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Comparison of in-planta sampling methods for delineating groundwater contaminants

Kendra Marie Waltermire

Department:

COMPARISON OF *IN-PLANTA* SAMPLING METHODS FOR DELINEATING GROUNDWATER CONTAMINANTS

by

KENDRA MARIE WALTERMIRE

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Glenn C. Morrison
Yinfa Ma

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ABSTRACT

Plants directly interact with surrounding water, air, and soil, collecting and storing chemicals and elements from the surrounding environment. Two new and innovative sampling methods have been developed in which this valuable data can be accessed to replace as well as supplement contaminated-site investigations. When determining the extent of the plume on a contaminated site, groundwater sampling may be limited due to time, site access, and expense. Using new techniques that place sampling devices in trees on site, we can sample trees naturally occurring on a contaminated site or those planted in phytoremediation or redevelopment efforts. Using these sampling devices, Solid Phase Microextraction (SPME) and Solid Phase Samplers (SPSs), the plume size can then be evaluated and changes in concentration can be detected. An array of data can be collected using these quick sampling techniques to help the efficiency in placement of groundwater monitoring wells. These new methods can save time and money as well as undue impact to the ecosystems at hand or personal property.

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I need to thank Hannah Bruce for her research that helped to supplement information for this research. Big thanks to Hala Abdelsalam and Allison Sperber who stepped up as undergraduates to help sample trees and lend an open ear for conversation. Thanks are definitely needed for my best bud in the lab, Aaron Archer, for all the support, help, and just being there as a friend. I would also like to give a big thanks to my family for their support throughout this process, especially when I was under immense stress. Most importantly, I would like to thank God for giving me strength and patience throughout my research.

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1. INTRODUCTION

1.1. BACKGROUND

Volatile organic compounds (VOCs) are compounds with high vapor pressure. Past extensive uses of these solvents lead to widespread releases through spills and leaks in the handling and transport of the immense volumes. As well, dumping of the contaminants "out the back door" after use in dry cleaners, auto mechanic shops, and many industrial facilities were common and accepted disposal practices. Due to this past indiscriminate disposal of VOCs, these contaminants are the most common pollutants in the country. Chlorinated volatile organic compounds, such as Trichloroethylene (TCE) and Tetrachloroethylene (PCE), are major contaminants of the soil and groundwater in the United States. Both contaminants are found on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Priority List of Hazardous Substances (ATSDR 2007). The chemical properties make PCE and TCE dense non-aqueous phase liquids (DNAPLs) which tend to sink to the bottom of aquifers where they form a contaminant plume in the aquifer. Once in the aquifer, PCE and TCE will undergo slow dissolution and persist in the aquifer for decades.

Due to the numerous and vast PCE and TCE plumes, detection and sampling are problematic. As well, many of these plumes are found in urban areas causing issues with public acceptance of groundwater monitoring and sampling. Tree core analysis can be conducted to delineate these chlorinated ethylene groundwater plumes (Vroblesky et al. 1999). Vegetation interacts with environmental media including air, water, and soil. Through the process of phytovolatilization, plants move volatile contaminants from soil and groundwater into the atmosphere. Transport of contaminants has been shown to

occur from the vadose zone, vapor phase, as well as the saturated zone, aqueous phase (Stuckhoff et.al. 2005). This previous research has proven that cores can be taken from the tree and analyzed using gas chromatography to determine contamination within the subsurface, particularly for chlorinated solvents (Vroblesky et al. 1999; Larson et al. 2008). The cores are a good qualitative analysis, but the heterogeneity of the cores leaves a range of unpredictability and error. As well, diversity amongst varying species sampled on a site can also affect peak areas detected from trees under similar contamination conditions. In order to reduce these variables, new methods have been designed.

One of the new methods is using a Solid Phase Microextraction (SPME) sampler to directly sample the VOC concentration qualitatively in cores. SPME samplers consist of fibers of varying matrixes that have high sorption capacities. SPME samplers passively extract the VOCs through absorption and then the concentration of the sample can be determined by using gas chromatography for analysis (Skaates et al. 2005; Legind et al. 2007). SPME sampling of trees can also decrease the mobilization costs, site impacts, permanent capital costs and repeat sampling costs. As well, the sensitivity was increased over coring analysis by 20-100 times (Sheehan 2009).

In this research, sampling methods were brought into the trees, rather than taking a small portion of the tree to the laboratory. SPME samplers and a new sampling device called Solid Phase Samplers (SPSs) were placed into trees to show they have potential for rapid, improved sampling of trees for groundwater delineations. The following results show there clearly is great potential for this application and the patent-pending technology may greatly increase the accuracy of Phase I site investigations and concurrently decrease costs and damage to property and the environment. Another

possible use for this new technology is the use of the sampler for phytoremediation research projects. The samplers can be used for repeat analysis to determine uptake of contaminants and degradation compounds which will give more insight and understanding of phytoremediation processes.

1.2. GOALS AND OBJECTIVES

The overall goal of this study was to develop a new, innovative sampling technique to help the efficiency of placement of groundwater monitoring wells. Methods derived must have a low ecological impact as well as cost and time effective. Known sampling methods of sampling trees to determine VOC contamination in the groundwater through core removal was investigated further. New and old methods of sampling were compared against each other under the same conditions.

To accomplish this goal, specific objectives were established. The objectives of the current study are to:

- Evaluate increased sensitivity of SPME methods relative to tree cores.
- Design and test *in-planta* solid phase sampler for use in vegetative sampling approaches.
- Develop methods for sampling with solid phase samplers and identify potential limitations.
- Relate in-planta sampling results to groundwater on contaminated sites using data analyzed from SPME and SPS.

2. REVIEW OF LITERATURE

2.1. PHYTOREMEDIATION AND PLANT SAMPLING

Phytoremediation is the use of plants to de-contaminate a site that has previously been contaminated. Phytoremediation has many benefits such as cost effectiveness, minimal impacts and aesthetically appealing. Low maintenance, great ecological benefits, and public acceptance as a viable remediation solution are all positive aspects of phytoremediation (Burken 1999). Uptake and transpiration through shoots and subsequent volatilization to the atmosphere is a primary pathway in VOC removal from a phytoremediation site. Previous research found that plants can be used as biosensors for subsurface contamination. This information can be used for contaminant detection by using plants as sampling points. In the beginning, concentrations of contaminants in tree tissues were analyzed using direct measurement of volatilization through the use of diffusion samplers. Diffusion samplers are either a collar or a bag that is placed around a selected section of a tree. A pump is attached to the collar or bag and air is drawn through a matrix of an adsorptive material such as activated carbon for collection of contaminants. Tree core samples were also analyzed and were shown that VOCs can be detected in tree biomass when roots are exposed to contaminated groundwater and soil. (Stuckhoff et.al. 2005, Vroblesky et al. 1999, Orchard 2000). In order to understand this relationship between groundwater and the concentration of the contaminant in the tree cores, partitioning coefficients between the air, water, and woody biomass for several chlorinated solvents were investigated (Ma 2002). Through further modeling of the behavior of chlorinated solvents through a tree, Ma and Burken found in laboratory and field sampling that chlorinated solvents in the transpiration stream decreased both with

height and in the radial direction through diffusion and volatilization from leaves and stem tissues (Ma 2003). Diffusion coefficients have also been determined through direct measurement of the diffusion through a tree to better understand the transpiration of VOCs through plant tissues (Baduru 2008).

2.2. SOLID PHASE MICROEXTRACTION (SPME)

New sampling techniques can be developed from this new knowledge of transport and diffusion of VOCs through plant tissues. SPME technology can be used for *in-planta* sampling offering benefits such as fast and easy sample preparation, as well as increased sensitivity. SPME is a method in which organic molecules from a variety of matrices can be sampled in the laboratory and field site setting. SPME has distinct advantages over traditional air or water sampling methods primarily because it will not deplete the sample concentrations during extraction (Mayer 2003). SPME is a passive method of extraction of a chemical from a matrix through adsorption, and the majority of the contaminant mass extracted is delivered directly into the analytic instrumentation. After adsorption, the concentration of the sample can be determined by using a Gas Chromatograph (GC) or HPLC. The direct deliver and affinity of the SPME for the contaminant, can offer low detection limits with minimal steps.

