20 Mar 2012

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Recommended Citation

E. M. Sheehan et al., "Time-Weighted Average SPME Analysis for in Planta Determination of CVOCs," *Environmental Science and Technology*, vol. 46, no. 6, pp. 3319 - 3325, American Chemical Society, Mar 2012.

The definitive version is available at https://doi.org/10.1021/es2041898

Environmental Science & Technology

Article

pubs.acs.org/est

Time-Weighted Average SPME Analysis for *in Planta* Determination of cVOCs

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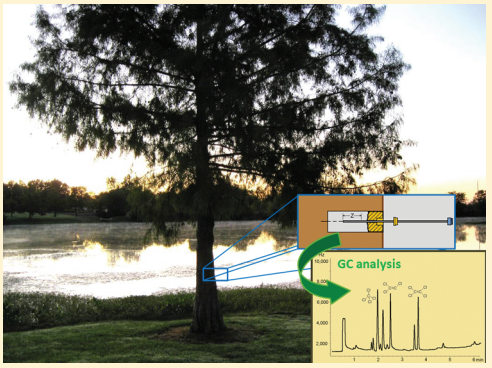
Supporting Information

ABSTRACT: The potential of phytoscreening for plume delineation at contaminated sites has promoted interest in innovative, sensitive contaminant sampling techniques. Solid-phase microextraction (SPME) methods have been developed, offering quick, undemanding, noninvasive sampling without the use of solvents. In this study, time-weighted average SPME (TWA-SPME) sampling was evaluated for *in planta* quantification of chlorinated solvents. TWA-SPME was found to have increased sensitivity over headspace and equilibrium SPME sampling. Using a variety of chlorinated solvents and a polydimethylsiloxane/carboxen (PDMS/CAR) SPME fiber, most compounds exhibited near linear or linear uptake over the sampling period. Smaller, less hydrophobic compounds exhibited more nonlinearity than larger, more hydrophobic molecules. Using a specifically designed *in planta* sampler, field sampling was conducted at a site contaminated with chlorinated solvents. Sampling with TWA-SPME produced instrument responses ranging from 5 to over 200 times higher than headspace tree core sampling. This work demonstrates that TWA-SPME can be used for *in planta* detection of a broad range of chlorinated solvents and methods can likely be applied to other volatile and semivolatile organic compounds.



INTRODUCTION

Recent research has shown that plants can translocate subsurface contaminants, thereby acting as biosensors to aid in understanding of subsurface chemistry,[1−3] a process termed phytoforensics.[4] A particular phytoforensic application, phytoscreening, employs existing trees or new phytoremediation-based plantings as sampling points to serve in plume delineation or monitoring. Plants are extremely efficient at actively removing water and obtaining nutrients from the subsurface, which simultaneously allows a range of contaminants to be translocated to above-ground tissues, even when present at very low chemical potentials. Some contaminants available for plant uptake include volatile and semivolatile organics, petroleum hydrocarbons, metals, polycyclic aromatic hydrocarbons, nutrients, and explosives, although chlorinated solvents are most frequently encountered for phytoscreening applications.[5−8] Detecting these contaminants requires sensitive methods, as a number of contaminant-specific loss mechanisms, such as volatilization, phytodegradation, or endophytic degradation, may reduce plant concentrations relative to groundwater concentrations.[9,10] Further understanding of contaminant interactions in the water−soil−gas−plant continuum may lead to more effective plant tissue sampling and analysis, thereby allowing better understanding of the underlying water, soil, and vapor chemistry. Phytoscreening offers great potential for rapid site assessments because of its effective, economical, and noninvasive nature.[11−14]

Concentrations of chlorinated volatile organics (cVOCs) in tree tissues have typically been analyzed by headspace analysis of tree core samples or by direct measurement of the volatilization of contaminants from the transpiration stream through the use of diffusion samplers.[3,15,16] Although these methods do provide valuable data, each has limitations. Tree core sampling requires time for each sample to equilibrate with the headspace (typically 24 h).[1] Similar equilibration periods apply to methods for sampling the branches or leaves of trees.[17] Headspace sampling, while straightforward and solvent-less, dilutes the contaminant concentration into the headspace volume and is limited to highly volatile compounds, as the majority of the semivolatile compound mass will remain in the tissue. Optimization of headspace methods is possible (e.g., heating, ref 11), but is difficult to apply to *in planta* sampling. Tree core analysis is also limited by sampling volume, as a tree core effectively samples only a very small percentage of the total tree mass. Contaminant concentrations have been shown to vary with height and radius, therefore the results from an

