME fibers agreed with measurements made using proton transfer reaction mass spectrometry (PTR-MS) within the estimated error of the method for well calibrated compounds. This technique can be applied for quantification of biogenic oxygenated terpene and sesquiterpene emissions from live branches in the field.

Keywords: Sesquiterpenes; PDMS/DVB solid phase microextraction fibers; SPME GC/MS; Field branch enclosure; Methyl chavicol

1. Introduction

Biogenic terpenes, byproducts of basic cell metabolism, play an important role in the atmosphere. Terpene compounds (i.e. monoterpenes $C_{10}H_{16}$, sesquiterpenes $C_{15}H_{24}$, and oxygenated terpenes) are emitted into ambient air by vegetation and are used to communicate with other plants and insects. They play an important role in the oxidative capacity of the troposphere because they react quickly with ozone and OH. Moreover, terpene oxidation products are a major source of secondary organic aerosols (SOAs) which affect the global radiation balance and still constitute a major uncertainty in assessing total climate forcing [1].

In order to understand the role of terpenes in ecosystems and in atmospheric chemistry, it is important to characterize and quantify their emissions and atmospheric abundance. Detecting highly reactive semi-volatile compounds, especially sesquiterpenes and oxygenated terpenes, in ambient air is an ongoing challenge. Methods generally include use of solid adsorbents to concentrate the terpenes, followed by transfer through either thermal desorption or solvent extraction into a gas chromatograph (e.g. [2–4]). Highly reactive compounds may not be stable enough to survive these sampling processes. Large and low-volatility compounds likely stick to materials commonly used in analytical sampling (i.e. tubing, trapping material, etc.), never reaching the detector [4,5].

Solid-phase microextraction (SPME) fibers have the potential to collect these highly reactive and sticky compounds for analysis by traditional chromatographic separation and detection methods. SPME fibers are small fused silica fibers thinly coated with a solid adsorbent or liquid absorbent. They provide an easy method for sampling the gas phase without requiring extraneous solvents or surfaces where compounds could be lost.

* Corresponding author. Tel.: +1 510 643 6449; fax: +1 510 643 5098.
E-mail address: nbouvier@nature.berkeley.edu (N.C. Bouvier-Brown).
[1] Present address: Institute for Marine and Atmospheric Research, Utrecht, The Netherlands.

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The compounds are directly adsorbed onto the fiber coating, then the fiber is placed into the gas chromatograph injector port for thermal desorption [6].

To detect terpenes using SPME fibers, one of three sampling techniques is generally used: (i) exposing fibers to the headspace of vials containing liquid or solid samples [7–16], (ii) exposing fibers to air that was circulating over the sample [17,18], or (iii) inserting the needle of the SPME apparatus into a vial containing the sample and allowing the compounds of interest to diffuse onto the retracted fiber [19]. These methods are typically employed to screen for terpenes volatilized from plant products or essential oils. SPME fibers have not been used to quantify naturally emitted terpenes from unstressed plants with the goal of understanding natural rates of emission to the atmosphere.

While many of the experiments mentioned above were qualitative, reporting relative composition of individual compounds based on chromatogram peak areas [7,8,11,13–15], two quantitative methods have been published. The most common approach relies on modeling the analytes' diffusion through the microscopic boundary layer that forms around the fiber [10,17–19]. To implement this method, analytes first must establish equilibrium between the fiber and the surrounding matrix. If the fiber is exposed to the sample until an equilibrium point is reached, then the extracted analyte is linearly proportional to the initial concentration in the matrix; the proportionality constant is a temperature-dependent distribution coefficient experimentally calculated for each compound and type of fiber. The second method for quantifying analytes collected on a SPME fiber is derived from the sorption profile of compounds onto the fiber [9,12,16]. Before equilibrium is reached, the amount of analyte adsorbed onto the fiber is linearly proportional to the time the fiber was exposed and the amount of analyte in the sample matrix. Thus, by exposing fibers to a set of standards for a specific exposure time, a calibration curve can be developed and then used to quantify the amount of analyte in the samples.

While analytical techniques have been well established for measuring monoterpene emissions from plants, less volatile and more reactive terpenes continue to present an analytical challenge for atmospheric chemists. We set out to quantify and identify sesquiterpenes and oxygenated terpenes from a living Ponderosa pine branch. The resulting emission profiles of live vegetation provide useful inputs for biogenic volatile organic compound (VOC) emission models. We report a method for using SPME fibers to quantify emissions of sesquiterpenes and methyl chavicol ($C_{10}H_{12}O$) using a linear calibration curve based on short-term fiber exposures.