The appeal of the SPME sampler is its versatility and ability to take readings of a wide range of contaminants, including hydrophobic contaminants (Mayer 2003). The majority of SPME analyses performed in the environmental field are equilibrium-based sampling. The SPME sampler is a portable sampler, resembling a needle with a fiber that extends out when the plunger is pushed, Figure 2.1. After adsorption, the sample then is run through analyses in using a Gas Chromatograph (GC), Figure 2.2. The fiber

equilibrates with the surrounding environmental sample. The retractable fiber is then withdrawn back into the sampler barrel when equilibrium between the coating and the sample is reached. From then on, longer extraction times do not result in larger amounts of contaminants extracted. This process is limited to the surface of the coating. Depending upon the SPME coating type, this means that a molecule with higher affinity to the coating can displace a molecule with lower affinity (Muller 2000).

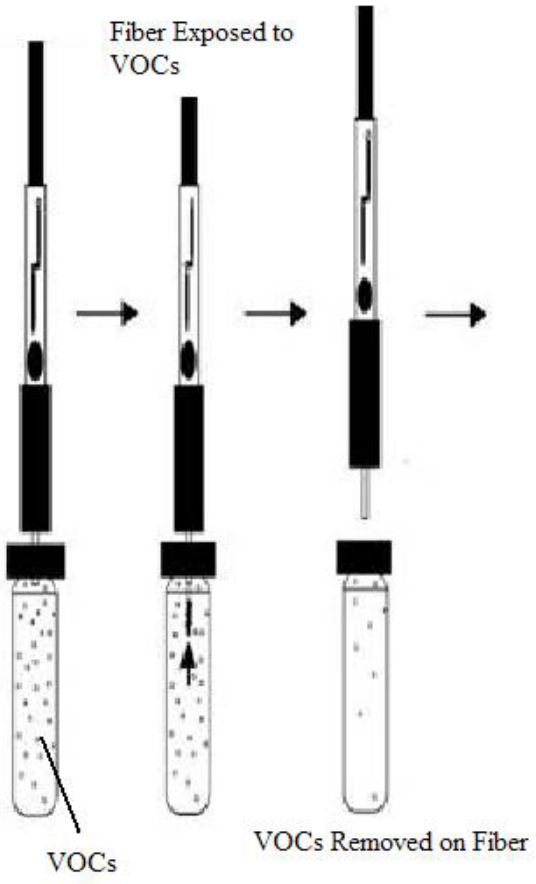

Fig. 2.1: Exposure of SPME fiber from sampler into contaminated matrix (Adapted from Ormsby 2005).

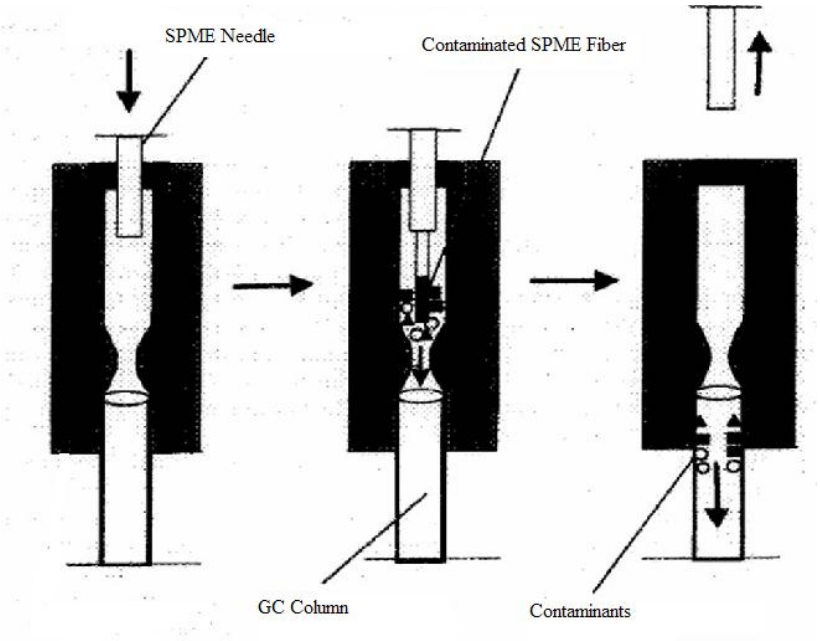

Fig. 2.2: SPME fiber desorption inside a GC injector (Adapted from Koziel 2001).

2.3. SPME-TWA

SPME can be also used as a time-weighted average (TWA) sampler for gas phase contaminants, specifically VOCs. In this method, the fiber is retracted a known distance into the needle during the sampling period which prevents the contaminants from reaching equilibrium with the fiber, Figure 2.3 (Koziel 2001). Therefore, sampling using TWA is accomplished by leaving the fiber inside the needle during the sampling session. Contaminate sampling rate is controlled by the diffusion coefficient of the contaminant and the concentration gradient inside the needle. Analysis by this method yields the concentration of a contaminant averaged over the entire sampling period (Muller 2000). Three TWA assumptions must be followed during sampling. The fiber is a zero sink; therefore the analytes extracted are 5-10% of equilibrium so it remains a first-order uptake rate. Also, the analyte concentration at the opening of the sampling device is equal to the bulk concentration of the analyte in the headspace sample (Koziel 2001).

The amount of contaminant reaching the fiber is directly proportional to the contaminate concentration outside of the sampler. Good sampling techniques are very important so that contaminate molecules trapped inside the sampler are not re-released to the surrounding atmosphere. As well, the contaminant molecules can not further affect uptake of other contaminant molecules.

TWA-SPME is very well suited for field applications, especially when the analysis is carried out on-site. The fiber can be exposed directly to the medium analyzed without knowing the exact volume of the sample the fiber is exposed to. Field analysis is rapidly gaining more and more importance, responding to the need for immediate results in environmental monitoring (Muller 2000, Jia 2000).

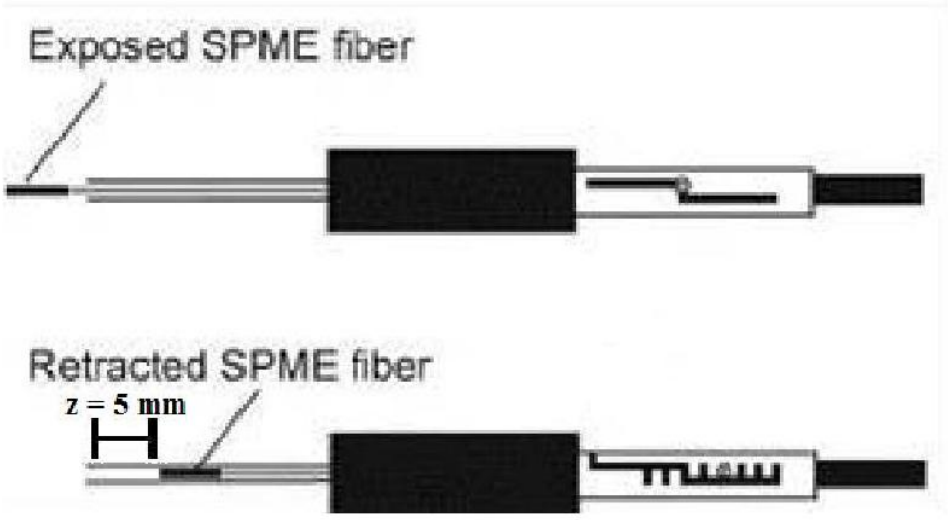

Fig. 2.3: SPME fiber is retracted into barrel a set distance for Time Weighted Average (TWA) Analysis (Adapted from Koziel 2001).

2.4. PASSIVE SAMPLERS

Semipermeable Membrane Device (SPMD) is a sampling device designed to sample hydrophobic semivolatile organic contaminants from water and air. The SPMD

consists of a neutral, high molecular weight lipid such as triolein which is encased in a thin-walled polyethylene membrane tube. The nonporous membrane allows the nonpolar chemicals to pass through to the lipid where the contaminants are concentrated (Cranor 2006). The SPMDs provide a highly reproducible means for monitoring contaminant levels and are largely unaffected by many environmental stressors that affect other forms of sampling. SPMDs provide a time-weighted average concentration of contaminants over a time period ranging from days to months (Huckins 2002). The SPMD also enables *in situ* concentration of trace organic contaminants that may otherwise be undetectable.

