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Analysis of sesquiterpene emissions by plants using solid phase microextraction

Brad Baker*, Mark Sinnott

California State University, Sacramento, Department of Chemistry, 6000 J Street, Sacramento, CA 95819, USA

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ABSTRACT

Solid phase microextraction (SPME) was characterized for the sampling and analysis of sesquiterpenes (SQTs) emitted by plants. Constant mixing ratio SQT standards were produced using a capillary diffusion system. Polydimethylsiloxane SPME fibers were characterized with respect to relative absorption of SQTs, and the effects of sample linear velocity and sample relative humidity on SQT absorption. SPME was then utilized to measure SQT emissions from gray pine (*Pinus sabiniana*) and ponderosa pine (*Pinus ponderosa*). Total SQT emission rates at a photosynthetic photon flux density of 1200 $\mu mol\,m^{-2}\,s^{-1}$ and 28 °C ranged 0.025–0.050 $\mu gC\,m^{-2}\,h^{-1}$ (α-farnesene) and 0.450–3.325 $\mu gC\,m^{-2}\,h^{-1}$ (α-farnesene, β-farnesene, and α-bergamotene) for gray pine and ponderosa pine, respectively.

1. Introduction

Sesquiterpenes (SQTs) include a broad range of biogenic volatile organic compounds (VOCs) made up of three isoprene units and having the general molecular formula $C_{15}H_{24}$. In the Earth's atmosphere SQTs react within minutes with O_3, OH, and NO_3 [1] to produce numerous products including multifunctional aldehydes, ketones, alcohols, and carboxylic acids that have vapor pressures much less than the parent compound [2–4]. Chamber studies have shown aerosol yields for various SQTs ranging from near zero to almost 100% [5–7]; and therefore, the key interest in SQTs is their contribution to secondary organic aerosol (SOA). SOA, including that produced through the oxidation of SQTs, is important to global climate. First, SOA can scatter sunlight, reflecting some back to space and effectively cooling the atmosphere. Second, SOA can act as cloud condensation nuclei and have an influence on both the albedo and lifetime of clouds. Quantitative estimates of the extent of aerosol effects on climate have very high uncertainties [8]. One of the many factors contributing to these uncertainties is that the source of SOA is not well characterized. This includes the contribution that VOCs, including SQTs, make towards global SOA. Recent estimates of the mass of SOA produced by VOCs range from under 100 $TgC\,yr^{-1}$ [8] to as high as 900 $TgC\,yr^{-1}$ [9].

One of the largest uncertainties regarding SQTs is their emission rate from vegetation. Ozone deposition data at a field site dominated by ponderosa pine in the Sierra Nevada foothills in California suggest that emissions of very reactive BVOCs are on average 10 times greater than those of measured monoterpenes [10,11]. Due to their very short lifetimes, it is suspected that these compounds are mostly SQTs. This relatively high emission of SQTs would also make them important as a sink for ozone and a source of hydroxyl radical [10,11]. Direct emission measurements of ponderosa pine suggest SQT emissions that are roughly equal to or much less than monoterpene emissions [12,13]. The most current estimate for SQT emissions for the continental United States based on scaling up plant level emission measurements shows that average mid-summer total SQT emissions are more than 10 times less than emissions for total monoterpenes on a carbon-mass basis [14]. However, this modeling effort only included 4 different plant functional types and utilized branch or leaf level emissions data from only 4 studies.

Considerable attention has been given to SQTs only recently due to the fact that these compounds are relatively difficult to quantify in air. In addition to their high reactivity that leads to their general absence in ambient air samples, SQTs also tend to have low vapor pressures. Both of these properties cause losses of SQTs in analytical systems that are routinely used to accurately quantify other BVOCs such as isoprene and the monoterpenes [15]. It additionally presents a challenge in making calibration standards, which are usually produced by diluting part per million level mixing ratios of an analyte that is contained in a compressed gas cylinder. SQT standards prepared in this way are predicted to be unstable [15]. One way to avoid the problem of compressed gas standards is to use a capillary diffusion system to create known mixing ratios of SQTs in air [15]. Once reliable standards are available, there is also the potential for analyte losses during the sampling and analysis process. One way to deal with this is to test all materials that the sample will contact and quantify losses [16]. Another way to deal with this

* Corresponding author. Tel.: +1 916 278 7409; fax: +1 916 278 4986.
E-mail address: bbaker@csus.edu (B. Baker).

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issue is to use an analysis technique that virtually eliminates contact of the sample with any surfaces. Solid phase microextraction (SPME) is a technique that can be used to accomplish this.

SPME was initially designed as a simple procedure to extract analytes directly from the liquid phase [17]. It involves exposing a polymer-coated fiber to the sample matrix where analytes absorb onto the fiber until equilibrium is reached between the fiber and sample matrix. Alternatively, the fiber can be exposed to the sample matrix for a fixed amount of time and removed before equilibrium is reached. The fiber is then inserted into a heated gas chromatograph (GC) injector where the analytes are desorbed and swept directly onto the separation column. This method has also been found to work well for sampling and analyzing trace constituents in gas matrices [18]. Sample collection by SPME reduces the number of surfaces analytes encounter, thus reducing the chance of systematic analyte losses. Another advantage to using SPME is that the technique avoids the use of bulky and expensive air sampling and analysis equipment. A GC instrument that is set up to analyze liquids can also be used to analyze either liquid or gas samples collected by SPME. Finally, polymers used with SPME do not absorb much water. In air samples that are collected for analysis by GC, water interference is a problem that commonly arises and must be dealt with.