Received: November 22, 2011
Revised: February 10, 2012
Accepted: February 14, 2012
Published: February 14, 2012

   dx.doi.org/10.1021/es2041898 | Environ. Sci. Technol. 2012, 46, 3319−3325

individual tree core may not accurately reflect the overall concentration in the tree.[1,2,18]

Diffusion samplers, another common method, operate by collecting contaminants volatilized from a tree's leaves and/or stems. Typically, the contaminants diffusing out from the biomass are collected in a sealed collar around the trunk of the tree or a bag placed over selected leaves of the tree.[19−21] Negative pressure is maintained in the collection device through a pump. The pumped air is drawn through an adsorptive material, such as activated carbon, for collection of contaminants. The method requires relatively long sampling times, portable equipment (pump), and aggressive desorption with a thermal desorber or solvents in the analytical or sample preparation steps. This sampling method is also subject to background contamination.

Solid-phase microextraction (SPME) has been applied to a wide range of environmental media for an array of analytic applications,[22−24] including *in planta* analysis to measure compounds in plants. A variety of compounds have been investigated, such as herbicides,[25] as well as numerous volatiles and semivolatiles.[26] The solvent-less extraction technique directly interfaces with a gas chromatograph (GC) to combine sample extraction and desorption. The technology uses a thin layer of high-sorption material, creating a sampler with a high surface to volume ratio for rapid kinetics. Detection limits can be low, although fiber kinetics may be affected by temperature, pressure, humidity, barriers to diffusion, boundary layer thickness, competitive adsorption, and sorption capacity.[27−29] Chemical properties that govern the interaction of compounds with the polymer coating include volatility, polarity, molecular weight, and structure.

SPME fibers can be operated in two broad regimes: equilibrium or kinetic. In the equilibrium regime, calibration requires partition coefficients that accurately describe analyte partitioning during sampling.[30] SPME equilibrium sampling of tree tissue for VOCs using the absorptive PDMS coating has been recently described.[14,24] Unfortunately, for highly volatile analytes it remains difficult to obtain sufficient detection limits with this approach due to the rather limited PDMS to air partitioning coefficients. Much lower detection limits are possible when using adsorptive, rather than absorptive, SPME coatings, but these coatings are difficult to apply to well-defined equilibrium sampling. In the kinetic regime, calibration requires knowledge of uptake rates that can be strongly affected by sampling conditions, such as air mixing/boundary layers, humidity, and temperature. Passive samplers are increasingly preloaded with performance reference compounds (PRC) to deduce uptake rates from the release kinetics of the PRCs.[31] Although this approach works well for absorptive sampling when rate-limited by mass transfer through the air, it is much more difficult to apply for adsorptive sampling of highly volatile analytes.

For such volatile analytes, reproducible uptake kinetics can be accomplished by including a diffusion barrier to achieve time-weighted average (TWA) sampling. The purpose is to combine a characterized, rate-limiting diffusion step with a "zero sink" sampling phase to ensure meaningful sampling rates and avoid back diffusion. This method of sampling has been widely applied to PAHs,[32] BTEX,[27,33] semivolatile organics,[33−35] volatile sulfur compounds,[28] C5−C11 n-alkanes,[29] and formaldehyde.[36,37] In TWA-SPME, the fiber is retracted into the needle to limit mass transfer such that Fick's first law applies to diffusion through the needle cross-section (Figure 1).[29,33,37−40] The measured average concentration in the media ($\bar{C}$) is dependent on needle cross-sectional area (A), diffusion path length (Z), sampling time (t), analyte diffusivity in air or water (D), and the analyte mass extracted (n), as shown in eq 1.[32]

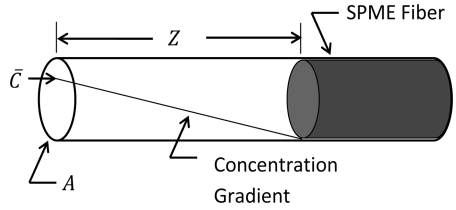


Figure 1. Schematic of TWA-SPME, showing Fickian diffusion through the needle and the idealized concentration gradient in the sampler. The fiber is retracted a distance Z into the needle.