2.5. SPME SAMPLING WITHIN TREES

Using the concepts of SPME sampling with phytoremediation, contaminates from inside the tree can be repeatedly analyzed. The fiber would be left in the tree long enough to equilibrate and then it would be removed for GC analysis (Muller 2000). On-site analysis and monitoring using SPME fibers can also allow for faster analysis. Also, better spatial data and time efficiency may be gained using a portable GC machine to determine if more or fewer samples need to be taken in a given area (Ouyang 2006). This new concept could mean more effective phytoremediation techniques and better estimates of the groundwater contaminants at sites.

When a core is taken, the data extracted through different analytical methods will only give a snapshot of the contamination. Many environmental factors such as temperature, light, and precipitation can have an effect on the concentration of contaminant in a tree. Vroblesky et al. showed the tree species, rooting depth, dilution by rain, and within-tree VOC degradation are all factors that affect the concentration of VOCs within tree cores (2008). Also, to gain a better idea of contamination in the

subsurface, a time-weighted average over a week will give a better understanding of the contamination in the tree. Using the Solid Phase Samplers, a better understanding of the concentration of the VOC in the tree can be quantified.

2.6. TETRACHLOROETHYLENE

The contaminant of concern during the course of this investigation was tetrachloroethylene or otherwise known as perchloroethene (PCE). PCE was chosen because both field site investigations mentioned in this report are contaminated primarily with PCE. Also, it degraded forms also exist such as TCE, cis-dichloroethene (c-DCE), trans-dichloroethene (t-DCE), and vinyl chloride (VC). PCE has the chemical formula of C_2Cl_4 while TCE has a chemical formula of C_2HCl_3.

PCE as an environmental contaminant, along with TCE is one of the most common occurring contaminants in the United States causing environmental concern. The number of PCE and TCE plumes is numerous because of the processes in which they were used and the methods they were disposed (Collins 2002). PCE is a suspected carcinogen with an EPA regulated maximum contaminant level in drinking water set as 5 parts per billion (ppb) (EPA 2006). PCE is a possible human carcinogen which typically affects the liver (Henschler 1990). PCE forms dense non-aqueous phase liquid (DNAPL) pools in groundwater aquifers because of its specific gravity of 1.623 making PCE denser than water (ToxProbe 2003). Rather than being confined to the upper portions as light non-aqueous phase liquids may be, non aqueous phase PCE sinks to the bottom of the aquifer due to its density. PCE is more likely to contaminate the entire depth of an aquifer because of its dense property. Also, if a clay lens or other isolated aquitards are present in an aquifer, the DNAPL can form perched pools contaminating

that level of the aquifer causing multiple contamination zones. DNAPLs also have the unfortunate characteristic of becoming concealed from traditional treatment methods by sinking into bedrock fractures that are not accessible to groundwater flow (Ma 2002). Another problematic characteristic of DNAPLs is the small droplets of pure product left behind after a recovery or remediation process occurs.

3. PAPER

In-planta Solid Phase Samplers to Delineate VOC Plumes

Kendra Waltermire and Joel G. Burken*
Missouri University of Science and Technology, Civil Engineering Department, 1870 Miner Circle, Rolla, MO 65409

3.1. ABSTRACT

Plants directly interact with surrounding water, air, and soil, collecting and storing chemicals and elements from the surrounding environment. Tree coring methods have shown that groundwater contamination can be assessed without directly sampling the groundwater. In this work, two new and innovative sampling methods that place sampling devices inside the plant, i.e. "*in-planta*", were developed to access this valuable data that can direct and perhaps replace traditional methods for contaminated-site investigations. Traditional site assessments may be limited due to time, site access, and expense, resulting in incomplete understanding of the contaminated plumes and inefficient remedial approaches. The new techniques presented include placing established solid phase microextraction fibers (SPMEs) and newly developed solid phase samplers (SPSs) that have greater sensitivity and reproducibility and can also provide repeated sampling of the same trees with minimal damage, offering new possibilities in using plants to monitor contaminated sites as well as doing initial investigations. These methods are also much faster and can be accomplished with little of no property and ecological damage, and with acceptance by property owners.

3.2. INTRODUCTION

Field site investigations using groundwater sampling can be very time consuming, expensive 'per sample' costs, and have big mobilization costs. As well, most of the time

there is not enough information and direction for initial placement of groundwater wells. Methods to reduce labor, time, cost, and environmental disruption are needed. Studies using tree cores collected from contaminated sites have shown VOC concentrations in plants correlate with the groundwater and soil vapor concentration of VOCs. Previous research has proven that cores can be taken from the tree and analyzed using gas chromatography to determine contamination within the subsurface, particularly for chlorinated solvents (Vroblesky et al. 1999; Larsen et al. 2008, Struckhoff et al 2005). Previous research has also modeled partitioning coefficients from wood to water of contaminants to understand more accurately the correlation between concentrations of contaminants in cores to groundwater concentration (Baduru 2008). Although this modeling can be used, the heterogeneity of the cores leaves a range of unpredictability and error, and the sensitivity is not fully understood relative to environmental conditions. Vroblesky and colleagues clearly showed that a simulated rainfall event can lead to changes in tree core analysis results in a matter of hours (Vroblesky et al. 2004). In order to improve the use of plants for environmental assessment and monitoring, new breakthroughs in analytical chemistry can be implemented.

One of the new analytical methods that have promise uses Solid Phase Microextraction (SPME) sampling. SPME samplers consist of fibers of varying matrixes that have high affinities for different chemicals. SPME samplers passively extract the VOCs from a sample matrix and then can introduce the entire sample into a gas chromatograph for analysis (Skaates et al. 2005; Legind et al. 2007) or can be extracted into minute volumes of solvent for liquid chromatography. Using SPME fibers can also be very rapidly analyzed and used repeatedly. This can allow for sampling of mixed

matrices as well. SPME fibers can sample water, air, slurries, and have even been used in plant sampling for food contamination (Lord 2004).

Another sampling method used for environmental monitoring is solid phase passive samplers. Semipermeable Membrane Device (SPMD) is a sampling device designed to sample hydrophobic semivolatile organic contaminants from water and air. The SPMD consists of a neutral, high molecular weight lipid such as triolein which is encased in a thin-walled polyethylene membrane tube. Another passive sampler uses Polydimethylsiloxane (PDMS) as the matrix to absorb the contaminant (Laak 2008). Using this concept of passive samplers, a new sampling device and method was developed to sample contamination in trees.

In this research, novel analytical methods were brought into trees, in the first *in-planta* sampling methods development. *In*-planta methods place a high affinity solid phase sampling device in the tree, rather than taking a small portion of the tree to the laboratory. Advantages herein reveal improved sensitivity and reproducibility. Additionally coring the tree results in damage to the trunk and frequent sampling is not possible without significantly damaging or causing the death of the trees (Gopalakrishnan 2007). The following results show there clearly is great potential for this application and the patent-pending technology may greatly increase the accuracy of Phase I site investigations and concurrently decrease costs and damage to property and the environment. Placing these sampling devices inside the trees on site, we can sample trees naturally occurring on a contaminated site or those planted in phytoremediation or redevelopment efforts, evaluate the plume size, and even monitor changes in concentration. These methods will have a minimal footprint and can be accomplished

with little materials cost, time, or labor demands. These quick sampling techniques can provide an array of data within a short amount of time to help the efficiency in placement of groundwater monitoring wells, saving time and money as well as undue impact to the ecosystems at hand or personal property.

3.3. MATERIALS AND METHODS

3.3.1. Tree Coring The tree cores obtained during this project were taken with a 0.5 cm diameter increment borer manufactured by Forestry Services, Inc. Tree cores were taken either 30 cm above the ground surface or at breast height depending on the diameter of the tree. Tree cores were immediately stored in 20 mL headspace vials caped with Teflon coated septa and crimp tops until analysis. Cores were allowed to equilibrate for ~24 hours in all analyses. Headspace concentrations were then determined using headspace analysis using a Tekmar 7000 headspace autosampler and a HP 5890 gas chromatograph with electron capture detection.

3.3.2. Solid Phase Microextraction (SPME) Dilution vials of chloroethenes were made up using chloroethenes in PDMS stock solution of concentration of 1 g/L. The standards were made with a dilution rate of 10% in 25 mL glass vials containing 5 mL of PDMS. The vials were then capped with Teflon septa caps to form a seal. Allowing the vials to equilibrate with the headspace overnight, the next day SPME-PDMS fibers were exposed for two minutes and run in the GC in duplicates. Gas Chromatography methods are presented in Appendix A.