2. Experimental

2.1. Instrumentation and chemical standards

SPME fibers were analyzed using a Varian CP-3800 gas chromatograph with a Saturn 2200 ion trap mass spectrometer. The carrier gas was ultra high purity helium flowing at 2.2 mL/min through a Cp-Sil-8 column (Varian, Palo Alto, CA, USA) with the gas chromatograph oven temperature at 40 °C for 4.25 min, increasing to 160 °C at 5 °C/min, then to 220 °C at 10 °C/min and held at this temperature for 11.75 min. After a 5 min solvent delay, the mass spectrometer was operated in mass scan mode from *m/z* 40–650.

In the field, VOCs were also measured using a proton transfer reaction mass spectrometer (PTR-MS) system (Ionicon Analytik, Innsbruck, Austria). The PTR-MS system uses H_3O^+ to ionize compounds with proton affinity higher than water that are then detected by a quadrupole mass spectrometer. This instrument is described in detail elsewhere [20]. The PTR-MS system was operated in either scan or selected ion mode focusing on the sum of all monoterpenes (*m/z* 81 + *m/z* 137), the sum of all sesquiterpenes (*m/z* 205), and methyl chavicol (*m/z* 149).

Calibration standards were made by diluting the following pure liquid compounds in cyclohexane: α-humulene, β-caryophyllene, aromadendrene, longifolene, α-pinene, β-pinene, and methyl chavicol (also known as 4-allylanisole or estragole). All chemicals were obtained from Sigma–Aldrich or from Fluka Chemicals through Sigma–Aldrich (St. Louis, MO, USA).

2.2. SPME protocol

Field portable 65 μm polydimethylsiloxane-divinylbenzene (PDMS/DVB) Stableflex fibers (Supelco, Bellefonte, PA, USA) were used for all SPME measurements reported here. New fibers were preconditioned at 250 °C for 30 min in a helium flow, following the manufacturer's instructions. Sampling time varied from 0.5–50 min. After sampling, SPME fibers used during tests in the laboratory were retracted into the fiber holder and stored on dry ice (unless otherwise noted). Following storage, each fiber holder was placed on the counter for 5 min to defrost, then the fiber was inserted in the injector port fitted with a 4.0 mm gooseneck split/splitless liner (Varian) for a 5 min desorption at 200 °C. After injection, each fiber was cleaned for at least 1 h at 250 °C in a helium flow, retracted into its holder, and placed back on dry ice in preparation for further sampling.

2.3. Laboratory experiments

Experiments were performed to characterize four aspects crucial to SPME fiber performance: (1) stability of compounds in a Tedlar bag (SKC, Eighty Four, PA, USA), (2) sampling temperature dependence, (3) compound stability on SPME fibers during storage, and (4) method of quantification. In each experiment, SPME fibers from the same lot number were exposed to a gaseous mixture of terpene standards (monoterpenes, an oxygenated terpene, and sesquiterpenes) with a typical concentration range of 20–120 nmol/mol (ppb) for each compound. After filling a 10 L Tedlar bag with 7.5 L of zero air (from a zero air generator) at 1 L/min, each diluted liquid standard was injected using an appropriate size Hamilton syringe (Restek, Bellefonte, PA, USA). Care was taken to ensure the liquid quickly volatilized by gently agitating the Tedlar bag while the liquid standard drop hung at the end of the syringe needle. Once all standards were added and volatilized, the remaining 2.5 L of zero air was added to help ensure adequate mixing. Tedlar bag standard mixtures were always made and kept in an oven at

23 °C. A complete mixture of standards was used in each experiment so that any competitive preferences for the fiber coating would occur in every sample. Because the amount of analyte adsorbed onto the fiber is dependent on both sampling time and the concentration present in the sample matrix, the product of these two quantities (ppb × min) was calculated for each sample. Typically its range was 60–450 ppb × min.

