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In planta solid phase sampling devices used in delineating groundwater contaminant plumes

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IN PLANTA SOLID PHASE SAMPLING DEVICES USED IN DELINEATING GROUNDWATER CONTAMINANT PLUMES

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ABSTRACT

The widespread and indiscriminate use of chlorinated volatile organic compounds as cleaning agents at dry - cleaning facilities, as metal degreasers and solvents in extraction and removal operations has been well documented in the past resulting in releases, while contaminating soil and groundwater. Current techniques to assess chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE) in the subsurface have been time and cost intensive and more importantly invasive to the surrounding environment. New methods use trees as sources of information to access contaminant plume size and plume delineation. The major goal of these research studies has been to save time and money and minimize impact to the surrounding ecosystem, establishing reliable and repeatable results. This study looks at the use of new sampling devices called Solid Phase Samplers (SPSs) and gives insights into the various materials that may find applicability for use as *in planta* samplers.

Laboratory studies included the estimation of the variable uptake kinetics for the materials tested as well as the determination of the material:air partitioning coefficients for chlorinated solvents of interests. These results were then applied in a greenhouse setting as well as in the field to assess sampler material performance The results indicate that linear low density polyethylene (LLDPE), polydimethylsiloxane (PDMS) and polyvinylchloride (PVC) are the most suitable for use as *in planta* samplers. These techniques used have great potential as sampling aids in the field of phytoforensics and may further supplement initial site investigations for chlorinated solvents in the subsurface.

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NOMENCLATURE

"Symbol"	"Description"
PCE	Perchloroethylene
TCE	Trichloroethylene
DNAPL	Dense Non- Aqueous Phase Liquid
PED	Polyethylene Devices
SPME	Solid Phase Microextraction
PSD	Passive Sampling Device
SPS	Solid Phase Sampler
cDCE	cis- Dichloroethylene
VC	Vinyl Chloride
cVOC	chlorinated Volatile Organic Compounds
SPMD	Semi – Permeable Membrane Device
PDMS	Polydimethlysiloxane
LDPE	Low Density Polyethylene
POM	Polyoxymethylene
PVC	Poly Vinyl Chloride
LLDPE	Linear Low Density Polyethylene
PISCES	Passive In-Situ Concentration / Extraction Sampler
PUF	Polyurethane Foam Disks
HS-SPME-GC	Headspace Solid-Phase Microextraction Gas Chromatography
CEC	Cation Exchange Capacity
1,2, DCA	1,2 - Dichloroethane

1. INTRODUCTION

Locating and assessing subsurface contaminants with a high degree of accuracy and efficiency has always been a critical concern with regard to the remediation of contaminated sites and the protection of health. Chlorinated volatile organic compounds (cVOCs) like perchloroethylene (PCE) and trichloroethylene (TCE) have been traditionally used as dry-cleaning solvents and degreasing agents due to their ability to dissolve oil and grease. Chlorinated solvents were designed to be chemically stable and low cost chemicals. Close to 80% of active dry cleaning facilities in the United States are estimated to use one of these two chloroethenes as their primary solvent of choice [1]. Unregulated use in large quantities from the 1930s through the 1970s and spills resulting from leaks and improper disposal practices has made these solvents a major environmental concern the world over. cVOCs are classified as DNAPLs (Dense Non-Aqueous Phase Liquids) due to their density being higher than that of water and low solubility in water. As a result cVOCs sink to the bottom of the aquifer, from where they undergo slow dissolution into the surrounding groundwater for decades to come. Thus, chloroethenes are evasive, stable compounds that undoubtedly pose a serious threat to health. The International Agency for Research on cancer classifies PCE under group 2A – "probably carcinogenic to humans" and exposure to these chlorinated solvents has been related to the development of bladder, liver and kidney cancer in the past [2]. The indiscriminate and improper disposal has made them the most prevalent groundwater contaminants in the United States.

Efforts to remediate chloroethenes from groundwater have been active for decades. Traditional methods leading to the detection and subsequent remediation of chemicals in groundwater are cumbersome, invasive and expensive. In efforts to discover innovative techniques for detection and monitoring, there has been a considerable body of research that includes technologies like dialysis samplers, polyethylene devices (PEDs) and Solid Phase Microextraction (SPME). Vroblesky et al. were the first to use tree cores to delineate shallow groundwater plumes contaminated with PCE and TCE [3]. Plants directly interact with the surrounding water, air and soil, collecting and storing chemicals and elements from the surrounding environment. Research has shown that the use of plants for the cleanup of contaminants (phytoremediation) has attracted considerable attention due to the lower costs incurred as well as aesthetic benefits [4]. From this research, a better knowledge and understanding of the plant-chemical interactions was documented. Known fate mechanisms include direct uptake followed by degradation in the tree, evapotranspiration, binding to tree tissue, as well as bioremediation in the rhizosphere by microbes. Based on this enhanced understanding of plant- chemical interactions, novel techniques may be developed to successfully use plants as biosensors for the detection and analysis of subsurface contamination.

The distinct advantages inherent in the use of these passive sampling devices (PSDs) are their robust nature and reliability as well as the ability to be used as long term integrative samplers. PSD's are able to collect the target chemicals in-situ and do not affect the bulk solution [5]. A major advantage of PSDs is the accumulation of trace organics within the PSD matrix, which may be otherwise undetectable, thereby increasing the mass of chemical in the sampled volume or mass. Important requirements

of these equilibrium sampling methods include stable analyte storage after a known accumulation time; shorter response times for the sampler than the changes in concentrations being measured and that sampler capacity remain well below that of the bulk sample in order to avoid depletion [6].

With regard to specific applications of the PSDs in the field of phytoremediation, the unique edge that these methods hold over tree-coring is that they provide a method of sampling that is not limited by the wood:air partitioning coefficient as is evident in tree coring but is instead a direct function of the target chemical's affinity to the sampler material. This allows for a greater mass of analyte being collected by the PSD. The PSD can then be analyzed. Passive sampling techniques have also found applications in the detection and analysis of contaminants in different matrices of interest like air and soil, in addition to their extensive use as aqueous-phase contamination detectors.

This research specifically looked at combining unique approaches and new techniques that involve the placement of PSDs termed solid phase samplers (SPSs) in trees growing at contaminated sites followed by laboratory analysis post-equilibrium. The performance and sensitivity of a number of different materials commonly used as SPSs was studied to demonstrate their viability as *in planta* samplers, in supplementing contaminated-site investigations for chlorinated solvents. The consistent results obtained in the study clearly demonstrate that the use of these solid phase samplers (SPSs) holds great potential for rapid, accurate and cost effective long term site assessment and monitoring.

2. GOALS AND OBJECTIVES

The primary goal of this study was to determine polymeric materials for suitability as *in planta* SPSs. The viability of polymeric *in planta* samplers needed to be evaluated simultaneously arriving at the optimal of the sampler materials. To achieve these goals, certain specific objectives were established. The objectives of the current study are to:

- Quantify uptake kinetics and time to reach equilibrium for each of the sampler materials by developing respective transient uptake curves.

  Hypothetical basis: Each polymeric material has a variable time to reach equilibrium which can be observed using a transient uptake curve.

- Determine equilibrium partitioning coefficients for specific polymeric materials.

  Hypothetical basis: The concentration of chlorinated solvents accumulated in a sampler material is related to its material:air partitioning coefficient.

- Compare *in planta* SPS sampling results to those from tree core analysis in a greenhouse setting to confirm kinetics and applicability in the field.

  Hypothetical basis: Results from *in planta* SPS sampling are comparable to *in planta* tree core analysis on site.

- Compare results from SPS sampling to those from tree core sampling at various contaminated sites and demonstrate plume mapping capabilities successfully.