3.3.3. SPS development and Testing A new sampling device, Solid Phase Sampler (SPS), consisting of PDMS tubing was designed for *in-planta* sampling. The tubing is permeable and absorbs the contaminant into its matrix. The mass of the tube is

much greater than a SPME fiber; therefore, more contaminant can absorb into the tube allowing for detection levels higher than SPME.

SPSs were constructed and exposed to a steady concentration of PCE and TCE to evaluate absorption rates. SPSs were constructed using polydimethyl silicone (PDMS) tubing cut into sections with mass ~0.5g. Mass was measured, and each section was placed on a threaded stainless steel #4, 1 ¼" bolt and secured with a nut, Figure 3.1. SPSs were placed in methanol for two days and allowed to dry under a hood to remove any contamination from production or shipping and storage. The SPS's were then placed in an incubator for 2 days at 100°C. The cooled tubes were then placed into a 100 mL beaker within a 300 mL screw top jar also containing 50 mL of PDMS oil dosed with PCE/TCE at a concentration of 10 ppm, Figure 3.2. This controlled the chemical activity (i.e. concentration) in the gas phase at low levels, without depleting the mass from PDMS via absorption into the SPSs. There was no direct contact of SPSs with PDMS oil containing PCE/TCE. The SPSs were placed within the PCE/TCE environment at the same time. To determine the uptake rates, one SPS was removed at varying times: 1 hour, 2 hour, 12 hour, 24 hr/1 day, 2 days, 3 days, 4.25 days, 7 days, 11 days, and 14 days. When a SPS was removed from the vial with tweezers, the tube was placed within a 20 mL headspace sampling vial and immediately capped then stored at 4 ˚C. Once all SPSs were removed, they were run at once in a headspace autosampler at 35 ˚C with direct injection to an HP 5890 GC with ECD for detection. The data was plotted versus exposure time.

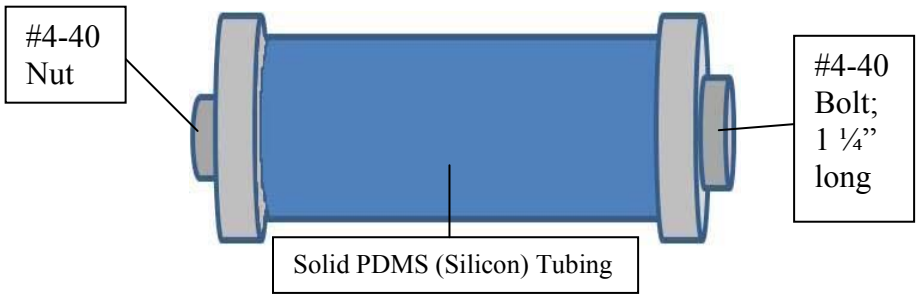

Figure 3.1. Solid Phase Sampler (SPS) assembly. PDMS mass was 0.5 g with a thickness of 3 mm and an outer diameter of 4 mm.

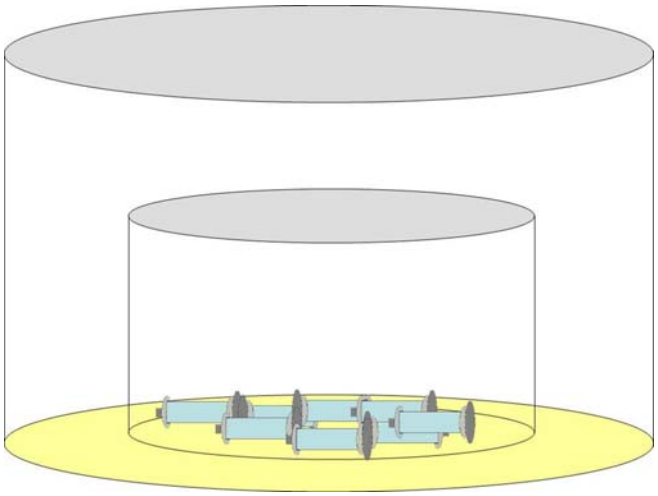

Figure 3.2. SPSs were placed in an open beaker inside a closed beaker containing PCE and TCE dosed PDMS oil.

3.3.4. Comparison of SPSs Versus Cores To compare the affinity of tree cores and the SPSs, the two materials were compared in side by side testing. As tree cores are highly variable in their collection and the chemical composition (Gopalakrishnan et al. In Press) surrogate, uniform xylem tissue was used and constructed by cutting poplar dowel rods at a mass of ~0.5g, diameter 0.4 cm, and the mass of each was recorded. The SPSs and surrogate cores were placed in a 100 mL beaker, as noted above, with an added aluminum foil divider placed in the center to separate the cores from the SPSs, Figure 3.3. The SPSs and cores were exposed for 3 weeks to PCE and TCE at a concentration of

10 ppm allowing them both to come to equilibrium with the surrounding environment. Partitioning coefficients for the solvents and PDMS oil were determined in related studies and is shown in supporting information. The resulting vapor concentration was calculated using partitioning coefficients of 2000 for PCE and 1200 for TCE. SPSs and cores were removed using tweezers and placed into separate vials and capped for analysis as noted above.

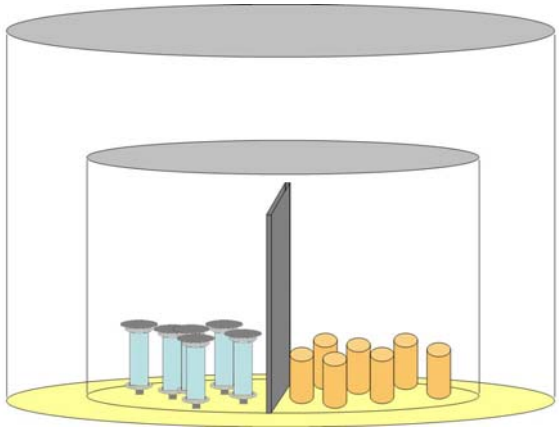

Figure 3.3. Solid Phase Samplers and dowel rods were placed in an open beaker inside a closed beaker containing PCE and TCE contaminated PDMS oil.

3.3.5. Comparison of PDMS-SPME, Carboxen-SPME, and Tree Cores To evaluate the relative sensitivity of different SPME methods, SPS analysis, and traditional tree coring methods, 4 methods were tested in the same contaminant activities. This testing also evaluates the linearity of the methods over a wide range of concentrations. Dilution vials of chloroethenes were made using chloroethenes in PDMS stock solution of concentration of 1 g/L. The standards were made with a dilution factor of 10% in 25 mL glass vials containing 5 mL of PDMS. The vials were then capped with Teflon septa caps to seal off air exchange.

Allowing the vials to equilibrate with the headspace overnight, the next day headspace analysis with a 1 mL air-tight syringe was performed on the vials in duplicate. After the initial headspace analysis, SPME-PDMS fibers were exposed for two minutes and run in the GC in duplicate. The inlet temperature was increased from 220°C to 250°C. Time-weighted average (TWA) analysis was then performed using a Carboxen fiber with z=5 mm for ten minutes. Next, multiple fibers were exposed at the same time in a large-mouthed glass vial with a Teflon septa cap. In order to compensate for more headspace, 25 mL of PDMS oil was used at the same concentrations as the original stock solutions. The fibers were exposed at 1, 2, 3, 4, 6, and 16 hours for 10 ppm concentration at z=5mm. One and two hour exposure times were also observed at concentration 100 ppm and 1 ppm.

3.3.6. Sequential Repeated Headspace Analysis of SPSs To evaluate the potential for multiple analyses of single SPS samplings, three SPSs were exposed to PCE and TCE in the environment using the method explained above (Fig. 3.2.). After the SPSs had been allowed to equilibrate with the PCE/TCE environment, the SPS were removed and immediately vialed and capped. The tubes were then run with the GC in the autoheadspace sampler. Without removing the tubing from the vial, the tubes went through eight sequential runs in the autosampler with two hours in-between analysis runs. The results were found using the mean value of peak area for the SPSs. The initial peak area was the baseline results. For every analysis, the percentage was found by dividing the peak area of a run by the baseline peak area.

3.3.7. Field Sampling Using SPME In New Haven, MO, PCE contaminated groundwater has impacted the city water supply and tree-core sampling was critical in

delineating the sources on the contamination (Schumacher et al. 2004). On the Kellwood Site (OU2) five trees were cored and then tested using *in-planta* SPME analysis. Cores were collected as previously described and in the borehole remaining, SPME analysis was conducted using time weighted average (TWA) methods using 100 μm Carboxen SPME fibers supplied by Supelco Analytical (Sigma-Aldrich Co., Bellafonte, Pennsylvania). The fibers were exposed in the trees at the New Haven Kellwood Site (OU2) site for 70 – 75 minutes, Figure B.3 in Appendix B, capped and transported to the Missouri S&T environmental engineering laboratory for analysis using an Agilent 6890 GC with ECD detection.