2.4. Field experiments

Field experiments were performed at the Blodgett forest site, a Ponderosa pine plantation located on the western slope of the Sierra Nevada mountains of California [21]. Branch enclosures were constructed from Teflon film (Richmond Aircraft Products). Zero air, with ambient CO_2 concentrations, flowed at ~4 L/min through the enclosure with a 20 s residence time (Fig. 1). Periodically, the branch chamber was artificially shaded with aluminum foil to investigate light and temperature dependencies of primary emissions. A SPME fiber sampling port was constructed by placing a septum on the outer nut of a PTFE bulkhead union (Swagelok). This union was then inserted in the chamber supported by a PTFE plate. The needle of the SPME fiber holder was fully extended to position it directly after the branch and perpendicular to the dominant flow of air. Simultaneous measurements of VOC emissions were made using an *in situ* PTR-MS instrument.

Tedlar bags containing terpene standard mixtures were utilized in the field to calibrate the fiber measurements. At the beginning and end of each 2 week sampling period, four fibers were exposed to different concentrations of standard air contained within four different Tedlar bags, then stored with the sample fibers in a refrigerator. All fibers were transported on ice to the laboratory at UC Berkeley and stored at <4 °C until analyzed.

The Tedlar bag standards were also analyzed with PTR-MS to calibrate the total sesquiterpene signal (*m/z* 205). Sesquiterpenes

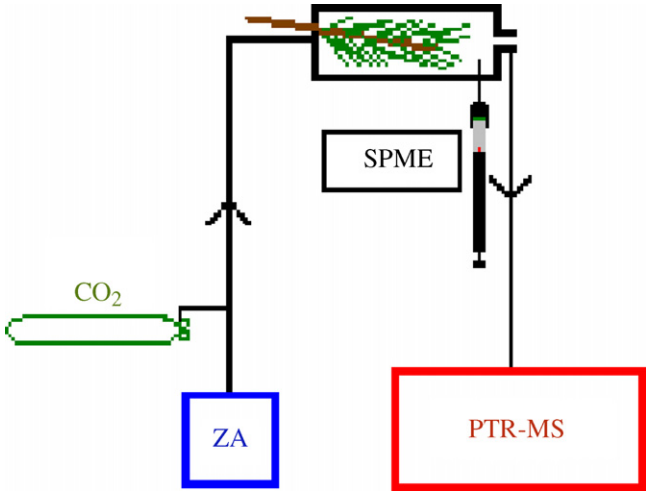

Fig. 1. Simplified schematic of the branch chamber and sampling setup. Zero air (ZA) with ambient CO_2 concentrations flowed through the enclosure, and sampling for quantification of terpenes was done with SPME fibers and a PTR-MS system.

used in this standard mixture were observed to fragment in the PTR-MS system resulting in signals at *m/z* 149 that interfered with the methyl chavicol observation. The standard mixtures always included both sesquiterpenes along with methyl chavicol, thus these were not useful for quantifying observations of methyl chavicol (*m/z* 149). Because mixing ratios of methyl chavicol calculated using an estimated rate constant for the proton transfer reaction [22] resulted in a significant underestimation, PTR-MS measurements at *m/z* 149 were scaled to methyl chavicol observed with the SPME fibers which were calibrated with an authentic standard.

Results from 6 September 2005 will be used to demonstrate how we implemented our SPME method. SPME fibers were exposed to the chamber enclosing a Ponderosa pine branch at 10:40, 12:10, 13:10, and 14:10 Pacific Standard Time (PST) for 15 min, and at 11:10 and 14:30 PST for 45 min.

3. Results and discussion

3.1. Laboratory experiments

In this section, we discuss results from tests of terpene stability in Tedlar bags, sampling temperature, and storage, describe the method of quantification, and assess the use of this method in field experiments. Air-filled Tedlar bags are a convenient way to make known concentrations of volatile compounds. However, we found the reproducibility of terpene standards measured from multiple Tedlar bags (two samples per bag, $n = 6$ bags) was not ideal, with average relative standard deviations (RSDs) of 13.8%, 27%, and 33% for monoterpenes, methyl chavicol, and sesquiterpenes, respectively. A more accurate method of creating gaseous terpene standards has been presented by Helmig et al. [5]. The data presented in each of the following individual experiments results from repeated sampling from a single Tedlar bag, thus this reproducibility issue was avoided.

3.1.1. Stability in Tedlar bags

To establish how stable the chosen compounds were in Tedlar bags over time, fibers were exposed to the same Tedlar bag containing a mixture of standards 0, 0.75, 1.5, 4.5, and 21 h after the bag was filled. Immediately following exposure, the fibers were analyzed by GC/MS. To assess the change over time, the concentration of each compound in the sample was normalized to the initial sample concentration at time zero. The monoterpene (α- and β-pinene) concentration did not significantly change over the 21-h period (RSD = 6.6%, where $n = 4$ fibers) (Fig. 2). Methyl chavicol was the least stable compound, and by 1.5 h, it had been significantly lost, presumably to the walls of the Tedlar bag. Sesquiterpenes, while more stable than methyl chavicol, were significantly lost within 1 day.