  Hypothetical basis: *In planta* concentrations obtained from tree coring may be qualitatively compared to those obtained from SPS analysis.

- Assess and compare sampler material applicability for use as an *in planta* SPS to detect chlorinated solvents in the subsurface.

  Hypothetical basis: A single sampler material can be described as most suited for *in planta* sampling using characteristics such as high partitioning for chloroethenes, short equilibration time and repeatability.

3. LITERATURE REVIEW

3.1 CHLORINATED VOLATILE ORGANIC COMPOUNDS

Chlorinated volatile organics like perchloroethylene (PCE) and trichloroethylene (TCE) were two of the most intensively used cleaning and degreasing solvents in the United States [7]. PCE and TCE are non flammable, highly volatile liquids with an inherent ability to dissolve grease and oil. Their low cost and easy availability has ensured their widespread and unregulated use in the United States making them suitable for use in applications ranging from an anesthetic in the medical community, to a degreaser in industry and the military as well as a solvent in dry cleaning, since the 1930s. It is estimated that of the approximately 34,000 dry cleaning facilities operational in the United States, around 82 % of them use PCE or TCE as the primary solvent [1]. Due to spills, leaks and poor disposal practices these chlorinated ethenes were released into the environment from dry cleaning and industrial facilities. As they were designed to be chemically stable, they are highly recalcitrant in many natural environments.

Chlorinated solvents are a major environmental and health concern the world over. The International Agency for Research on Cancer (IARC) classifies PCE under group 2A – "probably carcinogenic to humans". Exposure to these chlorinated solvents has been related to the development of bladder, liver and kidney cancer in the past [2]. Although the distribution and absorption of chlorinated solvents into the blood stream has not been disputed, the after effects of elevated levels of these chemicals in the blood are still under review. Some studies have looked at the relationship between proximity to dry cleaning facilities and the incidence of kidney cancer among residents in metropolitan

areas. The results appear to agree with the hypothesis that living in close proximity to dry cleaning facilities using chlorinated solvents, does in fact increase the risk of exposure to chlorinated solvents and of developing kidney cancer [8].

PCE has been reported to cause toxic hepatitis in adults when test subjects were exposed to the chemical over a prolonged period. Researchers have also cited reports of the death of a 16 year old boy following intoxication from a freshly dry cleaned and inadequately aired sleeping bag. Besides, Bagnell et al., also reported a study which indicated the possibility of obstructive jaundice in children due to the presence of PCE in breast milk [9]. Other studies by Blando et al. indicate that many states in the US including New Jersey have seriously considered the banning of PCE for use as a dry cleaning solvent. The motivating factors mentioned in the report include the widespread use of PCE in the dry cleaning industry as well as the listing of PCE by the US Environmental Protection Agency's (EPA) Urban Air Toxic Strategy as one of 33 chemicals thought to pose the most significant health risks among the general public [10]. A proposed rule in New Jersey would gradually phase out all PCE usage by 2021 and ban its use by cleaners in residential buildings after July 2009 [11].

3.2 TRADITIONAL TECHNIQUES OF REMEDIATION - DRAWBACKS

Prior to RCRA and toxic compound inventory tracking common practices included dumping these chlorinated solvents "out the back door" or disposal at remote locations once they had served their purpose and utility. Such disposal practice, coupled with indiscriminate usage and lax regulations on the part of the regulators has made these chemicals the most prevalent soil and groundwater contaminants in the United States [4]. PCE and TCE are classified as DNAPLs (Dense Non- Aqueous Phase Liquids) due to

their density being higher than that of water. Due to a very low solubility in water the chemicals have the ability to sink to the bottom of an aquifer from where they undergo slow dissolution into the surrounding groundwater for decades. The stable, persistent and evasive nature of these contaminants makes them a serious threat to human health and as a result a large body of research can be found in the literature, dedicated to the detection and remediation of chlorinated solvents. A very significant fraction of the cost associated with the remediation of contaminated soil and groundwater has been attached to site assessment, plume delineations and monitoring costs. Due to the diverse nature of the groundwater contamination found in the United States as well as the cost and technology limitations associated with the clean up, the eventual goal of such an effort has been modified from being remediation to a more long term risk management approach.

Traditional methods leading to the detection and subsequent monitoring of contaminants in groundwater have been cumbersome, time – consuming, evasive and rather expensive. The monitoring of contaminated groundwater often includes long-term monitoring, which eventually leads to monitored natural attenuation; the process by which contaminants are remediated by natural processes such as degradation and dilution. This process of long term monitoring usually includes the expensive sampling at tens or even hundreds of wells installed on site, which will end up costing millions of dollars not only on well installation and monitoring but also on data management. Also, once the wells are drilled in, the pumping of water and subsequent disposal has always been a cost constraint. Water storage and purging requirements increase with increasing depths of the monitoring well according to studies by Harte et al., [12].

The enormous task of removing these chlorinated solvents from the subsurface is currently accomplished most often by pump-and- treat procedures and the time required for adequate clean up to be achieved may range from a few decades to even centuries [13]. Existing methods usually include the pumping of the contaminated water to the surface after which it is stripped to the atmosphere, sorbed onto activated carbon, or destroyed by chemical or microbial means. *In situ* methods usually involve the stimulation of the aerobic or anaerobic environments within the aquifer or even the installation of chemically reactive zones. Unfortunately, some of these applications require the use of potentially toxic inducer compounds. The time line for remediation is also fairly long with tremendously high investments of manpower and financial resources required [4].

Degradation in the subsurface is one of the fate mechanisms for these chlorinated solvents and while aerobic degradation has been observed in the past, anaerobic reductive dechlorination is the most common degradation pathway. In this process PCE is degraded to TCE, which is further dechlorinated to cis - dichloroethylene (cDCE), vinyl chloride (VC) and finally to ethene. This process as a whole is termed as reductive dechlorination and is the single most important mechanism responsible for the natural attenuation and degradation of chlorinated solvents. Typically, preliminary site investigations at a contaminated site involve the collection of soil and groundwater samples from boreholes. While the drilling of the boreholes is in itself expensive, other issues with these traditional approaches include the enormous amounts of time required for such an exercise as well as the need for heavy equipment and vehicle access to the site, which can be difficult, invasive and ecologically damaging [14]. Most traditional monitoring

programs involve the collection of discrete grab samples at a given time. Hence, at contaminated sites where the target contaminants are present at trace levels, large volumes of water need to be collected. The subsequent laboratory analysis of samples offers only a snapshot of the pollutant concentrations at that point in time. This may become a problem in areas where contaminant concentrations are changing with respect to time. Due to the presence of these and other problems with traditional techniques, the need was felt for more innovative methods of plume detection, delineation and remediation to be developed.

3.3 NEW INNOVATIVE TECHNIQUES EMPLOYED

Some of the new and innovative techniques involved in the detection of contamination in groundwater involve approaches whereby test biota are deployed in the field for extended periods of time, during which they are able to passively bio-accumulate the pollutants from the surrounding water. By analyzing the tissues or the lipids of the test species, an estimation of the equilibrium level of waterborne contamination can be made. However there are some drawbacks to this approach, as a number of factors may possibly impact the results. Metabolism, stress, excretion and the condition of the original test subjects are only some of the apparent ones. The extraction of target contaminants from the tissue of the biota is also a complex process [5].

Other techniques involve the measurement of contaminant concentrations in the benthic sediments followed by the use of equilibrium distribution coefficient to estimate the concentration of target analytes. The major drawbacks of this approach are the assumptions that the sediments are in equilibrium with the water column at all times as also that the impacts of organic carbon present in the sediments and its implied effects on

partitioning values are negligible [5]. However the impact of the organic carbon on the partitioning values cannot be discounted and may have profound impacts on the results.

