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Use of In-planta Solid Phase Sampling Devices to Delineate VOC Plumes

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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 in which this valuable data can be accessed to replace as well as supplement contaminated-site investigations have been developed. When determining the extent of the plume on a contaminated site, groundwater sampling may be limited due to time, site access, and expense. By using new techniques that place 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.

INTRODUCTION

Tree cores collected from contaminated sites have shown concentrations of VOCs that correlate with the groundwater 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; Larson et al. 2008). The cores are a good qualitative analysis, but the heterogeneity of the cores leaves a range of unpredictability and error. In order to reduce these variables, new methods have been designed. One of the new methods is using a Solid Phase Micro Extraction (SPME) sampler to directly sample the VOC concentration qualitatively in cores. SPME samplers consist of fibers of varying matrixes that have highly absorptive characteristics. 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). Fibers can also decrease the mobilization costs, site impacts, permanent capital costs and repeat sampling costs. As well, the sensitivity was increased from coring analysis by 20-100 times.

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

that 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.

MATERIALS AND METHODS

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 (Struckhoff et al 2005, 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 (Struckhoff et al 2005, Schumacher et al. 2004) and in the borehole remaining, SPME analysis was conducted using time weighted average (TWA) methods (Koziel and Pawliszyn, 2001), using 100 μm Carboxene SPME fibers supplied by Supelco Analytical (Sigma-Aldrich Co., Bellafonte, Pennsylvania). In TWA analysis, a SPME fiber with a high contaminant affinity is exposed to a sample media with the fiber retracted into the SPME needle for a given period of time. For TWA analysis, the contaminant concentration in the fiber must not be near the equilibrium concentration or the TWA rules of sampling are violated. The fibers were exposed in the trees at the New Haven Kellwood Site (OU2) site for 70 – 75 minutes, capped and transported to the Missouri S&T environmental engineering laboratory for analysis using an Agilent 6890 GC with detection via ECD. Details are presented elsewhere (Sheehan 2009).

SPS development and Testing SPSs were constructed and exposed to a steady concentration of PCE to evaluate absorption rates. SPSs were constructed using polydimethyl silicone (PDMS) tubing cut into sections with mass ~0.5g. Mass was accurately determined and recorded, and each section was placed on a threaded stainless steel screw and secured with a nut, Figure 1. SPSs were placed in methanol for two days and allowed to dry under a hood to remove any contamination from production, shipping and storage. The SPSs were then placed in an incubator for 2 days at 100°C. The tubes were then cooled off and placed into a 100 mL beaker within a 300 mL screw top jar also containing a layer of PDMS oil dosed with PCE/TCE, Figure 2. This controlled the chemical activity (i.e. concentration) in the gas phase at low levels, without depleting the mass via absorption into the SPSs. There was no direct contact of SPSs with PDMS oil containing PCE/TCE. The tubes were placed within the PCE/TCE environment at the same time. To determine the uptake rates, the tubes were 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 tube 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 over time.

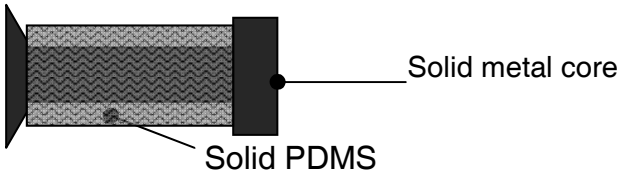

Figure 1: Solid Phase Sampler (SPS) assembly

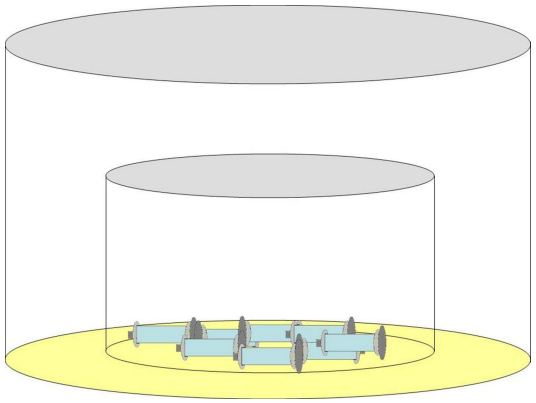

Figure 2: Solid Phase Samplers were placed in an open beaker inside a closed beaker containing PCE and TCE dosed PDMS oil.

Comparison of SPSs Versus Cores

As tree cores are highly variable in their collection and initial evaluation was set to evaluate tree xylem tissue versus the SPSs as a material, surrogate cores were used and constructed by cutting dowel rods at a mass of ~0.5g, diameter 0.4 cm, and the mass of each was recorded. The SPSs and 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. The SPSs and cores were exposed for 3 weeks allowing them both to come to equilibrium with the surrounding environment. SPSs and cores were removed using tweezers and placed into separate vials and capped for analysis as noted above.

RESULTS

Field Comparison of *In-planta* SPME Methods and Tree Core Analysis Sampling of trees at the New Haven Kellwood Site (OU2) was conducted on 4 trees known to be in a polluted area that had been previously analyzed and one tree that had been sampled and never shown to contain contaminants (Schumacher et al, 2004). Results of tree core analysis using accepted methods revealed contamination of both TCE and PCE in the trees. Based on peak areas using the same GC methods, the *in-planta*

SPME methods had peak areas from 4 to 230 times higher, with an average increase of 13 times for TCE and 62 times greater for PCE, Table 1. For the one duplicate analysis, the SPME also had a similar variation between the two analyses, 85% vs 91% for TCE and 55% vs 53% for PCE. This analysis shows that SPME *in-planta* analysis has definite potential for providing improved method detection limits with similar variability in analysis. The SPME analysis also has the benefit of potentially rapid analysis. The headspace methods for tree core analysis generally have a 24 hour equilibration period, although recent method development has shown that heating samples can reduce the equilibration period required (Vroblesky, 2008).