$$\bar{C} = \frac{nZ}{ADt} \tag{1}$$

Three important assumptions are made in writing eq 1.[33] First, the concentration at the sampler face must equal the concentration in the bulk phase (i.e., well-mixed system). Second, the sampler must respond proportionally to ambient concentrations (i.e., rapid response time). Third, the fiber must remain a "zero sink" for the analyte during the extraction process. If the fiber concentration becomes greater than 5% of the equilibrium fiber concentration, the response over time will be nonlinear due to decreasing analyte flux.[41]

This study evaluates the effectiveness of TWA-SPME for qualitative and quantitative analysis of several chlorinated solvents commonly found in contaminated groundwater. In addition, the use of TWA-SPME for *in planta* sampling is demonstrated. For *in planta* sampling, TWA-SPME analysis can sample a larger portion of the tree in a potentially quantifiable way, as mass transfer can be limited by the needle, not by diffusion through the tree. Coupled with a portable GC, *in planta* SPME-TWA can improve phytoscreening by yielding groundwater information onsite, allowing adaptive sampling plans that are better able to locate concentrated areas of contamination.

MATERIALS AND METHODS

Two SPME fibers were used in the analyses: a 100-μm polydimethylsiloxane (PDMS) fiber and an 80-μm composite PDMS/Carboxen (PDMS/CAR) fiber (Supelco, Bellefonte, PA). A Supelco SPME fiber holder was used to handle the fibers and set the retraction lengths. Prior to sampling, all SPME fibers were conditioned in the GC injection port by fully exposing them for 10 min at 250 °C.

The compounds used in this study included three classes of chlorinated solvents: chloromethanes, chloroethanes, and chloroethenes. Within each compound class, three compounds were chosen for study because of their physical properties and likelihood of contamination in the environment. The compounds studied were dichloromethane (DCM), chloroform (CF), carbon tetrachloride (CT), 1,2-dichloroethane (DCA), 1,1,2-trichloroethane (TCA), 1,1,2,2-tetrachloroethane (TetCA), *cis*-1,2-dichloroethene (cDCE), trichloroethene (TCE), and tetrachloroethene (PCE). All compounds were acquired from Fisher Scientific and were reagent grade or higher purity.

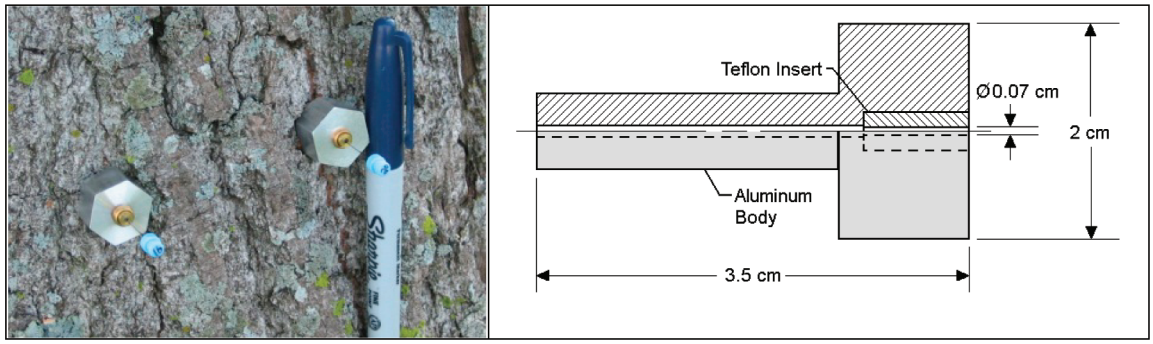


Figure 2. Left: *In planta* sampler and SPME sampling port during sampling at the Kellwood Site. Right: Half-section view of SPME sampling port.

All samples were analyzed by an Agilent 6890N GC with μECD detection. The GC inlet was set at 250 °C with a 0.75-mm diameter inlet liner for SPME samples. The GC was operated in constant pressure mode with an average carrier gas (nitrogen) velocity of 30 cm/s. Oven temperatures varied by compound class: 30 °C (isothermal) for chloromethanes; 30 °C for 1.5 min, 20 °C/min to 100 °C for chloroethanes; and 50 °C for 2 min, 20 °C/min to 100 °C for chloroethenes. All runs were 6 min in duration using an HP-5 column (30 m × 0.32 mm × 0.25 μm).