The use of trees as aids in the detection and remediation of groundwater contamination has received attention over the last decade. The primary reasons for this have been the multiple mechanisms by which trees are able to accumulate or destroy a variety of contaminants. The known fate mechanisms include direct uptake from the subsurface followed by degradation within the tree by various methods, evapotranspiration of the contaminants into the atmosphere, the binding of contaminants to the plant tissue, and the bioremediation of the contaminants by way of the enhanced microbial activity in the rhizosphere [15], [16], [17], [18], [19]. This approach to remediation is of increasing interest to researchers because of the economic, aesthetic and environmental benefits that are inherent in its use. The methods used are intrinsically simple and may be used to concurrently re-vegetate the contaminated site. There is no mechanical pumping involved and at the same time the methods incorporate low initial capital costs as well as low operation and maintenance cost [20].

3.4 PHYTOFORENSICS

It was Vroblesky et al. who demonstrated the presence of chlorinated solvents in tree trunks growing above shallow contaminated groundwater in 1999. The researchers were the first to show that the headspace analysis of *in vitro* tree cores was a fairly rapid and more importantly inexpensive method to delineate shallow plumes contaminated with chlorinated solvents [3]. Other studies demonstrated that the chlorinated solvents were in fact taken up by the trees and also volatilized to the atmosphere by way of evapotranspiration. The diffusion of the cVOCs along the transpiration pathway was

shown to be the primary loss mechanism along with transpiration from the stems and leaves [21].

The use of hybrid poplar trees to study the uptake of multiple organic compounds commonly found at hazardous waste sites demonstrated that fairly accurate relationships predicting the translocation and partitioning of chlorinated solvents to tree tissue can be made. Research was successfully able to show that the VOC's are able to undergo translocation through the tree and that transpiration from plant tissues was a significant fate mechanism [22].

Although phytoforensics does have wide applications in the field some intrinsic drawbacks of the approach have also been studied. One of the major issues with the application of phytoforensic techniques is that they may be applied only in areas where the contamination is in a relatively shallow aquifer. The roots of trees are not able to source contaminants that travel deep below the ground surface and as a result the trees are unable to recover very deep contaminant plumes. A USGS report published by Vroblesky et al., in 2008 indicates that the maximum depth to groundwater where phytoremediation can be thought of as a viable remediation mechanism is 10m below ground surface [23]. Also, the direct evaluation of phytoremediation is hampered because of the inability to pull samples at different depths at high resolution within the rhizosphere. Wells and piezometers although useful, are unable to provide the vertical resolution necessary to distinguish between essentially microbial and abiotic reactions within the aquifer. Hence the study of plant – microbe interactions in the rhizosphere and their effect on the contaminants at hand is severely hampered. The use of trees as

phytoforensic aids may provide better insight into these complicated plant- chemical-microbe interactions [24].

3.5 PASSIVE SAMPLING DEVICES

The monitoring of various pollutants present in groundwater has become a very challenging affair due to a number of factors involved. In order to observe qualitative and quantitative trends of pollution, a large number of samples need to be collected in order to obtain a large enough volume of contaminant. This is especially true for contaminants that are present in trace amounts. These samples need to be collected on a regular basis over a long period of time when the grab sampling approach is adopted. Not only are these methods time consuming, laborious and expensive, the grab samples provide information about contamination only for that instant in time and may fail to report an isolated incident of contamination. It is also important to note that the activity of a compound is a measure of how active a compound is in a given state as compared to its reference state. The grab sampling approach is unable to capture information about the activity coefficients of specific compounds being sampled [25].

The techniques used to solve these problems involve a passive sampling approach whereby chemicals of interest are analyzed as a weighted average over the period of sampling. In studies conducted by Vrana et al. the concentration of the target analyte is integrated over the entire time of exposure, thus making the method less prone to bias generated by the fluctuations in analyte concentrations [26]. These passive sampling devices may be used in different configurations. They may be single – phase devices where the membrane is the receiving phase or some more complex designs incorporated include semi-permeable membrane devices (SPMDs) which consist of triolein lipids

(receiving phase) enclosed within a low density polyethylene (LDPE) tubing (membrane). The concentration gradient present between the analyte in the water and the sampler which is initially free of analyte is the driving force for this diffusive process. Thus, diffusion coefficients of the analytes of interest within the sampler material as well as the sampler:water partitioning coefficients are important parameters in the selection of such passive samplers. The receiving phase of these samplers can be a solvent, a polymeric material, a chemical reagent or a porous adsorbent [27], [28].

Marked advantages of the passive sampling methodology include the simplification of the sampling and sample preparation step, the elimination of power requirements like a pump and a significantly reduced cost of analysis [29]. Ideal passive samplers are cheap, and easy to use with regards to deployment, retrieval and analysis. Once the initial isolation or enrichment step is in place, no further sample preparation is required [30]. The different types of passive sampling devices reported in the literature include those based either on permeation or diffusion, such as SPMDs, passive in-situ concentration/extraction samplers (PISCES), sorbent-filled devices, polyurethane foam (PUF) disks, and SPME [31], [32], [33], [34]. The SPME methodology has further advantages in that sample collection, isolation and enrichment are all combined into a single step thus avoiding the accumulation of any derived waste. It is also solvent- free and does not require further sample treatment post analysis.

In order to effectively quantify the analytical results obtained from passive sampling techniques, there is an intrinsic need for an appropriate calibration methodology. Calibration methodologies based on extraction at equilibrium are simple and have found wide applications among passive samplers. As part of these methods, the

sampler is required to be deployed in the environmental medium for long enough, so as to ensure that thermodynamic equilibrium is established between the receiving phase and the environmental medium. A thorough understanding of the uptake kinetics was demonstrated to be critically important [34].

3.6 EQUILIBRIUM SAMPLING AND SPME

As discussed previously, the conventional strategy used in environmental risk assessments and regulatory programs usually involve the sampling of an environmental medium and the determination of the quantity of analyte present, followed by calculation of the total concentration. The major drawback to this technique is that it does not distinguish between the freely dissolved molecules and those that are bound, hence focusing more on the presence of chemicals rather than their bioavailability or chemical activity. Hence, where conventional approaches employ a more exhaustive extraction and aggressive solvent approach, passive sampling techniques are able to take into account the bioavailability of the analytes being studied. Thus, the use of passive equilibrium samplers holds potential according to research carried out by Mayer et al. because these samplers are able to determine two thermodynamic parameters namely chemical potential and fugacity. The researchers focused not so much on the actual concentration in the medium itself, but more on the concentration in a reference phase, which was brought to equilibrium with the medium. Equilibrium by definition is established when the Gibb's free energy for the system reaches the minimum possible value [35]. The "availability" of a chemical may be directly accessed using these parameters because the chemical potential is logarithmically related to its fugacity and linearly related to its freely dissolved concentration in the media of choice [6].

The two major factors that characterize a sampler include the affinity of the sampler material for the target analytes as well as the sampling rate [36]. The former is controlled by the strength of interactions between the sampler and the chemicals such as Van der Wall's forces and hydrogen bonding. The sampling rate is dependent on sampler size and geometry, conditions of mixing, the sampler matrix as well as other physico – chemical properties of the chemicals and the sampler. Other important sampler properties for use in equilibrium sampling studies according to work performed by Dettmer et al. include low affinity to water to avoid displacement by hydrolysis reactions, low adsorption capacity for other solvents, the ability to completely enrich the analytes of interest while showing high inertness to reactive species, high mechanical and thermal stability as well as quick and complete desorption times [37]. Materials that are soluble in the organic solvents are not suitable for passive sampling because the samplers may swell and this may even impact the inherent properties of the sampler material [38].