3.1.2. Sampling temperature dependence

To determine how temperatures affect sampling, Tedlar bags filled with terpene standards were placed in an oven simulating typical summer conditions. Fibers were exposed at temperatures from 23–36 °C, and then analyzed by GC/MS. Methyl chavicol and sesquiterpene compounds gave consistent results over the

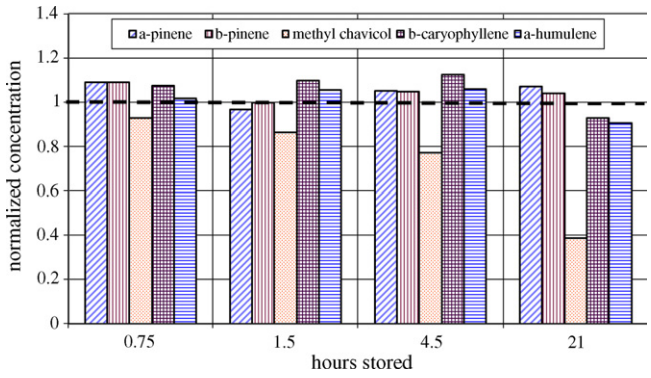

Fig. 2. The loss of terpenes from a standard mixture onto the walls of a Tedlar bag as a function of storage time. Concentration was normalized to the average initial sample concentrations at time zero.

temperature range, presumably due to their strong affinity for the fiber (Fig. 3A). Monoterpenes steadily decreased as temperature increased, exhibiting a preference for desorption from the fiber at higher temperatures (Fig. 3B). Similar mono-and sesquiterpene trends were reported for a 30–35 °C temperature span with the 50/30 μm divinylbenzene–carboxen–polydimethylsiloxane (DVB/CAR/PDMS) fiber [11].

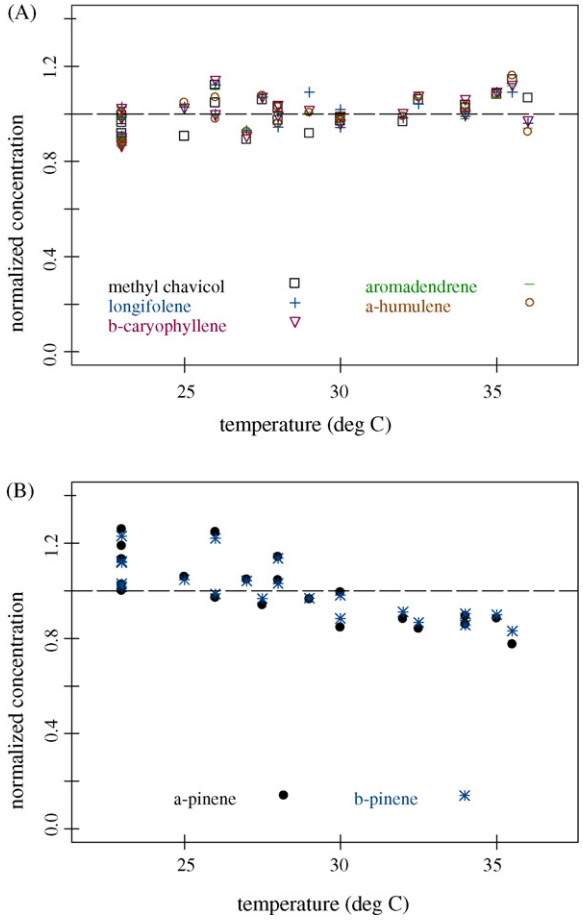

Fig. 3. Adsorption of methyl chavicol and sesquiterpenes onto SPME fibers (A) is not affected by summer daytime temperatures (23–36 °C), but monoterpene adsorption (B) is. Concentration was normalized to the average of all samples in these plots.

3.1.3. Stability in storage

To determine the appropriate storage conditions when using SPME fibers in the field, a series of fibers were exposed to a Tedlar bag containing standards, with several analyzed immediately, and the rest stored in various places under various temperature conditions for 1–2 weeks before analysis. The fibers that were analyzed immediately exhibited good reproducibility for all compounds (for eight replicates of $n = 2$ fibers, RSDs = 7.3%, 7.2%, and 4.7% for monoterpenes, methyl chavicol, and sesquiterpenes, respectively).