Extraction Method Sensitivity. Sensitivity of the SPME methods was evaluated against headspace sampling. Standard solutions were prepared using silicone oil as the solvent (Acros Organics, Geel, Belgium). The silicone oil was then applied as a passive dosing phase for the buffering of analyte concentrations in the headspace. The buffered concentrations allowed for longer sampling times without depleting the headspace.[24]

All extraction techniques were tested at four concentrations: 1, 10, 50, and 100 mg/L of PCE and TCE in silicone oil. Headspace sampling was performed using a 0.25-mL injection, while the PDMS fiber was exposed to the vial headspace for 5 min to reach equilibrium.[14,23] TWA-SPME sampling utilized the PDMS/CAR fiber at a retraction distance of 0.5 cm and extraction times of 10 min, 1 h, and 2 h. All sampling was performed at 30 °C.

TWA Linearity. To use TWA-SPME in the field quantitatively, method linearity for chlorinated solvents was tested using the 80-μm PDMS/CAR SPME fiber. This composite fiber is a good candidate for TWA-SPME, as it has a higher affinity for small VOCs than a PDMS fiber.[42,43] Sampling was conducted by exposing the fiber to the headspace above spiked silicone oil for a specified duration with the fiber retracted a known distance into the needle housing. Sampling times were 0.5, 2, 5, 15, 30, 60, and 120 min for each retraction length (0.5, 1.0, and 1.5 cm) and each compound class.

Samples were prepared by placing approximately 1 mL of spiked solution into 22-mL glass vials capped with Teflon-lined septa. Neat chlorinated solvents were added to silicone oil to give a stock solution for each compound class. These solutions were then diluted 100-fold in silicone oil to arrive at the experimental concentrations, as shown in Table SI1. Before sampling, the vial was rotated to allow the sample to coat the sides of the vial, increasing mass transfer to the headspace. During sampling, the vial, holder, and fiber remained motionless and at room temperature on the lab bench. Immediately after sampling, fibers were analyzed by GC.

For consistency, a single fiber, vial, and spiked solution sampled each contaminant class, which increased the potential for depletion of the solution as contaminant mass was removed by each sampling event. Equilibrium sampling was conducted in duplicate before and after each TWA-SPME experiment to verify that the sample headspace was not substantially depleted during TWA-SPME sampling and to obtain a measurement of headspace concentration. Equilibrium sampling was conducted by fully exposing a PDMS SPME fiber in the headspace for 4 min. Analysis was performed using the GC methods described above.

To examine linearity, linear regression was performed in SAS using PROC REG (SAS Institute, Cary, NC). Equation 1 was rearranged such that TWA peak area (PA) normalized by equilibrium sampling PA was regressed against sampling time divided by retraction distance (eq 2).

$$\frac{\mathrm{PA_{TWA}}}{\mathrm{PA_{EQ}}} \propto \frac{n}{\overline{C}} = DA\left(\frac{t}{Z}\right) \tag{2}$$

To ensure homoscedasticity, both quantities were $\log_{10}$ transformed. The resulting linear equation was fitted by the procedure, where M is a parameter with a value of unity if the two quantities are linearly related (eq 3).

$$\log_{10}\left(\frac{n}{\overline{C}}\right) = M\cdot\log_{10}\left(\frac{t}{Z}\right) + \log_{10}(DA) \tag{3}$$

TWA-SPME was considered linear for the analyte if the 95% confidence interval of M included unity.

Field Sampling. Field sampling was conducted at the Kellwood Site (OU2) of the Riverfront Superfund Site in New Haven, Missouri. Previously, the subsurface PCE contamination at the Riverfront Superfund Site (OU1) and at the Kellwood Site was characterized using tree core sampling.[2,44]

Tree cores were taken using a 5-mm increment borer as described previously.[1] Cores were immediately transferred to a 22-mL vial and capped with Teflon-lined septa. The samples were stored for 24 h at room temperature before analysis to allow equilibration between the vial headspace and the tree tissue. Tree cores were analyzed by sampling the headspace with a 0.1-mL syringe followed by direct injection into the GC.