3.3.8. Field Sampling Using SPS Tygon (silicon) tubing was cut into pieces with a mass of .45g. The mass of the tubing was limited by the length of the bolts to be used. The bolts used for this experiment were size #4, 1 ¼" length bolts. The SPSs were cleaned and assembled as mentioned previously. Each SPS was individually wrapped in foil and then placed into the oven for two hours at 100°C. Once the SPSs were removed from the oven, one SPS was removed from the foil and placed in a vial as a blank. The other SPSs remained individually wrapped in foil. This foil was placed in a 1 L jar with a screw-on Teflon cap. This is to prevent any contamination of the SPSs.

On arrival at New Haven, one SPS was removed from its foil and placed into a vial and capped for a field blank. Tree cores were taken and SPS was placed into all core holes, Figure B.6 in Appendix B. Tags were attached to the SPS for flagging on return trip to remove SPSs from trees. The SPS were unwrapped partially from its individual wrapping and then using the foil to hold onto the SPS, the SPS will be placed inside the

core hole completely exposed. Then, a screw with a ¼" diameter was placed in the hole to seal the headspace inside from the outside exposure.

Using gloves, the foil was removed from three SPSs and wire was wrapped around them. One SPS was then hung from each of the three trees from the wire to evaluate the background concentration and potential for cross contamination from the surrounding air at the VOC contaminated site. The SPSs were placed so they would not touch the tree. At the end of the sampling trip, a SPS was removed from the foil and placed into a vial as the trip background.

On the return trip to remove the SPSs from the trees, another SPS was removed from its foil and used as a third background. This was then vialed and capped. To remove the SPS from the tree, tweezers were used to extract the SPS from the tree hole. The SPSs were then immediately vialed and capped with the wire being cut from the tag. All of the samples were analyzed at the Missouri S&T environmental engineering laboratory using an Agilent 6890 GC with ECD detection.

3.4. RESULTS AND DISCUSSION

3.4.1. Sorption Rates for SPSs Results for the absorption rates showed a clear relationship for both PCE and TCE absorption, Figure 3.4. Absorption as measure by the mass transferred to the SPSs increased rapidly over the first 96 hours and then reached apparent equilibrium at approximately 10 days. Equilibrium was determined as being reached if the change was less than 1 % over 72 hours.

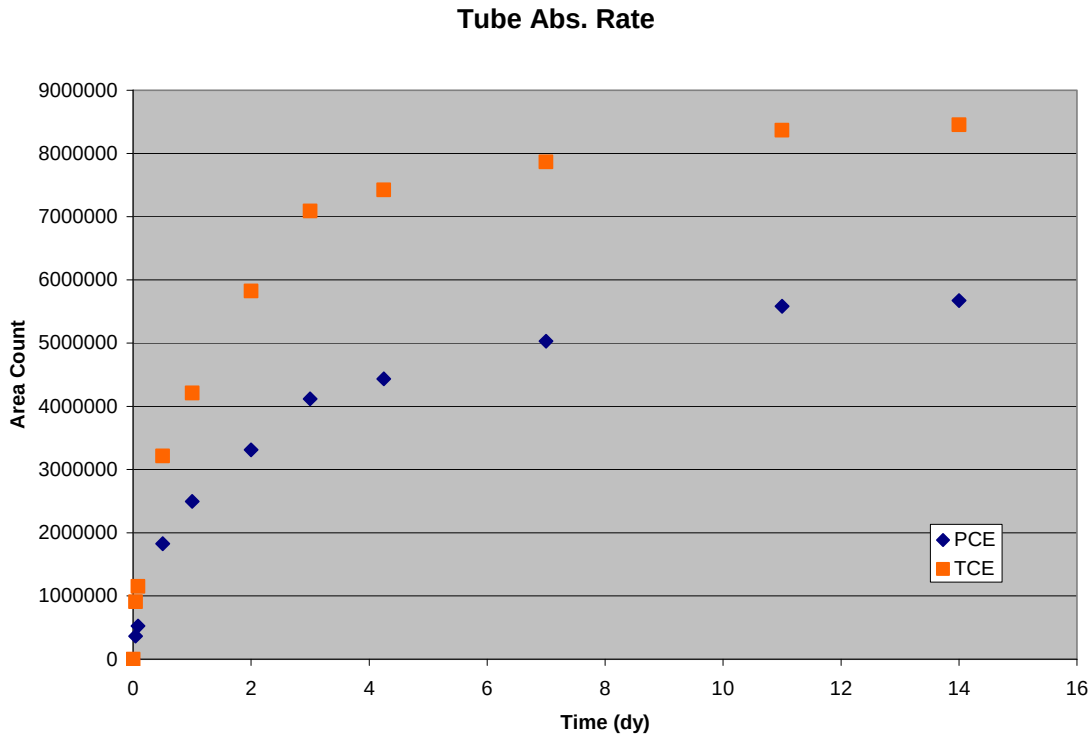

Figure 3.4. SPS-controlled absorption rate of PCE and TCE, showing equilibrium in approximately 10 days.

This experiment shows that the SPSs do take at least 8-10 days to equilibrate with their surroundings, assuming there are no limitations in the kinetics to supply the contaminants. This study also shows that while equilibrium may take many days, the predictable uptake can allow for rapid sampling after 1 or 2 days to get initial results, perhaps positive negative presence, and longer terms are needed for active equilibrium sampling with maximum sensitivity. While the sensitivity is beneficial for getting the lowest possible method detection limits, the predictability of the uptake lets short term sampling (24 hours) be extrapolated to actual equilibrium concentrations.

3.4.2. Comparison of SPS and Core Equilibrium Concentration The equilibrium comparison of cores and SPSs exposed to the same headspace concentration revealed that the SPSs were more sensitive for PCE while core with headspace analysis

was slightly more sensitive for TCE, Figure 3.5. The SPS peak area response was 97% higher than the core analysis for PCE. The SPSs had lower variability for both PCE and TCE. As well, the SPSs were more reproducible. Although ten SPSs and dowel rods were dosed, only four are shown. The four dowel rods and SPSs shown are the four sets of samples that have a peak area closest to the mean peak area. All ten samples were analyzed for statistical findings. The average standard deviations for the peak area of the cores were 122428 and 84835 for PCE and TCE respectively. The average standard deviations for the peak area of the SPSs for PCE and TCE were 77987 and 20942 respectively. The 95% confidence interval was only 0.9% and 0.8% of the mean for SPS analysis of PCE and TCE respectively, where as these values were 2.7% and 2.4 % for the cores analyzed.

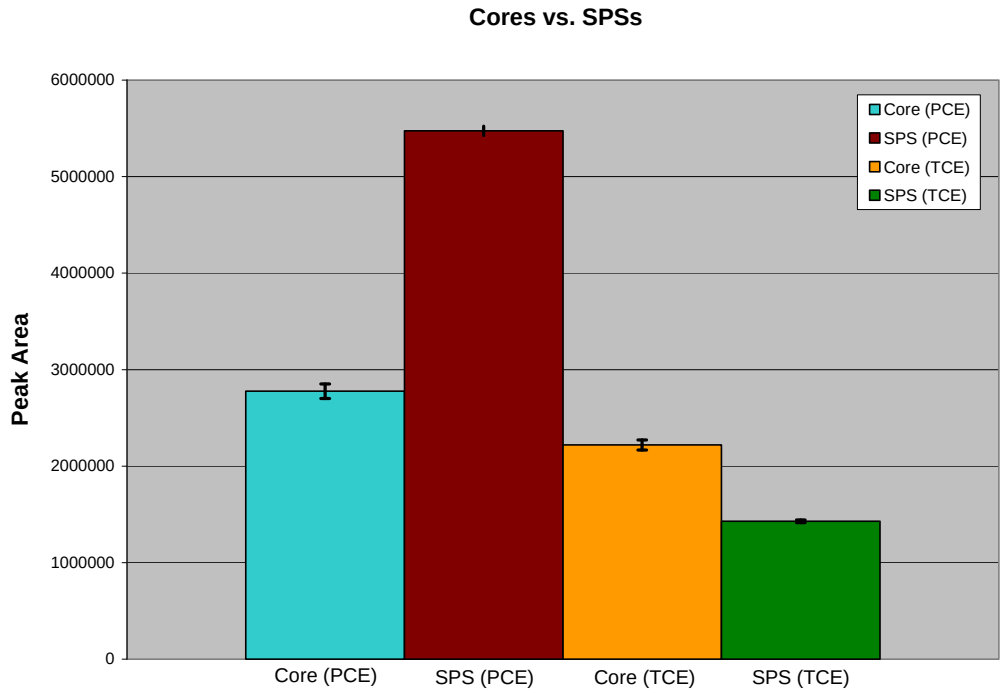

Figure 3.5. Ten samples of SPSs and Dowel Rods were averaged. When exposed to PCE and TCE under the same conditions, multiple replicates of SPSs have peak area sensitivity 97% higher for PCE and 61% less for TCE than cores. For both PCE and TCE reproducibility was increased in SPSs compared to cores. SPSs had a variability of only 1.2% versus 4.9% for the cores with PCE and 2.4% versus 7.2% for the cores with TCE.

