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In planta passive sampling devices for assessing subsurface chlorinated solvents

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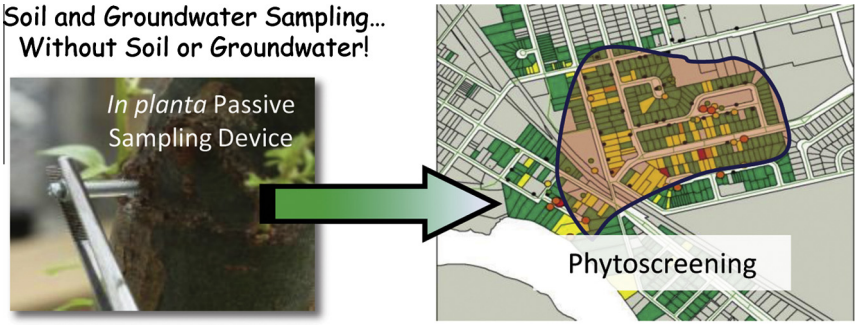
HIGHLIGHTS

- Kinetic and equilibrium characteristics of five passive samplers were determined.
- The PDMS sampler was capable of measuring plant PCE and TCE concentrations.
- Passive sampling devices in trees are a helpful phytoscreening tool.

GRAPHICAL ABSTRACT



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ABSTRACT

Contaminant concentrations in trees have been used to delineate groundwater contaminant plumes (i.e., phytoscreening); however, variability in tree composition hinders accurate measurement of contaminant concentrations *in planta*, particularly for long-term monitoring. This study investigated *in planta* passive sampling devices (PSDs), termed solid phase samplers (SPSs) to be used as a surrogate tree core. Characteristics studied for five materials included material-air partitioning coefficients (K_{ma}) for chlorinated solvents, sampler equilibration time and field suitability. The materials investigated were polydimethylsiloxane (PDMS), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polyoxymethylene (POM) and plasticized polyvinyl chloride (PVC). Both PDMS and LLDPE samplers demonstrated high partitioning coefficients and diffusivities and were further tested in greenhouse experiments and field trials. While most of the materials could be used for passive sampling, the PDMS SPSs performed best as an *in planta* sampler. Such a sampler was able to accurately measure trichloroethylene (TCE) and tetrachloroethylene (PCE) concentrations while simultaneously incorporating simple operation and minimal impact to the surrounding property and environment.

1. Introduction

The efficient and accurate detection of subsurface contamination is a crucial step in risk assessment and in the remediation of contaminated sites. Chlorinated volatile organic compounds (cVOCs), such as perchloroethylene (PCE) and trichloroethylene (TCE), have been historically used as dry cleaning solvents, degreasing agents and paint strippers due to their ability to dissolve oil and grease, low cost, and high volatility (Doherty, 2000a,b). These chemicals were intentionally manufactured with high chemical stability, leading to their persistence in the natural environment. However, many of these chemicals also pose a threat to human health due to their potential carcinogenicity (NTP, 2011), resulting in low drinking water maximum contaminant levels (MCLs) (EPA, 2013). Delineation of subsurface cVOC plumes via traditional groundwater monitoring is a time- and resource-intensive process, involving the drilling of multiple wells on-site that provide data of

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limited spatial and temporal resolution. To minimize cost, time, labor and environmental impact, new and improved environmental assessment methods are needed to better screen potentially contaminated sites.

Previous research has shown that plants directly interact with the surrounding water, soil and air, collecting and storing chemicals from the environment (Schnoor et al., 1995; McCutcheon and Schnoor, 2003; Henry et al., 2013). Phytoremediation of these chemicals has also attracted considerable attention due to the low costs incurred and other ancillary benefits (Henry et al., 2013). Sustained interest in this area of research has led to several published reports of plant–VOC interactions (Nietch et al., 1999; Ma and Burken, 2003, 2004; Doucette et al., 2004; Struckhoff et al., 2005; Baduru et al., 2008). Using this knowledge, novel techniques have been developed to successfully use plants as biosensors for the detection and analysis of subsurface contamination (i.e., phytoforensics) (Balouet et al., 2009; Burken et al., 2011). One example of phytoforensics is phytoscreening, which has been used to delineate shallow groundwater plumes of PCE and TCE (Vroblesky et al., 1999; Sorek et al., 2008; Vroblesky, 2008; Holm and Rotard, 2011; Wahyudi et al., 2012). Phytoscreening typically involves the removal and analysis of a core from the tree trunk using an increment borer (Vroblesky, 2008). However, this sampling technique is not practical for long-term monitoring using trees (i.e., phytomonitoring) due to the repeated damage to the tree. In addition, analysis and comparison of the tree core concentrations generally requires knowledge of the partitioning coefficients, which are dependent on the wood composition, particularly lignin and lipid content (MacKay and Gschwend, 2000; Trapp et al., 2001). Partitioning coefficients between wood cores of five different genera have been shown to vary by a factor of four (Gopalakrishnan et al., 2009). To more accurately measure contaminant concentrations in trees, a more reproducible sampling matrix is needed.