In planta sampling of the tree using the PDMS/CAR SPME fiber was performed in the tree void space after the core had been removed. A SPME *in planta* sampler was designed and constructed to create a volume of sealed headspace for SPME sampling. Several other design considerations included that the sampler be constructed of an inert material, be rugged and reusable, and support the SPME fiber to prevent contact with the tree.

A total of six tree cores were taken from five individual trees at the Kellwood site. All trees were poplars, with heights between 3 and 20 m. Following the collection of tree cores, the

in planta sampler was inserted into the tree core void space. Figure 2 shows a photograph taken at the Kellwood Site demonstrating *in planta* SPME sampling and a schematic of the sampler. A fiber retraction distance of 0.5 cm was set prior to insertion into the *in planta* sampler, with the exception of tree 5 near the plume boundary, where the fiber was fully exposed. The sampling time began when the SPME device was inserted into the *in planta* sampler and continued for approximately 70 min. After sampling was complete, the SPME devices were removed from the *in planta* samplers and capped with a Teflon cap, shown to reduce analyte losses during transportation (see ref 45 and Supporting Information for details).

SPME fibers were transported to the Missouri S&T campus for analysis, approximately 1−2 h after sampling. Analysis was conducted using the GC method for chloroethenes, described above. After analysis, each fiber was dosed with a chloroethenes standard to check for fiber damage during field sampling or transport. Fiber integrity was confirmed by comparing GC results with previous analyses under similar conditions.

RESULTS AND DISCUSSION

Extraction Method Sensitivity. TWA-SPME with a PDMS/CAR fiber yielded higher GC response than equilibrium SPME-PDMS or headspace sampling. For TCE and PCE, the 1-h and 2-h TWA sample responses exceeded the response of the PDMS fiber and headspace sampling. The response curves are shown in Figure 3 and Figure 4. A 10-min

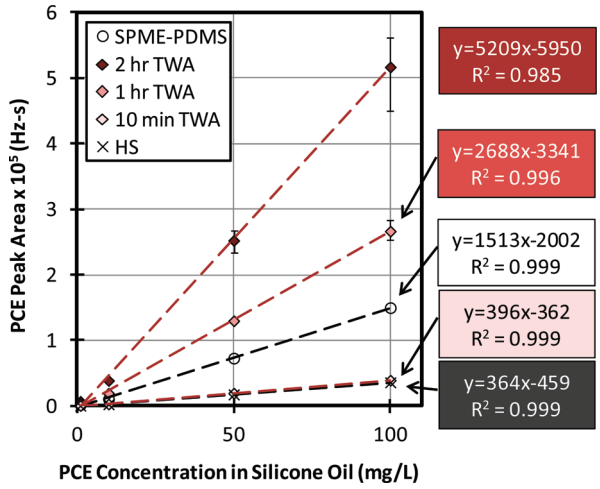


Figure 3. PCE: Effect of extraction method on GC response. Error bars denote maximum and minimum values (n = 3).

TWA sample was most comparable to headspace and equilibrium SPME sampling. This large response of TWA-SPME analysis illustrates the advantage of the method, especially over headspace analysis, although longer extraction times are required. Although not shown here, SPME can also decrease peak width, allowing better peak separation and lower detection limits for these chlorinated solvents.[14]

TWA Linearity. The response of the PDMS/CAR fiber was generally found to be linear or near linear for many of the compounds. The linearity parameter, M, was within a confidence interval of unity for chloroform and carbon tetrachloride (see Figure 5). All other compounds exhibited nonlinearity, with M values less than unity, indicating decreasing uptake rates with time. Decreasing uptake rates imply a violation of "zero sink" conditions over the measurement period. The "zero sink" condition is most likely to be violated when mass loading is high as a result of high molecular diffusivities, low fiber affinity, long sampling times, or small retraction distances. This is most evident when comparing chloromethanes, as DCM has the highest diffusivity and lowest fiber affinity, resulting in nonlinear behavior (see Figure 6). Further discussion of linearity can be found in the Supporting Information.