3.4.3. Comparison of SPME, SPME-TWA Analysis, and Tree Cores

Comparison of Carboxen Time Weight Average (TWA) Analysis, SPME-PDMS analysis, and traditional headspace analysis resulted in the TWA analysis was much more sensitive to PCE and TCE, Figure 3.6. and Figure 3.7. respectively. If TWA analysis rules are adhered to, then as the time increases, the expected linear response will increase in sensitivity for these compounds (Sheehan 2009). The peak area response was close to four times higher for TWA for two hours exposure and had a slightly higher sensitivity for TWA for one hour exposure compared to headspace analysis. On the other hand SPME-PDMS had similar peak area sensitivity compared to headspace analysis with

TCE and more than twice the sensitivity in peak area with PCE. TWA analysis performed at a short time of 10 minutes resulted in a peak area sensitivity of 22% lower compared to headspace analysis.

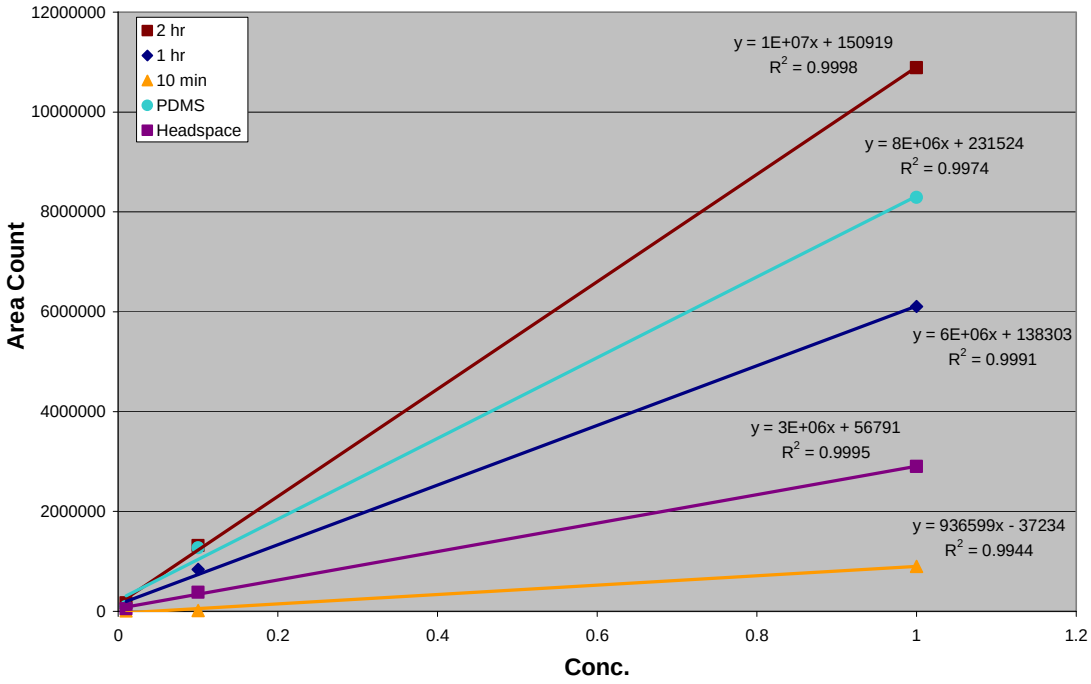

Figure 3.6. Comparison of Carboxen Time Weighted Average (TWA) Analysis, SPME-PDMS analysis, and traditional headspace analysis at different concentrations of PCE. TWA Analysis produces greater peak area sensitivity than SPME-PDMS and headspace analysis.

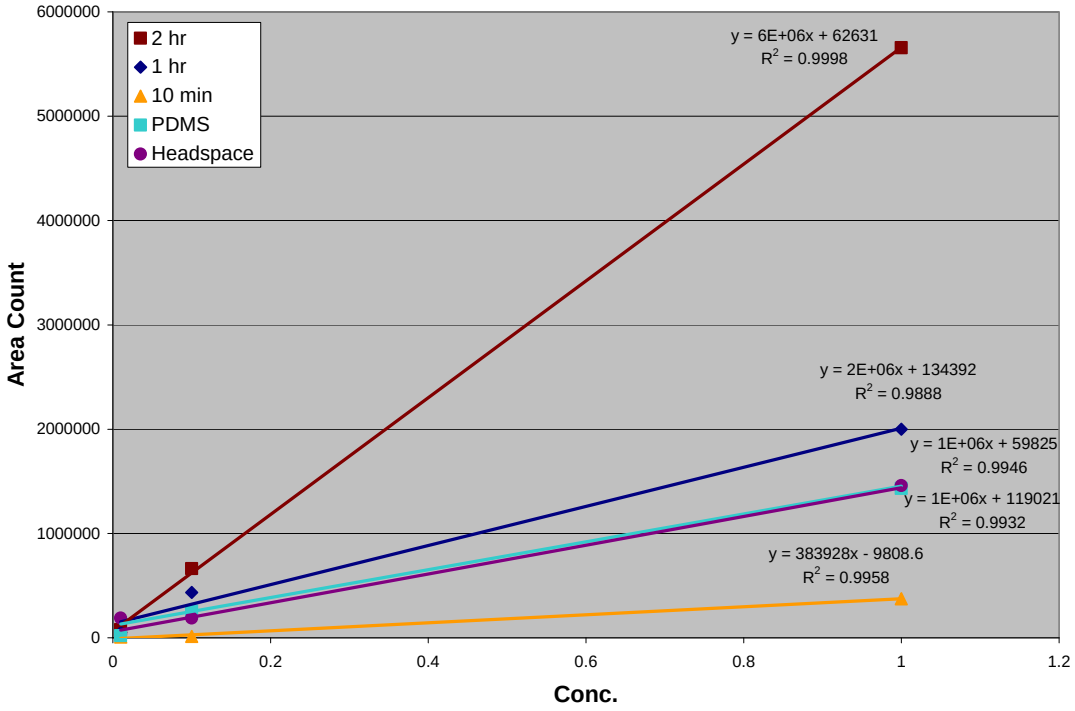

Figure 3.7. Comparison of TWA Analysis, SPME-PDMS analysis, and traditional headspace analysis at different concentrations of TCE. TWA Analysis produces greater peak area sensitivity than SPME-PDMS and headspace analysis.

3.4.4. Sequential Headspace Analysis of SPS Through repeat analysis of dosed SPSs, a set amount of PCE and TCE were removed after each sampling, Figure 3.8. After four runs, SPSs still contained over half of PCE and TCE within its matrix. This repeat analysis proves that even after an initial determination run, a known mass was removed which allows for determination of initial concentration. One thing to note, the more analysis runs on a tube increases uncertainty of back calculating the initial mass in the SPS. This predictive decrease can help to determine analytical results under multiple analysis using different detectors. Standard deviation was found for PCE and TCE. The averaged standard deviation was found to be 3.4% for PCE and 3.9% for TCE.