Arthur and Pawliszyn first demonstrated the use of solid-phase microextraction (SPME) in which hydrophobic volatile organics were absorbed onto a fused silica fiber coated with an organic polymer. The researchers were able to demonstrate its viability as a simple and solvent free sampling technique with a high analytical performance, small sample size requirement and reduced technician time [39]. Another distinct advantage with the SPME methodology is that a majority of the adsorbed analyte is delivered directly into the analytical instrument. The direct delivery of the contaminant coupled with the affinity of SPME for the target analyte ensures that low detection limits can be established for the volatile organics of interest. Studies have indicated that the headspace SPME gas- chromatography (HS-SPME-GC) method has a high sensitivity for dirty

samples and since there is no direct contact with the liquid or solid matrix, fiber contamination may be avoided which in turn is shown to lead to enhanced fiber- life [40], [41]. This technique for analysis of chlorinated solvents has shown wide applications in environmental sampling.

3.7 POLYMERIC MATERIALS AND PROPERTIES

Six different polymeric materials were used in this study include Polydimethylsiloxane (PDMS) tubing, Polyvinyl Chloride (PVC) tubing, Low Density Polyethylene (LDPE) tubing, Linear Low Density Polyethylene (LLDPE) tubing, Polyoxymethylene (POM) rod and Polystyrene rod. The structural properties of these materials can be outlined as follows:

PDMS – The material is composed of $(CH_3)_2SiO$ repeating units and is traditionally known for its stability to UV, hydrophobicity, thermostability, good gas permeability and biocompatibility among others. It is considered to be non-polar due to the methyl groups set outside the siloxane chain and has been reported to have a partial uniformly positive charge in all directions.[42] The methyl groups that are part of the PDMS structure are able to generate a highly hydrophobic cover at the interface of the polymer and air, in turn yielding very low surface energy. [43]

PVC - Polyvinyl chloride is a thermoplastic used widely in industry due to its low combustibility and combustion resistance. PVC is amorphous in structure and has polar chlorine atoms attached to it owing to which it is reported to have a very high durability and resistance to oxidation by atmospheric oxygen. Reports also indicate that it has low permeability to gases and good resistance to oils and oxidizing agents. [44]

LDPE and LLDPE – LDPE is reported to be one of the first manufactured polyolefins that were produced by the polymerization of ethylene. It has a small amount of branching from the carbon chain and hence has a lower density than other polyolefins. It may be attacked by strong oxidizing agents that may cause swelling, but has good resistance to concentrated acids and esters. LLDPE is a copolymer of ethylene with α-olefins like butane, hexane and octane. The material has higher impact strength and puncture-resistance than LDPE, and is also resistant to ultraviolet radiation. Some reports have also shown that LLDPE exhibits high heterogeneity in intermolecular distribution of monomer units along the polymeric chain. [45]

POM – POM has been described as a highly crystalline thermoplastic material having very high toughness, rigidity, elasticity coupled with high chemical resistance and low gas permeability. Due to this excellent combination of properties POM has found wide applications in the electrical, electronics and automotive sectors[46]. Previous research has reported that POM shows a high affinity for hydrophobic compounds POM has a hard and smooth surface and also shows excellent resistance to organic solvents[47].

Polystyrene – Studies have indicated that polystyrene is a polymeric material having low impact strength, poor weatherability, low resistance to chemicals and poor adhesion to metal surfaces. Commercially, it is used for low cost applications. [48]

4. PAPER

IN PLANTA PASSIVE SAMPLING DEVICES TO DETECT CONTAMINATION BY CHLORINATED SOLVENTS IN THE SUBSURFACE

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ABSTRACT

Rapid, inexpensive detection of contaminants in our biosphere is important to protect human health from fugitive contaminants. To determine the extent of the contamination and effectively delineating the subsurface plume has been an ongoing challenge due to the traditionally cumbersome, time, money and labor- intensive techniques. Vegetation growing on sites may be used as biosensors for detection and sampling of subsurface contamination as plants actively extract all water and nutrients needed from the subsurface. The development of innovative methods in order to effectively use trees as sources of information leading to accurate delineation of the plume boundary and size is a worthy endeavor, to protect human health. This study particularly looked at a new innovative technique using solid phase samplers (SPSs) that may be used as *in planta* passive sampling devices. Several materials were studied to estimate the most suitable sampler material.

Sampler characteristics that were studied during these experiments included a high material:air partitioning coefficient for chlorinated solvents PCE, TCE, cDCE and chloroform, rapid equilibration time once placed *in planta,* and a degree of reproducibility with regard to performance in the field. Six materials in total were tested with these characteristic at the forefront. While the polydimethylsiloxane (PDMS) sampler appears to reach equilibrium the fastest *in planta* within 4 days of deployment, the linear low density polyethylene (LLDPE) sampler demonstrates the highest partitioning for the primary chlorinated solvents of interest at 2261:1 for PCE and 928:1 for TCE. The polyvinylchloride (PVC) sampler also shows favorable characteristics. All results were validated both in greenhouse experiments as well as multiple on-site field trials. The results obtained indicate that these SPSs prove to be applicable for use as *in planta* samplers for use in the field of phytoforensics to supplement initial site investigations while simultaneously incorporating decreased costs, simple operations and minimal impact to the surrounding property and environment.

I. INTRODUCTION

The efficient and accurate detection and assessment of contamination in the subsurface is a crucial step in the remediation of contaminated sites, in keeping with the ultimate goal of the protection of human health. Chlorinated volatile organic compounds like perchloroethylene (PCE) and trichloroethylene (TCE) have been traditionally used as dry – cleaning solvents, degreasing agents and paint strippers due to their phenomenal ability to dissolve oil and grease, low cost and also their high volatility. These chemicals were so to speak, manufactured with excellent chemical stability as an important property and their persistence in the natural environment should not be surprising. Chlorinated

solvents are extremely evasive in the subsurface and their detection and analysis has been a challenge. Due to the threat that the chlorinated volatile organic compounds (cVOCs) pose to the health and welfare of human beings, their quick and accurate detection as well as remediation is a worthy goal.

Traditional groundwater monitoring has been a time- consuming and expensive process, involving the drilling of multiple sampling/ monitoring wells on- site with the help of very limited existing data. With a view to save on cost of time, labor and environmental impact the need for new and improved techniques was felt.

Previous research has shown that plants directly interact with the surrounding water, soil, and air, collecting and storing chemicals from the environment (Refer to Figure 1). The use of plants in the cleanup of these chemicals has also attracted considerable attention due to the low costs incurred and the aesthetic benefits [3], [20], [49]. Sustained interest in this area of research has lead to a considerable knowledge of plant – volatile organic compound interactions being found in the literature. Using this extensive knowledge, novel techniques maybe developed to successfully use plants as biosensors for the detection and analysis of subsurface contamination [50], [51]. Tree coring has been used in the past as a means to delineate shallow groundwater plumes contaminated with PCE and TCE [3]. Other innovative techniques used to detect groundwater contamination include the use of dialysis samplers, polyethylene devices (PEDs) and solid phase microextraction (SPME) among others. These passive sampling devices (PSDs) collect the target analytes in-situ and do not affect the bulk solution, at the same time providing robustness, reliability and the ability to be used as long term integrative samplers [24], [6]. A major advantage of the PSDs is the concentration of

trace organics that maybe otherwise undetectable. Traditional grab sampling methodologies of sample collection are able to provide only a snapshot of the contaminant concentration present at that moment in time. A more reliable approach is to collect samples over a period of weeks or months in order to obtain a time weighted average (TWA) concentration that is able to indicate average exposure to a chemical over a period of time. [52] Studies by Heringa et al. state that passive sampling techniques are simpler to use and more cost-effective than active sampling.(Heringa, 2003) The matrix of the sampler material is immensely helpful in the pre – concentration of the target compound hence increasing its detectibility. The successful application of such PSDs as aids in detection and monitoring of contamination in the environment has been demonstrated in the past [26], [53], [54], [55].