Innovative *in situ* sampling methods have been developed to detect and quantify groundwater contamination passively, such as dialysis samplers, polyethylene devices (PEDs) and solid phase microextraction (SPME). These passive sampling devices (PSDs) collect the target analytes without affecting the bulk solution, allowing PSDs to be used as long-term integrative samplers (Mayer et al., 2003; Jackson et al., 2005). A major advantage of the PSDs is the enrichment of trace organics that may be otherwise undetectable. However, quantification requires that the equilibrium and transient response of the passive sampler be known for the environmental volume being sampled (Mayer et al., 2003). Non-equilibrium sampling and environmental factors such as wind and temperature can affect measured contaminant concentrations (Krupa and Legge, 2000). The time period of interest also influences the choice of sampler, as traditional grab sampling methodologies are more sensitive than PSDs to transient conditions. Assuming concentrations in PSDs can be accurately measured and interpreted, PSDs can sample over a period of weeks or months to yield a time weighted average (TWA) concentration (Martos and Pawliszyn, 1999; Khaled and Pawliszyn, 2000; Fox et al., 2010; Sheehan et al., 2012). Passive sampling techniques have also been found to be simpler to use and more cost-effective than active sampling (Heringa and Hermens, 2003; Vrana et al., 2006; DiFilippo and Eganhouse, 2010; Qin et al., 2010; Gschwend et al., 2011).

This research specifically investigated a new passive sampler, termed solid phase samplers (SPSs), intended to be placed into trees at contaminated sites. The SPS would then be removed and analyzed *in vitro* to provide quantitative *in planta* chemical concentrations. The performance and sensitivity of different materials commonly used as PSDs was studied to evaluate their viability as *in planta* samplers. In evaluating materials, high material:air partitioning coefficient for target analytes, short time to equilibrium, and field viability were considered most desirable.

2. Materials and methods

2.1. Solid phase sampler (SPS) materials

The SPS consisted of tubing or rods of different rubbery polymers, cut to a standard length of 2.6 cm to fit into the space created by removing a tree core (typical diameter <0.5 cm, 5–10 cm long). The sampler materials tested in this particular study included amorphous polydimethylsiloxane (PDMS) tubing, plasticized polyvinylchloride (PVC) tubing, semi-crystalline low density polyethylene (LDPE) tubing, semi-crystalline polyoxymethylene (POM) rod, and semi-crystalline linear low density polyethylene (LLDPE) tubing. All sampler materials used in the study were purchased from McMaster–Carr Inc. (Chicago, IL). Sampler dimensions, masses, densities (after cleaning) and the glass transition temperature (T_g) are shown in Table 1.

SPS pieces were cleaned in ACS Grade methanol (Fisher Scientific) for a period of 48 h to remove oligomers after which they were allowed to air dry (Rusina et al., 2007). All pieces were then placed in an oven at 100 °C for 48 h. Material dimensions and mass were measured before and after cleaning, revealing less than 1% mass loss in most polymers, except PVC (16% mass loss), and no significant change in density (see Appendix A). The samplers were stored in aluminum foil prior to deployment in the laboratory or in the field.

2.2. Uptake kinetics

Following the methodology of ter Laak et al. (2005) a static dosing chamber assembly was used to provide a continuous source of chlorinated solvents. The chamber consisted of three 100-mL beakers placed inside a 2-L screw top jar that contained 100 mL of PDMS oil (Acros Organics) dosed with PCE, TCE, *cis*-1,2-dichloroethylene (cDCE) and chloroform (CF) at approximately 1, 20, 500 and 50 mg m^{-3}, respectively. SPSs were placed into the beakers to avoid direct contact with the dosed oil (see Fig. A1). A maximum of forty SPSs of the same sampler material were placed in the dosing chamber at one time. The large volume of oil relative to the sampler volume ensured that the gas phase concentration of all chlorinated solvents remained constant throughout an experiment. PDMS oil was specifically chosen because it has a high affinity for chlorinated solvents (i.e., a low activity coefficient in the PDMS oil).

To estimate kinetic uptake, sampler pieces were pulled out in triplicate after 12 different exposure durations: 1 h, 2 h, 5 h, 12 h, 1 d, 2 d, 4 d, 6 d, 8 d, 10 d, 12 d and 14 d. Once removed from the dosing chamber, each piece was placed inside a 20-mL vial with a screw top cap and PTFE septa (Supelco, Bellefonte, PA). The samplers were found to equilibrate with the vial headspace within 24 h at room temperature (data not shown), after which the vial headspace was analyzed using negligible depletion solid-phase microextraction (nd-SPME) gas chromatography with micro electron capture detection (GC-μECD) (Limmer et al., 2011). A polydimethylsiloxane SPME fiber was able to equilibrate with the headspace within five minutes, followed by separation on a VOCOL

Table 1
SPS Material Properties.

Material	Type	Outer diameter (in)	Wall Thickness (in)	Sample mass (g)	Density (g/mL)	T_g (K) (Peyser, 1989)
LLDPE	Tubing	1/8	1/32	0.15	0.83	148-240
PDMS	Tubing	7/32	1/16	0.65	1.25	146
PVC	Tubing	3/16	1/16	0.60	1.26	354-371
LDPE	Tubing	1/16	1/32	0.18	0.91	148-240
POM	Rod	3/16	–	0.65	1.42	191