3.1.3.1. Storage temperature. To determine the temperature best suited for the preservation of the adsorbed sample, fibers were stored for 1 week on: (i) the lab counter, (ii) ice in an ice chest, (iii) a refrigerator shelf, and (iv) dry ice in a Styrofoam container.

3.1.3.2. Packaging material. To determine if packaging material influences fiber stability, pairs of fibers were packaged in a variety of materials with one stored on ice and the other on dry ice for 2 weeks. Materials used to surround the fiber before storage included: (i) a glass tube covered in PTFE film, (ii) an envelope made by heat sealing PTFE film and closed with PTFE tape (3M Scotch), and (iii) aluminum foil. Another pair of fibers was placed on ice and on dry ice as controls without packing material.

3.1.3.3. Diffusion during storage. To determine if diffusion of air into the needle surrounding the SPME fiber may cause contamination of the fiber during storage, fibers loaded with standards were sealed by either (i) placing a Thermogreen septum (Supelco) on the tip of an exposed needle, (ii) keeping the needle open to ambient air, or (iii) allowing the open needle to be continuously flushed with ultra high purity nitrogen. Two fibers with needles retracted behind the pierced septum in the SPME holder were used as the control. All of these fibers were kept in a fume hood at room temperature for 10 days.

To summarize results of the storage experiments, average RSDs were calculated for each compound class in each experiment, where n = the number of storage experiments in each test (Table 1). With the limits of fiber reproducibility, there was no significant difference among storage experiments for sesquiterpene and methyl chavicol (average $p = 0.28$), but monoterpenes were impacted by storage conditions with β-pinene increasing significantly compared to the control in most cases. The laboratory refrigerator was a source of contamination, likely due to its use in storing chemicals standards. At room temperature, all storage methods increased the amount of total monoterpenes detected from the fiber, irrespective of the presence or placement of the septum.

3.1.4. Method of quantification

There are two methods for quantifying the amount of analyte adsorbed onto SPME fibers. The first involves exposing the fibers to samples until the analytes reach equilibrium with the surrounding matrix ([23–25], and references therein). At the equilibrium point, a longer sampling time will not significantly

Table 1
Average relative standard deviations (RSDs) calculated for each terpene class in each storage experiment (see Section 3.1.3.)

	Monoterpenes (%)	Methyl chavicol (%)	Sesquiterpenes (%)
Storage temperature (Section 3.1.3.1.), two replicates of $n = 6$ tests	12	6.0	5.8
Packaging material (Section 3.1.3.2.), $n = 10$ tests	18	5.8	5.1
Diffusion during storage (Section 3.1.3.3.), $n = 5$ tests	12	3.2	3.6

increase the amount of analyte on the fiber. Before equilibrium is reached, the amount of analyte adsorbed is linearly proportional to the amount of analyte in the matrix and the exposure time. The second method of quantification utilizes this linear relationship.

To ascertain the maximum exposure time permissible to ensure the use of linear calibration curves, sorption profiles were created by exposing fibers to our mixture of terpene standards in Tedlar bags for 0.5–50 min. By comparing the detector response to the product of concentration times exposure time (ppb × min, an analog for sampling time at a constant concentration) (Fig. 4A), threshold values were estimated up to which a clear linear relationship is observed. For monoterpenes, the threshold value reached is essentially the equilibrium point at 1000 ppb × min. Over longer time periods, the monoterpene response decreased due to competitive sorption, consistent with