This research specifically looked at combining new approaches that involve the placement of passive sampling devices called Solid Phases Samplers (SPSs) in trees on a contaminated site (Refer to Figure 1) followed by laboratory analysis post – equilibrium. The performance and sensitivity of different materials commonly used as samplers was studied to demonstrate their viability as *in planta* samplers, in supplementing contaminated-site investigations for chlorinated solvents. In evaluating materials, specific properties like high material:air partitioning coefficient for target analytes, short time to equilibrium and a degree of reproducibility were evaluated. SPSs may hold great potential for rapid, accurate and cost-effective detection of cVOCs in the subsurface for initial site assessment studies, as well as long term monitoring goals.

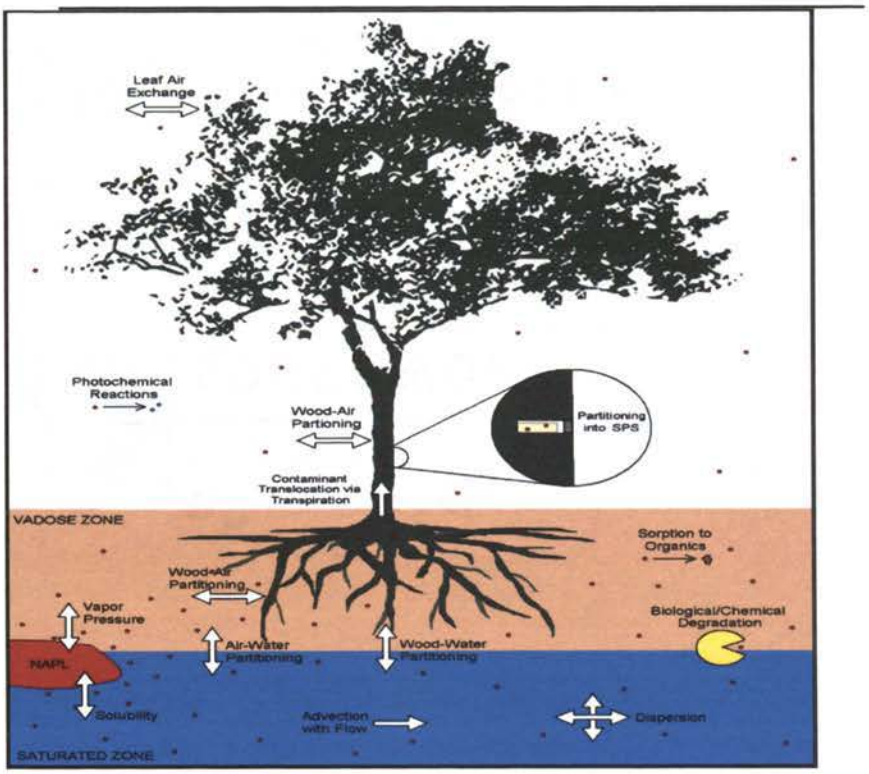

Figure 1 - A schematic demonstrating the various processes and governing relationships present in the complex environment that is found in the subsurface. Diverse interactions take place between the tree, the contaminants, soil microbes, and the groundwater. The contaminants are transported up the length of the tree. An SPS is inserted into the tree once the tree core has been extracted.

II. EXPERIMENTAL METHODOLOGY

1. SOLID PHASE SAMPLERS (SPSs)

The SPS consists of tubing or rods of different polymeric materials, cut to a standard length of 2.6 cm to arrive at a piece of standard mass (± 0.01mg) for each material being tested as *in planta* samplers (Refer to Figure 2). Since the mass of the sampler is greater than that of the SPME fiber, it is able to collect a much larger mass of contaminant, hence increasing the detection level of target volatile organics. All SPS

masses were measured using a Metler Toledo XS 205 Dual Range balance at a resolution of 0.01mg. The sampler materials tested in this particular study included polydimethylsiloxane (PDMS) tubing, polyvinylchloride (PVC) tubing, low density polyethylene (LDPE) tubing, polyoxymethylene (POM) rod, polystyrene rod and linear low density polyethylene (LLDPE) tubing with each piece of the respective SPSs having masses of 0.65g, 0.60g, 0.18g, 0.65g, 0.70g and 0.15g, respectively. All sampler materials used in the study were purchased from McMaster – Carr Inc., Chicago, IL. Sampler pieces were cut to a standard length of 2.6 cm and placed in methanol for a period of 48 hours after which they were allowed to air dry under a fume hood to remove any contaminants that they may have picked up during production and transport. All pieces were then placed in an oven at 100°C for 48 hours. The samplers were then cooled and were ready for use. The samplers were stored in aluminum foil prior to deployment in the laboratory or in the field.

Figure 2 - Photograph showing the SPSs used in testing (to scale). (From top to bottom) Polydimethylsiloxane (PDMS) tubing, polyoxymethylene (POM) rod, polyvinylchloride (PVC) tubing and low density polyethylene (LDPE) tubing.

2. UPTAKE KINETICS EXPERIMENTS

A dosing chamber assembly was used as a continuous source of chlorinated solvents. It consisted of three 100- mL beakers placed inside a 2000- mL screw top jar that also contained 100 mL of PDMS oil dosed with PCE, TCE, cis- DCE and chloroform (Refer to Figure 3). This ensured that the gas phase concentration of all chlorinated solvents remained low without depleting the mass of contaminants from the PDMS oil due to absorption into the SPSs. PDMS oil was specifically chosen because it has a very high affinity for chlorinated solvents and these chemicals have a very low activity coefficient in the PDMS oil. There was no contact between the SPSs and the oil at any stage. Forty SPSs of the same sampler material were placed in the dosing chamber at the same time. To estimate the rate of uptake, sampler pieces were pulled out in triplicate at 12 different time intervals namely – 1 hr, 2 hrs, 5 hr, 12 hr, 1 day, 2 days, 4 days, 6 days, 8 days, 10 days, 12 days and 14 days. As soon as they were removed from the dosing chamber with the help of a pair of tweezers, the each piece was placed inside a 20- mL vial with a screw top cap and PTFE septa (Supelco, Bellefonte, PA) to ensure a good seal. The samplers were allowed to equilibrate at room temperature for 24 hours after which the vial headspace was run via GC as noted below. (Refer to 6). The headspace in the dosing chamber was tested at regular intervals to ensure that the concentrations in headspace were close to saturation at all times during the course of the tests. Periodic checks were run every 48 hours to ensure that the headspace in the chamber was at equilibrium and there was no depletion of contaminant concentration in the headspace.

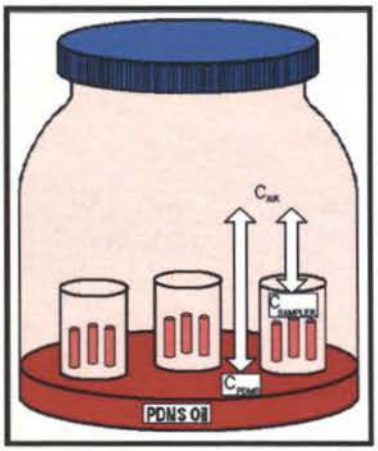

Figure 3- Schematic of the dosing chamber with 100- mL vials placed inside a 2-L screw-top jar. The oil was dosed with PCE, TCE, cDCE and chloroform.