Table 1 Comparison of standard tree core analysis and *in-planta* SPME analysis with TWA methods.

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

Sorption Rates for SPSs Results for the absorption rates showed a clear relationship for both PCE and TCE absorption, Figure 3. Absorption as measure by the mass transferred to the SPSs increased rapidly over the first 96 hours and then reached apparent equilibrium at approximately 240 hours, 10 days. Equilibrium was reached if the change was less than 1 % over 72 hours. A simple first order uptake model was applied to each, Equation 1, with a first order uptake coefficient of 0.017 hr^{-1} and 0.024 hr^{-1} for PCE and TCE respectively. The importance of this methodology is to show that the SPS is more sensitive and predictable in the uptake (i.e. absorption). 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.

$$A = A_{max} (1\text{-}e^{-kt}) \qquad \text{(Equation 1)}$$

Where A = peak area, A_{max} = peak area at equilibrium, k = 1st order rate coefficient (hr^{-1}), t = time (hours).

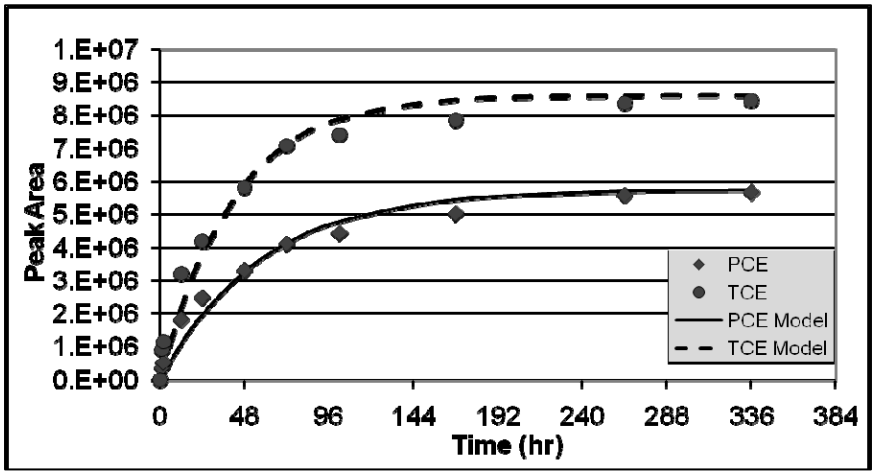

Figure 3: SPS-controlled absorption rate of PCE and TCE, showing equilibrium in approximately 10 days. The absorption followed a 1st order kinetic model.

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 and had lower variability for both PCE and TCE; while core and headspace analysis was slightly more sensitive for TCE, Figure 4. The SPS peak area response was 98% higher than the core analysis for PCE, whereas the SPS response was 35% lower than the core analysis. The SPSs were more reproducible. 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.

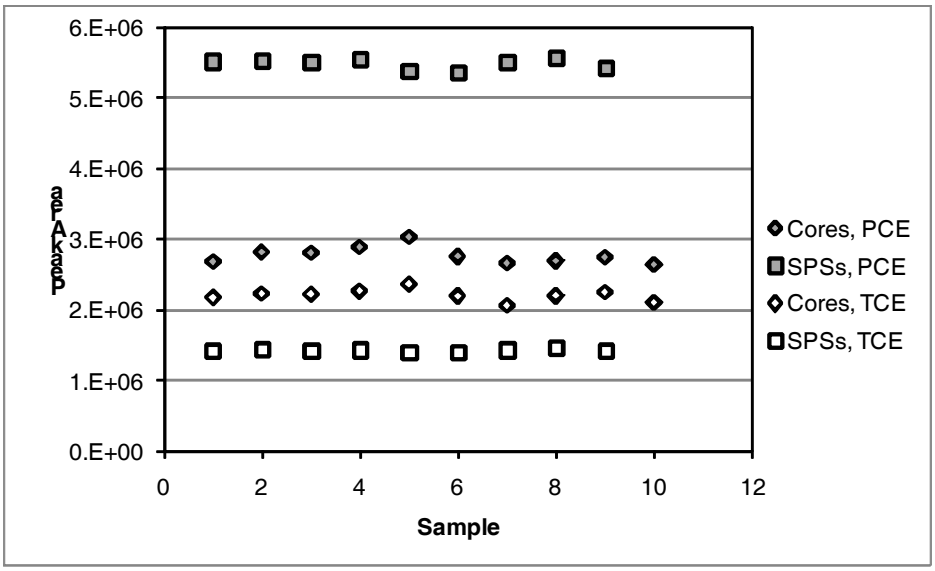

Figure 4: The SPSs and Cores were dosed and analyzed on the GC-ECD headspace autosampler.

CONCLUSION

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. Plant sampling overall has benefits of minimal environmental or property disturbance. Sampling is accomplished with very little materials cost, 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. This new approach is patent-pending and appears to have a bright future if optimized further.

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