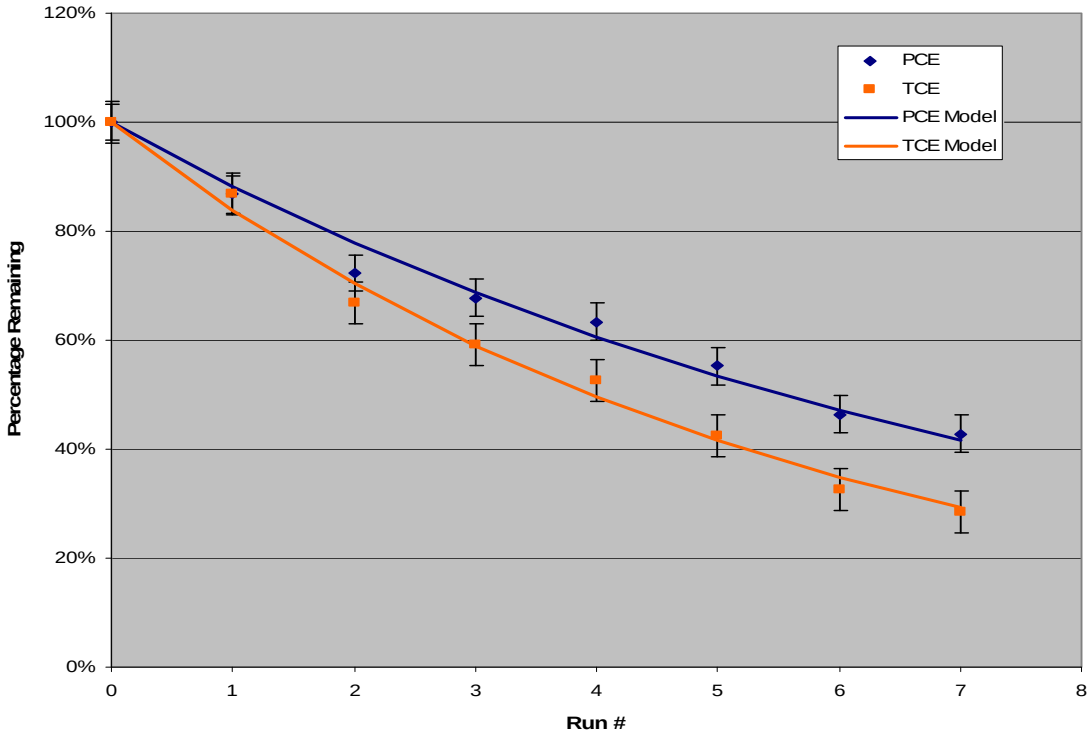

Figure 3.8. Repeat analysis of SPS analysis, showing that samples can be analyzed numerous times with predictable results. Standard Deviation for PCE is 3.4% and for TCE is 3.9%.

3.4.5. Field Comparison of *In-planta* SPME Methods, Tree Core Analysis, and SPS Methods Sampling of trees at the New Haven Kellwood Site (OU2) was conducted on 4 trees known to be contaminated from previous sampling as well as a tree believed to be free of contamination. Results of tree core analysis using accepted methods revealed contamination of both TCE and PCE in the trees as well as the tree previously believe to be free of contamination, Figure 3.9. and Figure 3.10. The *in-planta* SPME methods had peak areas 4 to 230 times higher using the same GC methods for analysis. Also, an average increase in the peak area of 13 times for TCE and 62 times greater for PCE was also detected. As well, SPSs used to sample reached similar results within the same log scale as the SPME fibers and resulted in higher sensitivity than tree cores. This analysis shows that SPME and SPS *in-planta* analysis have potential for

providing improved method detection limits with similar variability in analysis. The SPME analysis also has the benefit of potentially rapid analysis.

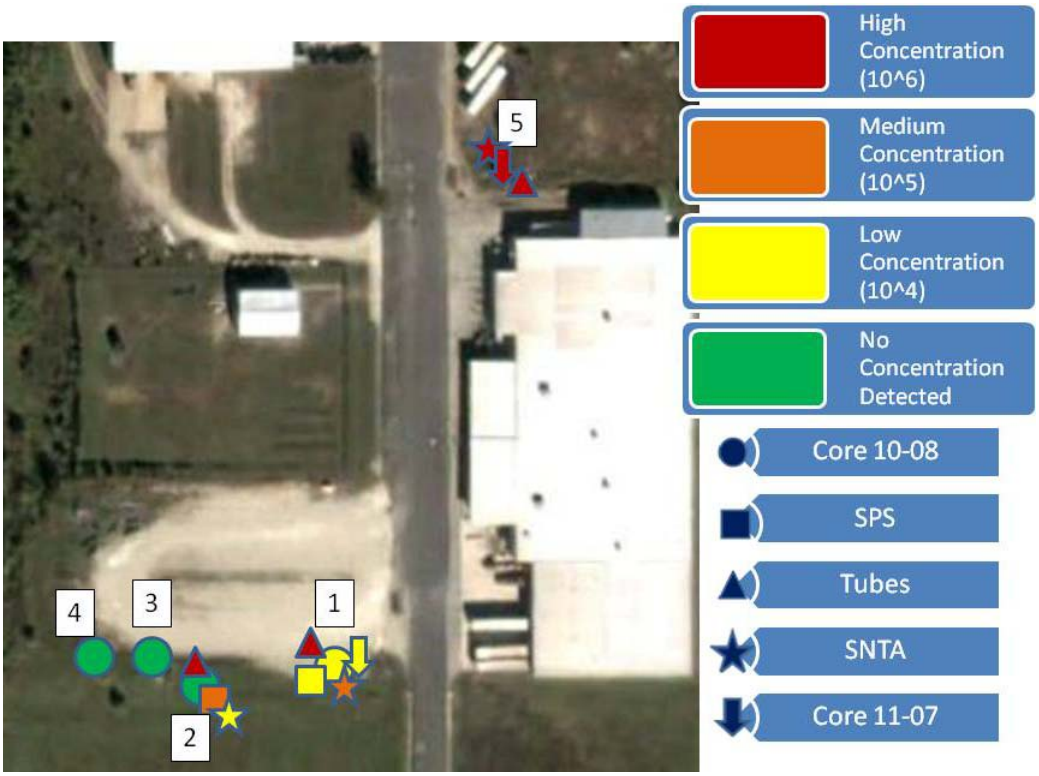

Figure 3.9. Site map of New Haven Kelwood Site (OU2) with repeat sampling information.

Tree #	Cores-TCE	Cores-PCE	SPME-TCE	SPME-PCE	SPS-PCE
Tree 1	3.8×10^2	2.1×10^4	5.8×10^3	1.2×10^6	2.1×10^4
Tree 2	6.1×10^2	1.9×10^4	1.7×10^4	4.4×10^6	2.8×10^4
Tree 3	9.4×10^1	5.2×10^2	5.8×10^2	2.5×10^3	ND
Tree 4a	5.3×10^1	2.8×10^3	3.7×10^2	3.3×10^4	ND
Tree 4b	3.6×10^2	6.2×10^3	4.3×10^3	7.1×10^4	ND
Tree 5	ND	1.4×10^2	ND	7.2×10^3	7.7×10^5

Figure 3.10. Comparison of peak areas from standard tree cores, SPME *in-planta* TWA, and *in-planta* SPS analysis.

3.5. FINDINGS

Using the SPME fibers and SPSs to sample trees in the field appears to have benefits relative to traditional tree coring analyses. These methods may improve the

vegetation-sampling approaches that have great benefits for Phase I site assessments and also for monitoring groundwater concentrations at phytoremediation sites. Actual groundwater concentrations still require sampling groundwater wells, but these methods can give relative quantifications (Schumacher et al. 2004, Ma 2002). Using plant sampling to gain relative quantifications, benefits can be gained that could not with groundwater monitoring such as minimal environmental or property disturbance as well as little materials cost. Sampling is accomplished with very little energy use or labor demands. As well, with the reproducibility of the SPME fiber and SPSs, groundwater monitoring can be replaced or become more efficient through these methods that are at the very infancy of development. Using these new methods, continuous groundwater sampling used in natural attenuation monitoring could also be replaced. This new approach is patent-pending and appears to have a bright future if optimized further.