3. MATERIAL:AIR PARTITIONING COEFFICIENT EXPERIMENTS

To determine the material:air partitioning coefficients for the sampler materials noted above, each 2.6 cm sampler piece was further cut into smaller pieces to establish a mass range spanning over 6 different masses for each sampler. Each mass weighed was placed in the dosing chamber apparatus in triplicate and allowed to come to equilibrium with the headspace of the dosing chamber. Time to reach equilibrium for each of the sampler materials were determined from the previously conducted uptake kinetics experiments as discussed above. Once equilibrium had been established, all sampler pieces were pulled out and placed inside a 20- mL vial with a screw top cap and PTFE septa to ensure a good seal. The samplers were allowed to equilibrate at room temperature for 24 hours after which the vial headspace was analyzed as discussed below. Methods used here were based off of research work performed by Legind et al. [56] to

determine the chemical activity of semi-volatile compounds by headspace SPME. In order to estimate $K_{material,\ air}$ the formula used was as stated below:

$$PA = PAo\left(1 - \frac{VolumeRatio}{VolumeRatio + K_{material,\ air}}\right) \quad \textbf{Equation 1}$$

Once peak area values for the various sampler materials were obtained from the GC, the values for $K_{material,\ air}$ were estimated using the variable volume ratios for the different masses of the sampler materials. This was done by running a non- linear regression for the formula stated above using the PASW Statistics 18 ™ software from SPSS – An IBM product, Armonk, NY, USA. The nonlinear regression yielded the final values for the material:air partitioning coefficients of the sampler materials for different chlorinated solvents.

4. GREENHOUSE STUDIES

To mimic field conditions, two large diameter poplar tree cuttings approximately 2-3 m in length and 5-7 cm in diameter were grown in two separate 200-L reactors filled with loam mix. The loam mix consisted of 40% sand, 45% silt, 15% clay and 5.8% organic matter. The salt pH was measured to be 6.8 while the cation exchange capacity (CEC) was 13.3 meq/100 g. All soil characteristics were tested at the University of Missouri Extension Soil Testing Laboratory (Portageville, MO). Both tree cuttings were allowed to grow in the reactors for 5 months before they were cored and used to test the various sampler materials. Water was continuously fed into the bottom of both reactors

by means of a tube with perforations connected to a water reservoir, in order to ensure the uniform distribution of water throughout the soil. All experiments were conducted out in the Baker Greenhouse at the Missouri University of Science and Technology.

Chlorinated solvents (PCE, TCE and chloroform) were injected into the source reservoir. Dosage was controlled such that concentrations for PCE, TCE, and chloroform in the reservoir water were maintained at 10 ppm, 60 ppm and 100 ppm, respectively. Henry's Law constants were assumed to be 0.58 for PCE, 0.34 for TCE and 0.12 for chloroform, (at 20°C) when estimates for reservoir water dosage were made [57]. Tree coring was carried out using techniques suggested by Vroblesky et al. [23] as discussed in Section 5. An SPS was inserted into the space left by the tree core after which a #10-32 x ½" machine screw was used to seal the hole. Stainless steel wire was looped through the tubing in order to aid with the insertion and removal of the SPSs. The screw was inserted to ensure a snug fit. The SPSs were allowed to equilibrate inside the tree for as many days as was estimated from the kinetic uptake experiments for the respective material. (See Table) Once the SPSs reached equilibration inside the tree, the SPSs were removed and immediately vialled and capped.

5. TREE CORING

Tree cores were obtained using a 0.5 cm increment borer manufactured by Forestry Services Inc. Each core was approximately 8cm in length and was taken at a height of around 1 – 1.5 m depending on the diameter of the tree. Once extracted, the core was immediately transferred to a 20- mL vial with a screw top cap and PTFE septa. (Supelco, Bellefonte, PA) Field blanks were taken during every sampling run for QA/QC analysis. Cores were allowed to equilibrate for 24 hours in all cases. Concentrations of

the target analytes present in the vial headspace were then determined by solid phase microextraction (SPME) of the vial headspace. The SPME fiber was desorbed into an Agilent 7890 gas chromatograph equipped with a micro electron captured detector (μECD).

6. ANALYTICAL METHODOLOGY

All samples of tree cores and SPSs were tested using solid phase microextraction (SPME) of the respective vial headspaces using a CombiPAL SPME autosampler (CTC Analytics, Zwingen, Switzerland). A 100μm PDMS SPME fiber was desorbed into an Agilent 7890 Gas Chromatograph (GC) equipped with a micro – electron capture detector (μECD)

A 5 minute extraction time was used along with a 3 minute desorption time at an injector temperature of 230 °C. Purge flow occurred after 0.75 minutes with a flow rate of 60 mL/ min. Nitrogen was used as a carrier gas and was passed through the VOCOL© column having dimensions of 10m x 200 μm x 1.2 μm (Supelco, Bellefonte, PA). The temperature was initially held at 40 °C for 0.75 minutes and was then ramped up at 20 °C/ min until it reached 160 °C, which was the termination temperature of the run. The μECD detector was maintained at 250 °C. Water stocks were used to obtain a calibration curve. 10 mL of water was added to a 20 mL vial and was spiked with PCE, TCE, chloroform and cis – DCE. The vial headspace of five different standards was sampled and a linear calibration plot was obtained from three standard replicates. Both the concentrations and peak areas were log-transformed in order to maintain homoscedasticity for least squares regression. Check – standards were placed after every 10 – 15 samples in order to ensure the validity of the calibration.

7. VALIDATION AT FIELD SITES

In order to demonstrate the validity of their use in the field, these SPSs were tested on - site at two locations which were reported to have contamination by chlorinated solvents in the subsurface.

7.1. BUSY BEE LAUNDRY SITE, ROLLA, MO

The Busy Bee Laundry site is located at Rolla, MO, USA. A number of chlorinated solvents including PCE and TCE are present at the site. Current remediation mechanisms in place include a pump and treat system powered by solar cells and a phytoremediation approach. For this particular study, 3 trees growing on-site were sampled for tree cores and using SPSs. Tree coring techniques as well as SPS insertion and recovery techniques were similar to those mentioned in previous sections. The trees tested include two bald cypresses (*Taxodium distichum (L.) Rich)* and an oak tree (*Quercus robur (L.)*). Since the chamber equilibration studies indicated that PDMS, LLDPE, and PVC samplers had the highest affinity for chlorinated solvents, only these samplers were used for further testing in the field.

7.2. DOW CHEMICALS SITE, SARNIA, ON, CANADA

The Dow Chemical Company field site is located at Sarnia, ON, Canada. Groundwater and soil sampling on – site have demonstrated the presence of chlorinated solvents like PCE, TCE and carbon tetrachloride in the subsurface. A plume map for the total chlorinated volatile organic compounds on – site has been created using at least 50 data points. The images from these studies conducted by Miller et al. demonstrating the spatial distribution of the total VOCs and PCE specifically have been shown in Figure 4 below[58].