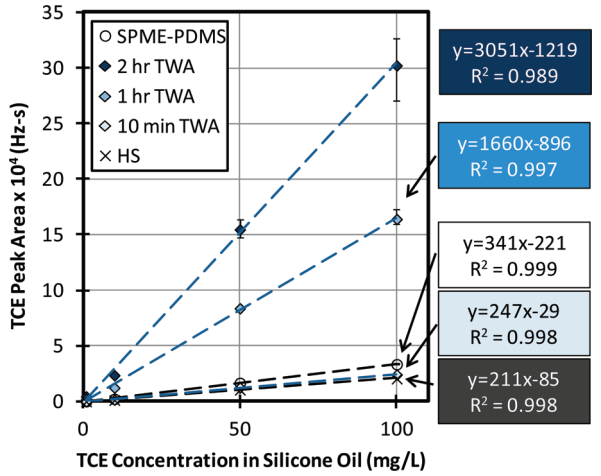


Figure 4. TCE: Effect of extraction method on GC response. Error bars denote maximum and minimum values (n = 3).

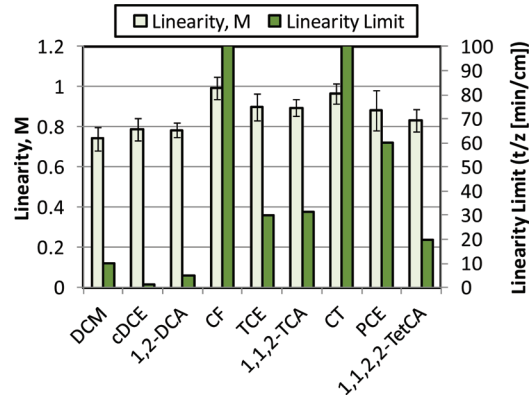


Figure 5. Linearity and upper linearity limit of TWA-SPME analysis for cVOCs. Compounds are listed from left to right in order of increasing molecular mass. Error bars on the linearity parameter denote the 95% confidence interval.

To estimate the upper limit of the linear region of TWA-SPME for each compound, high mass transfer (i.e., high t/z) samples were removed from the regression until the confidence interval included unity. Although fewer observations increase the confidence intervals, the findings provide some insight into the nonlinear behavior. The corresponding upper t/z values are plotted in Figure 5, although upper linearity limits were not determined for CF or CT as the samples were linear for all test conditions. Within each class of compounds, the linearity limit generally decreased with decreasing molecular size. Nonlinear behavior was likely due to violation of "zero sink" conditions, resulting from higher diffusivities of these small molecules and lower capacity of the fiber for these compounds. In theory, the linearity limit can be determined from eq 1, as parameters are known or estimable. However, in practice, determining the equilibrium concentration is complicated by competitive

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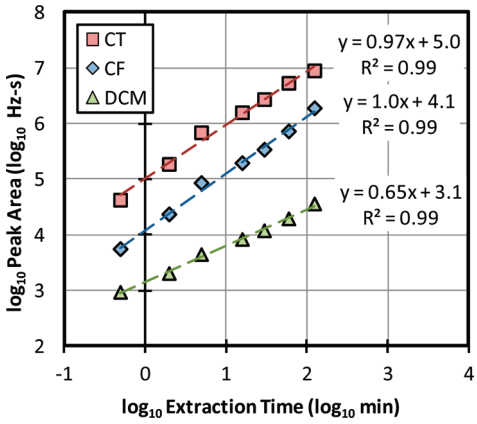

Figure 6. Linearity of TWA-SPME analysis for chloromethanes with Z = 0.5 cm.

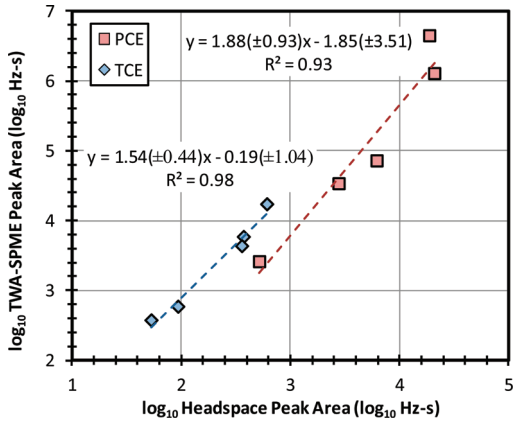

Figure 8. Method comparison for field sampling (95% parameter confidence intervals are indicated in parentheses).

adsorption. In addition, estimating the analyte concentration in the sample may be difficult. If quantitative analysis is desired, linearity should be examined in a representative matrix, as a carefully chosen matrix will help ensure all assumptions of TWA-SPME are upheld.