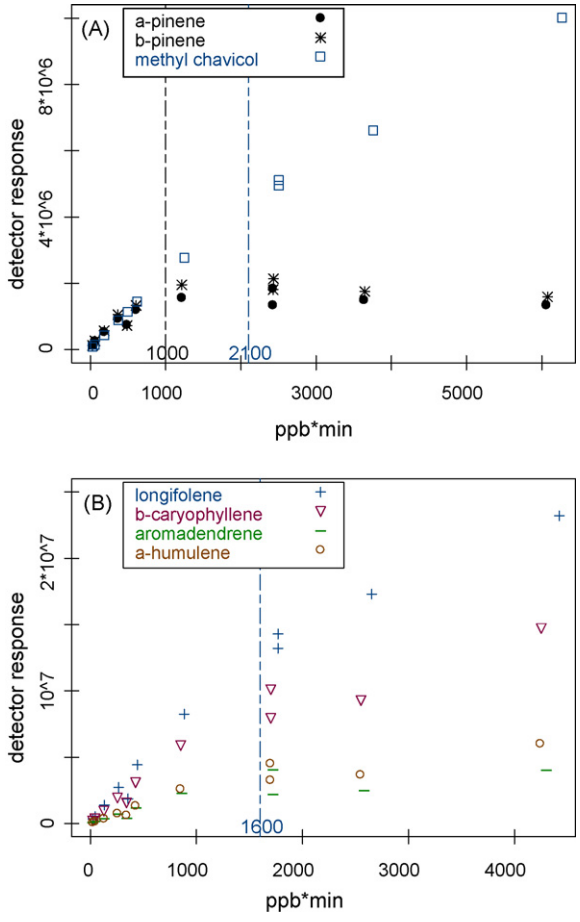

Fig. 4. (A) The threshold points for monoterpenes and methyl chavicol are 1000 and 2100 ppb × min, respectively (indicated by the dashed vertical lines). (B) The typical threshold value for the sesquiterpenes tested is 1600 ppb × min.

experiments by Adam et al. [11] with the DVB/CAR/PDMS fiber. Threshold values were estimated to be 2100 ppb × min for methyl chavicol and 1600 ppb × min for all four sesquiterpenes (Fig. 4 A and B).

The units of the threshold points (ppb × min) can be divided by the maximum concentration of each compound class expected in the branch enclosure to indicate the sampling time needed to reach this point. Estimates of total monoterpene, methyl chavicol, and total sesquiterpene concentrations in the branch chamber detected by the PTR-MS system were 50, 10–120, and 1–45 ppb, respectively. Concentrations of individual compounds in each terpene class would be lower. Based on weighted averages of these estimates (50, 15, and 5 ppb, respectively), calculated sampling times required to reach the threshold point for monoterpenes, methyl chavicol, and sesquiterpenes are 20 min, 140, and 320 min, respectively (Table 2).

Equilibrium sampling is not ideal for a field application, mainly because it is not possible to optimize the sampling time in order to quantify all compounds of interest. The sorption profile created (Fig. 4), with a maximum of 6000 ppb × min, was insufficient to reach clear equilibrium points for methyl chavicol and sesquiterpenes, but it was long enough to significantly oversaturate monoterpenes and cause competitive exclusion. Also, environmental factors that determine terpene emission rates will not be constant over the long exposure time needed to reach the equilibrium point for methyl chavicol or sesquiterpenes.

3.2. Field experiments

Based on the laboratory experiments, we developed a protocol for using the SPME fibers in field experiments. We did not quantify monoterpenes because the laboratory measurements showed that they were unstable on the PDMS/DVB fibers and had storage contamination problems. Our field experiment protocol was optimized for the quantification of sesquiterpenes and methyl chavicol. In order to use a linear calibration curve, the exposure time multiplied by the sample concentration must not exceed the smallest equilibrium point (1600 ppb × min), which limits the exposure time in the branch enclosure to a maximum of 107 min. For our study, we exposed fibers for 15 and 45 min and chose the concentrations of our standard mixtures so that after multiplying by the exposure time, the average quantity was less than 700 ppb × min. Since the expected range of daytime summer temperatures in the field (23–36 °C) did not affect the adsorption of methyl chavicol or sesquiterpenes, sampling could occur in the afternoon to capture peak emissions. Fibers were exposed to Tedlar bags filled with terpene standards on the first and last day of each 2 week sampling period throughout the summer. Because methyl chavicol was significantly lost to the walls

Table 2
Maximum SPME sampling times allowable to utilize the linear portion of the calibration curve for quantifying concentrations

Compound class	Threshold point (ppb × min)	Concentration in chamber (PTR-MS) (ppb)	Maximum exposure time (min)
Monoterpenes	1000	50	20
Methyl chavicol	2100	10–120	140
Sesquiterpenes	1600	1–45	320