3.6. ACKNOWLEDGEMENTS

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4. CONCLUSIONS AND RECOMMENDATIONS

4.1. CONCLUSIONS

From these results, SPS and SPME are definitely a viable option for sampling contaminated sites to determine a contamination plume. Uptake rates of SPSs were found with the result of equilibrium is reached at ten days. SPSs were also placed in the same PCE and TCE contaminated environment as tree cores to see a comparison between the two methods. SPSs were found to have almost twice the sensitivity for PCE compared to the tree cores. For TCE, the SPSs seem to actually have a slightly lower sensitivity compared to the tree cores. Repeat analysis was also performed on dosed SPSs. It was found that a predictable loss is removed from the tubing after every run. This will allow for repeat analysis of the tubing from different detectors while SPME and tree cores would have been depleted after the initial analysis. Different sampling methods of SPME were also looked into to compare peak area sensitivity to traditional headspace analysis. What was found is that TWA analysis at one and two hours gave greater sensitivity at up to four times compared to headspace analysis. The PDMS fiber was found to be comparable if not having better sensitivity for PCE and TCE compared to headspace analysis as well. Field sampling using the SPSs and SPME *in-planta* samplers demonstrated the use of solid phase samplers as a substitute for tree core sampling. Lower detection limits were also shown with the SPME and SPS methods in comparison to tree core sampling.

Sampling using tree cores is cost effective and takes little time, but it does damage the tree with repeat analysis. Using the new, innovative methods of SPME and SPS, repeat analysis of trees can occur saving money, time, and damage to the tree. As

well, the heterogeneity of tree cores allow for a large variability in peak area sensitivity between repeat sampling. SPME and SPS allow for uniformity between sampling with greater reproducibility. Through these new methods, groundwater monitoring can be all together replaced or these methods can supplement groundwater data.

4.2. RECOMMENDATIONS

There is much to learn about the improvement of these samplers, especially with the SPSs. The SPSs used PDMS tubing as the sampling matrix for these methods. With the PDMS tubing, PCE had increase sensitivity, but TCE was lower than tree core sampling. New matrices such as polyethylene, latex, or neoprene needs to be further investigated to determine if other tubing can be used for better sensitivity or better attractiveness for specific contaminants such as TCE. As well, depletion of headspace after removal of SPSs should be investigated to see how many repeat samplings can occur in the core space before the headspace is depleted. If SPME sampling occurs directly after removal of SPS, peak area might be affected with such a large removal of contaminant on the SPS from the core space.

To fully understand the quantified concentration of the groundwater with respect to the peak area observed using SPSs, partitioning coefficients for different contaminants to the SPS samplers need to be determined. This will allow calculations to be performed and relative close quantifications of the groundwater contamination concentration can be found. As well, non-volatile organic compounds should be investigated using SPME and SPS detection methods.

These achievements demonstrate that SPME and SPS sampling methods are successful and should be used for detection of certain chlorinated solvents in vegetative

systems. Also demonstrated by this work is the vast potential of SPME and SPS sampling techniques for use with other volatile organic compounds and the possibility with non-volatile organic compounds.

APPENDIX A

GAS CHROMATOGRAPHY METHODS

GC Set-up for Headspace and SPME-Carboxen Analysis

Time (min)	**Injector Temp.**	**Detector Temp.**	**Oven Temp.**
0-2	220°C	250°C	50°C
2-4.5	220°C	250°C	50→100°C
4.5-6.5	220°C	250°C	100°C

Flow: ~20

GC Set-up for SPME-PDMS

Time (min)	**Injector Temp.**	**Detector Temp.**	**Oven Temp.**
0-2	250°C	250°C	50°C
2-4.5	250°C	250°C	50→100°C
4.5-6.5	250°C	250°C	100°C

Flow: ~20

APPENDIX B

PHOTOS OF SAMPLING WITH SPME AND SPS

Figure B.1: Core removal from tree on site in Toronto, Canada

Figure B.2: Core extraction from tree

Figure B.3: SPME *in-planta* application photo from field application of SPME analysis

Figure B.4: SPS placed inside core space left after removal of the tree core

Figure B.5: Once SPS is placed inside open core, a screw used to seal the hole from the outside environment.

Figure B.6: *In-planta* schematic and application photo from field application of SPS

APPENDIX C

MAP OF NORTHSTAR SITE, CANADA

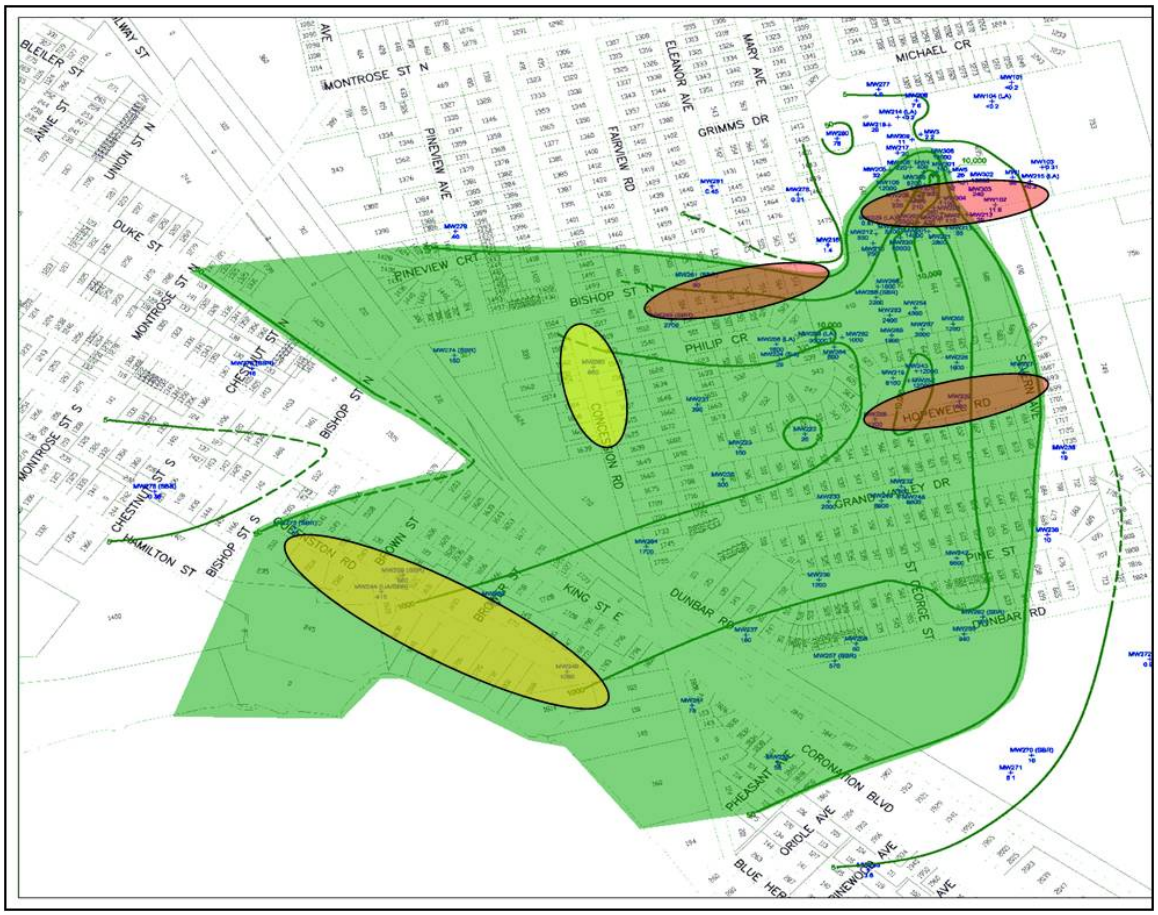

Figure C.1: Map of PCE plume on Northstar Site, Canada. Green lines and shading indicate contamination gradients found using groundwater well samples. The red, orange, and yellow circles indicate PCE concentrations found in trees sampled on site. Red: High concentration; Red-Orange: Medium concentration; Orange:Medium-low concentration; Yellow: Low concentration

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VITA

Kendra Marie Waltermire was born in Bartlesville, Oklahoma on June 4, 1985. At the age of one, she moved to Collinsville, Illinois. She then moved to Maryville, Illinois where she graduated from Collinsville High School in Collinsville, Illinois. She enrolled at University of Missouri-Rolla where she received her Bachelor of Science in Biological Sciences with a minor in Chemistry and Business. While an undergraduate at UMR she held many positions on the executive council of Kappa Delta Sorority. She also held numerous positions in Omicron Delta Kappa, a leadership organization, and Phi Sigma Biology Honors Society. For three years, she welcomed freshmen to campus as a PRO Leader. After finishing her Bachelor Degree, she went on to complete a Master of Science in Environmental Engineering at Missouri University of Science and Technology. During her graduate degree, she joined the United Church of Christ praise band. She also became a member and held positions, including president, of Water Environment Federation. After graduation, she moved to Houston, TX to work as an Environmental Engineer for CH2M HILL.