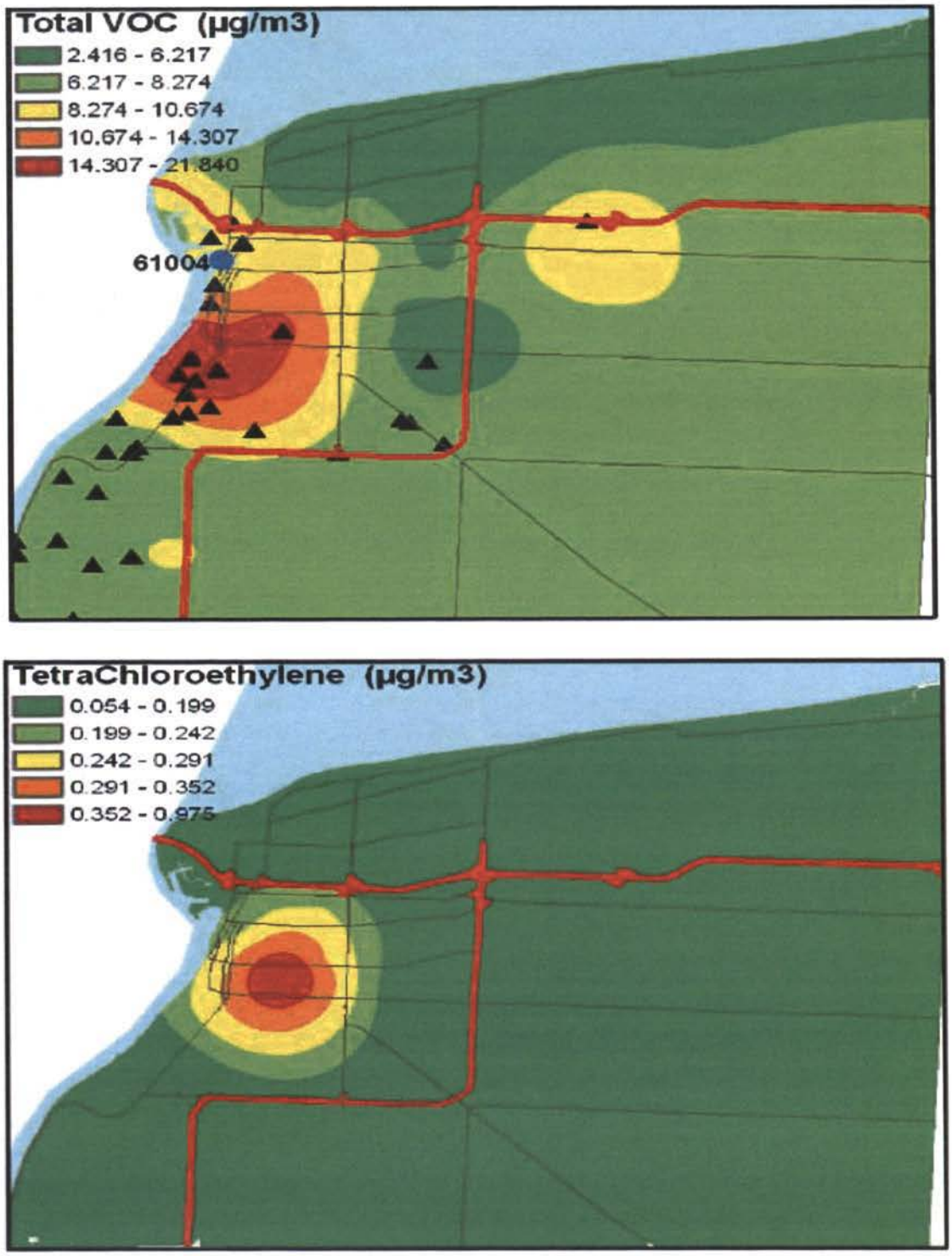

Figure 4– Plume maps showing total VOC (top) and PCE (bottom) concentrations in µg/m^3 at the Sarnia site in Ontario, Canada. Data referenced from Miller et al., 2009.

Rows of hybrid poplar trees were planted on – site in 2008. The site map before and after the trees were planted has been shown in Figure 5.

Figure 5- The Sarnia, ON, Canada site, block 150. Photograph of the site before and after the planting of trees.

At the time of sampling, the trees on site were between 3-5 m in height and 8-10 cm in diameter. Tree coring was carried out for 30 trees using the procedure described in section 5. Two such trips, one on August 26th, 2010 and the other on October 25th, 2010 were conducted in order to collect the tree cores. Approximately 30 trees were sampled during each of the trips to the site. Cores extracted from the trees were 8cm in length and they were taken at a height of approximately 1m. Although traditionally, trees are core at breast-height (~ 1.5m) these cores were taken at slightly lower heights due to the comparatively smaller diameters of the trees. SPSs (0.5g ± 2% PVC (Tygon©) tubing - Formulation R - 3603, I D: 1.6mm, O D: 4.8mm) were placed in the trees in place of the tree core during each trip. As noted above each hole was plugged with a machine screw.

The SPSs were allowed to equilibrate *in planta* for 3-4 weeks and were then transferred to 20-mL screw top vials with PTFE/ silicone septa and were shipped overnight for analysis. The vials (cores and SPSs) were refrigerated until analysis and were brought to room temperature prior to extraction.

It is important to note here that in order to arrive at concentrations in the tree core and the SPS, calibrations were obtained using water stocks. For this purpose, 10 mL of water was added to a 20-mL vial and was spiked with the 8 chemicals of interest. Using SPME, the vial headspace of the five calibration standards was sampled in order to obtain a linear calibration. Three replicates were used for each of the five calibration standards.

III. RESULTS AND DISCUSSION

1. UPTAKE KINETICS EXPERIMENTS

Results obtained from the absorption rate studies for all samplers tested clearly indicate an underlying relationship for the uptake of PCE, TCE, cDCE and chloroform by the SPSs. Uptake kinetics and the time to reach equilibrium is different for different materials thus supporting the initial hypothesis stated to that effect. The transient uptake curves for all materials tested clearly show a rapid uptake during the first 1-2 days followed by a gradual drop in rate and eventual equilibration. Equilibrium was assumed to be established if the change in peak area was estimated to be less than 2% over a 48 hour period. The equilibration chamber setup for lab experimentation was successfully used in order to obtain the time to reach equilibrium for the 6 sampler materials tested. It is important to note here that the inside of a tree is a complex environment that is difficult to replicate in the lab, and hence a dosing chamber apparatus, like the one used in this

study may serve as a learning aid although it is unable to represent the precise inner environment of a tree.

The results indicate that the PDMS uptake was most rapid when compared to the other sampler materials tested. As demonstrated in Figure 6, SPSs made from the PDMS tubing are able to reach equilibrium in close to 4 days. Both the LDPE and the LLDPE sampler, appear to reach equilibrium in 6 days, while the PVC, POM and Polystyrene samplers each require over 9 days to reach equilibrium in the dosing chamber. (Refer to Appendix A for kinetic uptake curves)