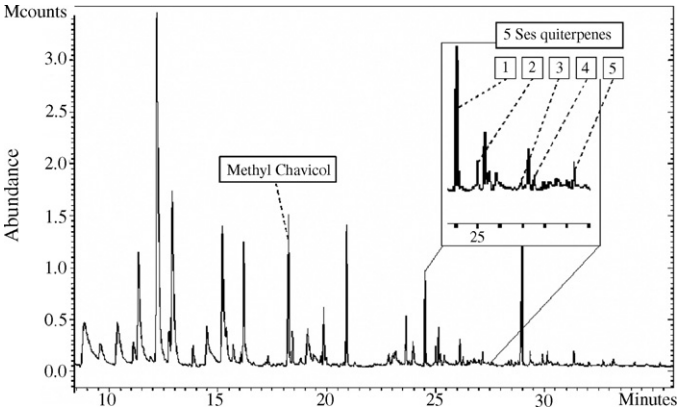

Fig. 5. The chromatogram from a 45 min exposure to the Ponderosa pine branch at 14:30 PST on 6 September 2005. Peaks corresponding to methyl chavicol and five sesquiterpenes are indicated. Some of the sesquiterpenes have been identified: #1, α-bergamotene; #2, β-farnesene; #4, α-farnesene.

of the Tedlar bag within 1 h after the bag was filled (see Section 3.1.1.), we were careful to expose fibers to the Tedlar bags immediately after the standard mixtures were made. Although the results from testing different storage materials were inconclusive, we stored our fibers in a refrigerator at the field site and on ice for transport.

Results are shown from 1 day of sampling (6 September 2005) and are provided principally as a demonstration of the use of our SPME method. Of the 5 distinct sesquiterpenes emitted from the branch (Fig. 5), α-bergamotene and β-farnesene were identified in every sample of the diurnal profile, and α-farnesene was detected in the samples taken at 11:10, 14:10, and 14:30 PST. Throughout the entire field campaign, 26 different sesquiterpenes were observed. A linear calibration curve (e.g. Fig. 6)

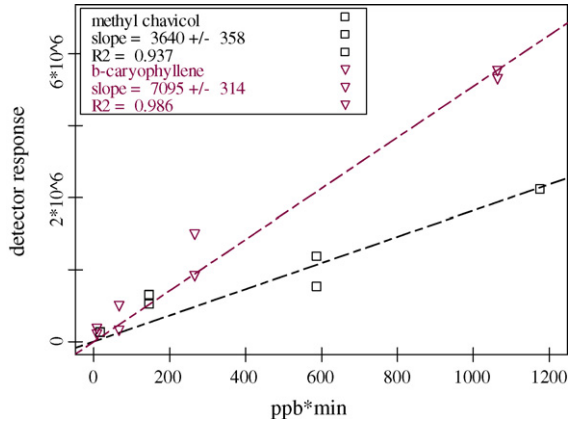

Fig. 6. An example of the calibration curves constructed from terpene standards during the summer 2005 field experiment used to calculate methyl chavicol and sesquiterpene concentrations.

constructed from the analysis of standard fibers was utilized to calculate methyl chavicol and total sesquiterpene concentrations (Table 3). β-Caryophyllene was used to create the sesquiterpene calibration curve because it was the only sesquiterpene compound present in both the standard Tedlar bags and some of the field samples. The highest methyl chavicol concentration was seen at 14:10 PST, while maximum total sesquiterpene concentration was seen at 14:30 PST. Table 3 shows all results from 6 September. These data reasonably reflect the temperature dependence of terpene emissions. Lower concentrations measured in the morning and when the chamber was artificially shaded with foil was due to the decrease in temperature experienced by the branch.

3.2.1. Method validation

Time series of observed concentrations from 6 September 2005 show that the amount of sesquiterpenes and methyl chavicol measured using PTR-MS and SPME fiber methods agree reasonably (Fig. 7). To adequately compare these methods, PTR-MS concentrations were averaged for the time periods when the fiber was exposed. Quantification by PTR-MS of total sesquiterpenes emitted from all sampled Ponderosa pine branches throughout the summer correlates well with the total amount of sesquiterpenes quantified using SPME fibers (slope = 1.01 ± 0.06 and R^2 = 0.82). Slight discrepancies in the individual measurements are likely due to the variation in the mixture of the emitted sesquiterpenes. While the PTR-MS system was calibrated using four sesquiterpene standards, only β-caryophyllene was used to calibrate the fibers. Each individual compound may have a slightly different affinity for the fiber and may also fragment differently in the PTR-MS instrument. PTR-MS measurements of methyl chavicol were scaled to match the SPME measurements, but the two methods agree in terms of temporal variations (R^2 = 0.87).