Equilibrium sampling was conducted before and after each TWA-SPME data set to test for sample depletion. Results of the equilibrium sampling were calculated as relative percent differences (RPD), with an average RPD of −7% indicating an acceptably small loss of analytes over the sampling period.

***In Planta* TWA-SPME Sampling.** Results of the field tree core and TWA-SPME sampling are shown in Figure 7. For each

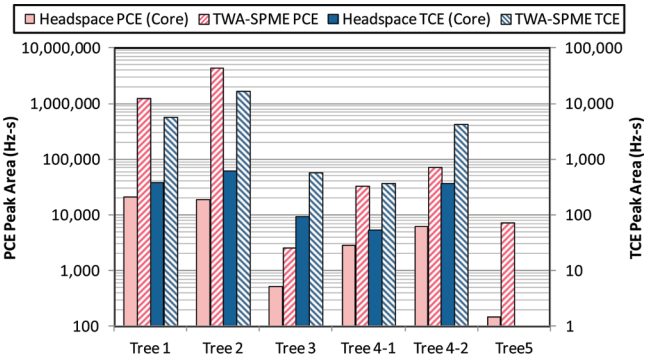

Figure 7. Field sampling results for PCE and TCE.

tree core analyzed, the corresponding SPME sample showed higher detection. Sampling with the TWA-SPME method resulted in GC responses a minimum of 6 times higher for TCE and 5 times higher for PCE when detected. On average, GC responses increased by 1.1 $\log_{10}$ units for TCE and 1.5 $\log_{10}$ units for PCE. For PCE in tree 2, the upper response limit of the detector was exceeded during SPME sampling. In multiple previous samplings, tree 5 had not resulted in PCE or TCE detection using headspace analysis. In this tree, full exposure of the PDMS-CAR fiber resulted in clear detection of PCE.

The concentrations of PCE and TCE measured by TWA-SPME were correlated with the measurements made by the headspace method (see Figure 8). While the slope of the fit is greater than unity, the 95% confidence interval of the parameter estimates is large given the small data set, so further interpretation of the data is difficult. Despite these limitations, these data do imply that TWA-SPME is an appropriate method for measuring cVOCs in trees. Previous research has established semiquantitative links between tree contaminant concentrations and groundwater contaminant concentrations,[46−48] although numerous factors can affect the correlation. The applicability of phytoscreening can be limited by subsurface heterogeneities, rooting depth, microbial degradation, azimuthal variations in tree contaminant concentration, infiltration of surface water, and seasonal changes in evapotranspiration.[2,11,18,48−50]

The consistently higher responses of TCE and PCE by TWA-SPME sampling relative to tree coring indicate that TWA-SPME is a potentially superior sampling technique to headspace tree core sampling for cVOCs, likely allowing lower detection limits. However, application of TWA-SPME for semivolatiles may be complicated by low analyte volatility and competitive adsorption of numerous semivolatile plant compounds, as competing analytes make violation of the "zero sink" assumption more probable. TWA-SPME is capable of detecting a wide range of volatile hydrophobic compounds with a single sample, although quantitative analysis may be limited with some compounds and sampling conditions. The method can detect nonpolar metabolites *in planta*, as evidenced by the detection of PCE along with its likely daughter product, TCE. Coupled with a portable GC, the method could be used to obtain real-time subsurface information during site investigations. In addition, repeated sampling of the same tree is possible without additional damage, which may be a useful way to perform long-term *in planta* monitoring. All of these benefits make TWA-SPME an attractive tool for cVOC passive sampling applications such as phytoscreening.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of analyte concentrations, evaluation of SPME fiber storage, and further discussion of linearity. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded through an OECD Fellowship (JA00029981-Burken), the EPA Midwest Hazardous Substance Research Center, and the European Union (European Commission, FP7 contract 213161, ModelPROBE). The authors thank Helmi Selin and Supelco for providing SPME fibers and technical insight. We also thank Dr. Charlotte Legind and Lotte Frederiksen from Aarhus University and Dr. Honglan Shi and Kendra Waltermire from Missouri S&T for analytical assistance in method development. We also offer thanks to John Schumacher from USGS (Rolla, Missouri) for site assistance and planning at New Haven, Missouri and Dr. Kathryn Northcut from Missouri S&T for her comments on the manuscript.

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