SPME has only been used infrequently for the analysis of BVOC emissions from live vegetation. Zini et al. [19] used SPME to analyze for a wide range of BVOC emitted by *Eucalyptus* including β and α caryophyllene. However, the analysis was not quantitative as they lacked appropriate gas phase standards. More recently, Bouvier-Brown et al. [20] utilized SPME to look specifically at SQTs emitted primarily by ponderosa pine growing in the foothills of the Sierra Nevada. Calibration standards were produced by injecting small volumes of diluted SQTs into Tedlar bags filled with zero air. Although quantitative, they found high variability in the prepared standards with a 33% relative standard deviation for the analysis of multiple SQT standards.

The goal of the study presented here was to characterize the use of SPME for the sampling and analysis of SQTs emitted by plants contained in a branch or whole plant enclosure. A focus was placed on generating calibration curves for SQT compounds, and determining the effects of different sampling conditions on the absorption of SQTs onto the SPME fiber. These conditions include: humidity, changing linear velocity over the SPME fiber, and analyte mixing ratio changes during sampling. In addition, SQT emission rate data is presented for gray pine (*Pinus sabiniana*) and ponderosa pine (*Pinus ponderosa*) trees.

2. Experimental

2.1. Standard generation

SQT standards were generated using a 4 channel capillary diffusion system (CDS). The system was based on the design presented by Helmig et al. [15]. Fig. 1 is a schematic diagram showing the flow path and key characteristics of this system. Approximately 200 μL of standard compounds in their pure liquid form (Sigma–Aldrich Corp., St. Louis, MO) were placed in small glass vials (Agilent Technologies, Santa Clara, CA) and attached to a diffusion capillary made from either fused silica (Agilent Technologies, Santa Clara, CA) or Silcosteel® (Restek, Bellefonte, PA). The diameter of the diffusion capillary was chosen such that the relative amounts of the 4 standards exiting the CDS were within the same general range. Higher boiling compounds (later eluting compounds) required shorter capillaries with larger inner diameters relative to SQTs with lower boiling points. Table 1 gives specific details regarding the SQTs used for standard compounds, and the dimensions of the diffusion capillaries for each SQT. 1,3,5-Triisopropyl benzene was always included in one channel of the CDS as an internal standard. This compound has the same molecular mass as the SQTs, a boiling point in the same range as the SQTs, but its structure does not represent three isoprene units and it is not known to be emitted by vegetation. Cis and trans nerolidol are oxygenated SQTs, and were also included as standards. Ultra high purity (UHP) N_2 was passed over each diffusion capillary and was used to carry the diffused standards through the system and to avoid oxidation of the highly reactive SQT standards that would occur if zero air were used [15]. The total flow of N_2 into the CDS was controlled by a mass flow controller (MFC, Unit Instruments, Yorba Linda, CA) set at a flow rate of 100 standard cubic cm per min (SCCM). Within the CDS, a capillary restrictor composed of 40 cm of 0.18 mm inner diameter fused silica was directly downstream of each diffusion tube and controlled the relative flows of N_2 through each channel of the CDS and established a pressure of approximately 212 kPa in the diffusion vials. A three-way valve (Swagelok, Solon, OH) was used in each channel such that any mixture of the 4 standards contained in the CDS could be either directed to vent or included in the standard mixture exiting the CDS. The entire system was enclosed in a heated box. The glass vials containing the liquid standards were held in depressions drilled into a brass heater block. A strip heater (Omega, Stamford, CT) was used to heat the CDS box and the brass block. The temperature of the block was controlled to $75 \pm 0.1\ ^\circ C$ using a standard PID controller (Omega, Stamford CT). All fittings within the CDS

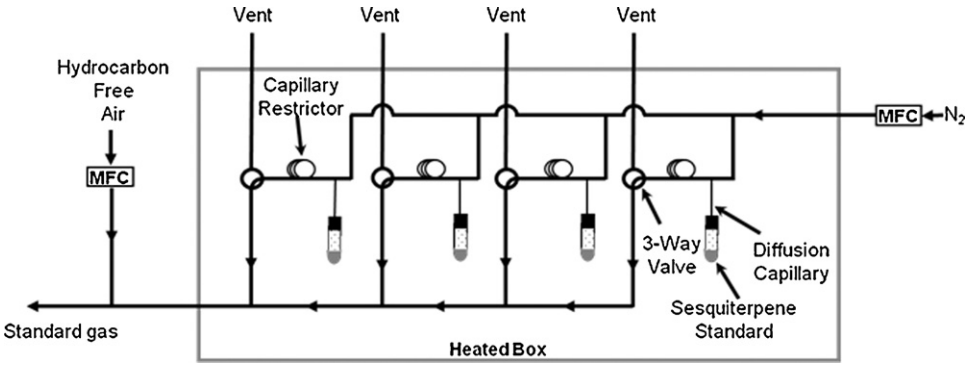

Fig. 1. Schematic of the capillary diffusion system (CDS). Pure SQT standards were placed in small vials and allowed to diffuse in a temperature controlled environment. Diffusion from each vial was controlled by a diffusion capillary (see Table 1). Capillary restrictors were used to regulate N_2 flow passing by each standard vial. A three-way valve was used to direct each standard for inclusion/exclusion from the standard mixture exiting the CDS. Flow through the system is depicted by arrows. Flow of UHP nitrogen through the system was controlled by a mass flow controller. Hydrocarbon free air was added to the effluent of the system and used for dilution.