Detection limits, defined as the amount of standard required to create a peak 3 times the baseline noise, were calculated on the basis of the field standards. The average detection

Table 3
Concentrations of methyl chavicol and total sesquiterpenes emitted from the Ponderosa pine branch enclosed on 6 September 2005

Exposure time (PST)	Sunlight	Methyl chavicol (ppb)	Total sesquiterpenes (ppb)
10:40–10:55	Shaded	1.98	2.10
11:10–11:55	Partly sunny	2.86	3.07
12:10–12:25	Full sun	6.43	4.53
13:10–13:25	Shaded Al foil	4.03	3.69
14:10–14:25	Full sun	6.80	7.66
14:30–15:15	Full sun	5.62	8.17

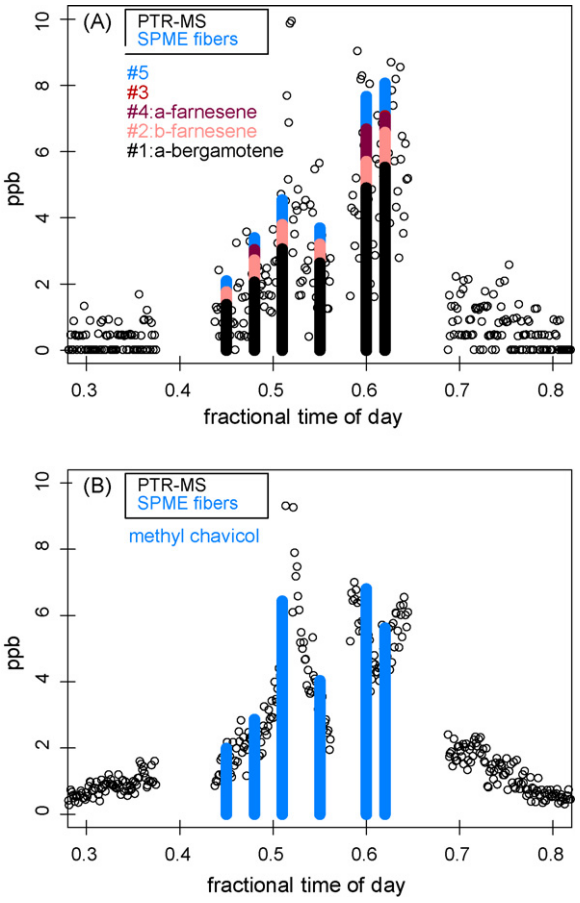

Fig. 7. Methyl chavicol and sesquiterpene concentrations emitted from the Ponderosa pine branch were measured using PTR-MS (open circles) and SPME fibers (bars). The SPME fiber data is broken into the individual sesquiterpene compounds detected.

limit for methyl chavicol was 4.36 pmol/mol (ppt) whereas the detection limit for β-caryophyllene was 16.6 ppt. Sources of random error include the accuracies of pipets and the multiple syringes used for terpene dilutions and injections into the Tedlar bag, the consistent accuracy of the flow controller (3–5% total), and reproducibility between different fibers (e.g. see Section 3.1.3.). All of these sources are minor compared to the reproducibility between standards sampled from multiple Tedlar bags using multiple SPME fibers (see Section 3.1.).

4. Conclusions

A protocol is defined for the quantification of sesquiterpene and oxygenated terpene compound emissions from live vegetation. This method is particularly useful due to the simple features of the SPME fiber—direct adsorption eliminates the loss of these compounds to the walls of sampling lines and instrument parts, while direct desorption eliminates the need for solvents. Semi-volatile compounds, such as sesquiterpenes and oxygenated terpenes, have been difficult to measure using traditional methods because they are easily lost in the sampling process, but their adsorptive characteristics also make them ideal analytes for sampling with SPME fibers due to their high affinity for adsorption onto surfaces. Methyl chavicol and sesquiterpenes were shown to be stable on the fibers in storage as long as they remain below ambient temperatures. Laboratory experiments also showed the importance of limiting the time between making terpene standard mixtures in Tedlar bags and exposing SPME fibers. Short exposure times ensure the usefulness of linear calibration curves for quantification of multiple types of compounds. A 10–45 min range of exposure times was used in the study described here. SPME fibers make fast and easy quantification of semi-volatile terpenes possible. The portability of the technique allows for the sampling of live vegetation using an enclosure in the field. This method can therefore be considered a well suited technique for emission measurements to help reduce the large uncertainties in the reactive terpene budget.

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