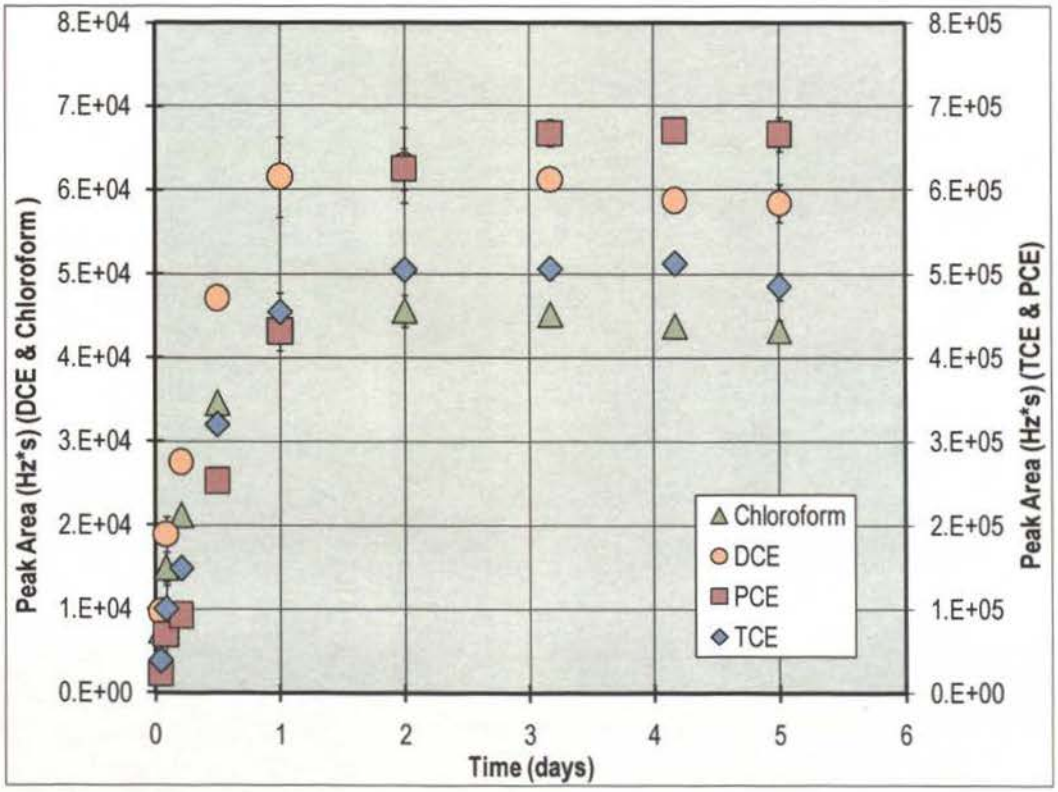

Figure 6- A graph demonstrating the transient uptake curve for the PDMS sampler. As is evident there is rapid uptake for the first 24 hours after which the rate of uptake slows down and equilibrium is established in 4 days.

2. MATERIAL:AIR PARTITIONING COEFFICIENTS EXPERIMENTS

The laboratory experiments to determine the material: air partitioning coefficients for the 6 sampler materials were also successful in yielding good results. The results indicate that the LLDPE sampler has the highest equilibrium partitioning for PCE and TCE while the PVC sampler has the highest partitioning numbers for cDCE and chloroform. All partitioning coefficient values can be observed in Table 1.

Table 1 - Table listing the material:air partitioning coefficients for the various sampler materials tested along with the respective R^2 values for chlorinated solvents using nonlinear regression. The approximate time to reach equilibrium is also listed.

Sampler	PCE (k)	R^2	TCE (k)	R^2	cDCE (k)	R^2	Chloroform (k)	R^2	Eqbm (days)
LDPE	679	0.98	81	0.99	50	0.99	42	0.99	4 -5
PDMS	801	0.97	309	0.97	158	0.98	130	0.98	3 - 4
PVC	1301	0.92	512	0.98	183	0.98	260	0.98	9 - 10
POM	95	0.99	65	0.99	131	0.91	100	0.9	8 - 9
LLDPE	2261	0.95	928	0.96	35	0.94	69	0.96	5 - 6
Polystyrene	163	0.5	132	0.74	0.012	0.67	13	0.92	7 -8

While the R^2 values for the partitioning coefficients for PCE and TCE of the nonlinear regression carried out using Legind's equation (equation 1) were higher in all cases for PDMS, PVC and LDPE (greater than 0.95), lower R^2 values were observed for cDCE and chloroform. This may be attributed to the lower affinity of cDCE and chloroform to the sampler materials. As is demonstrated by the graph in Figure 7 for the LDPE sampler, where peak areas have been plotted on the y - axis and volume ratios

have been plotted on the x- axis; the ideal curve derived from the model and the curve generated from the experimental results were in close agreement.

Model trends predicted data for the PDMS, POM, PVC and LLDPE samplers. Results for the polystyrene sampler were well off the curve generated using the model. (Refer to Appendix B for partitioning coefficient data). These conflicting results may be attributed to the possible loss of chemicals while being transferred from the dosing chamber to the respective vials, compounded by the extremely low affinity of the polystyrene sampler for the chlorinated solvents tested (Refer to Table 1).

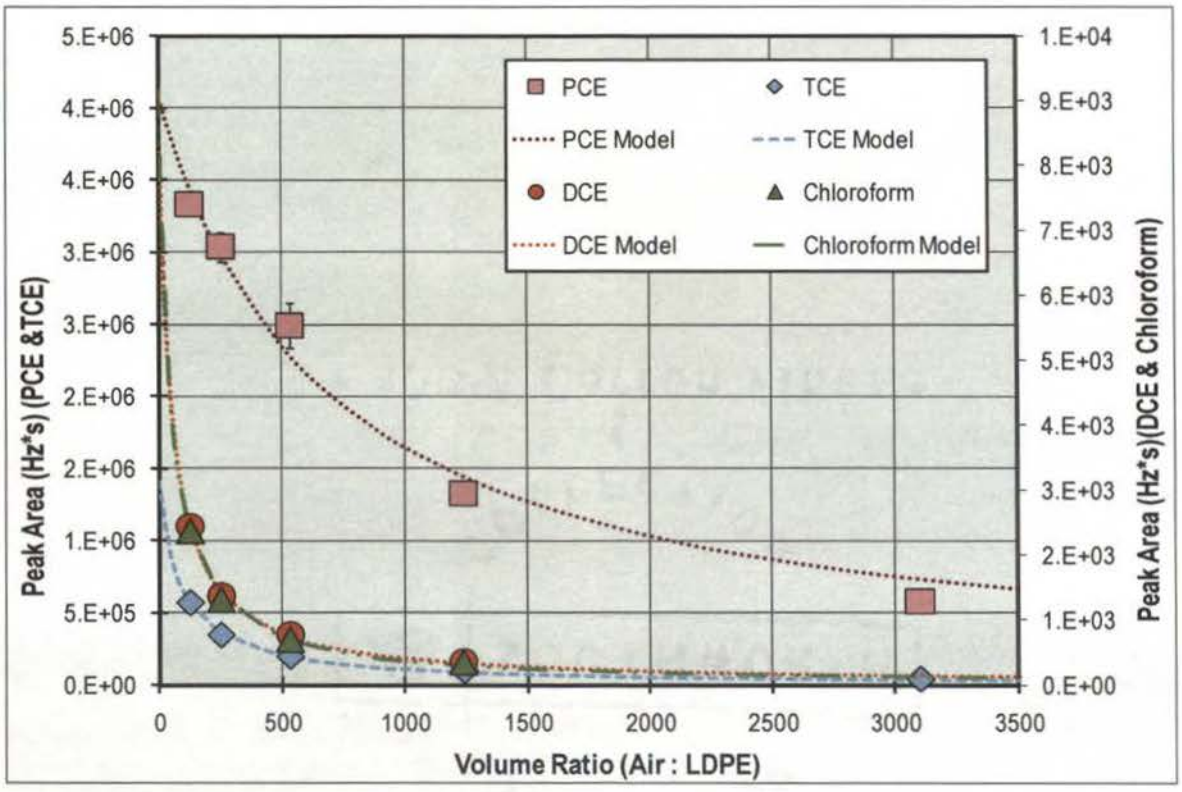

Figure 7- Graph demonstrating the partitioning coefficient data for the LDPE sampler. Volume ratio is plotted versus peak area and a comparison is made between actual data and the results from a model proposed by Legind et al.

From results obtained solely for the material:air partitioning coefficient experiments for PCE and TCE, the LLDPE sampler appears to be the best material for use as an SPS. LLDPE has relatively high partitioning coefficients of 2261:1 and 928:1 for PCE and TCE, respectively. It also reaches equilibrium *in planta* within a period of 6 days. The PVC and the PDMS sampler also have relatively high values for partitioning coefficients for the chlorinated solvents of interest. (Refer to Figure 8.)

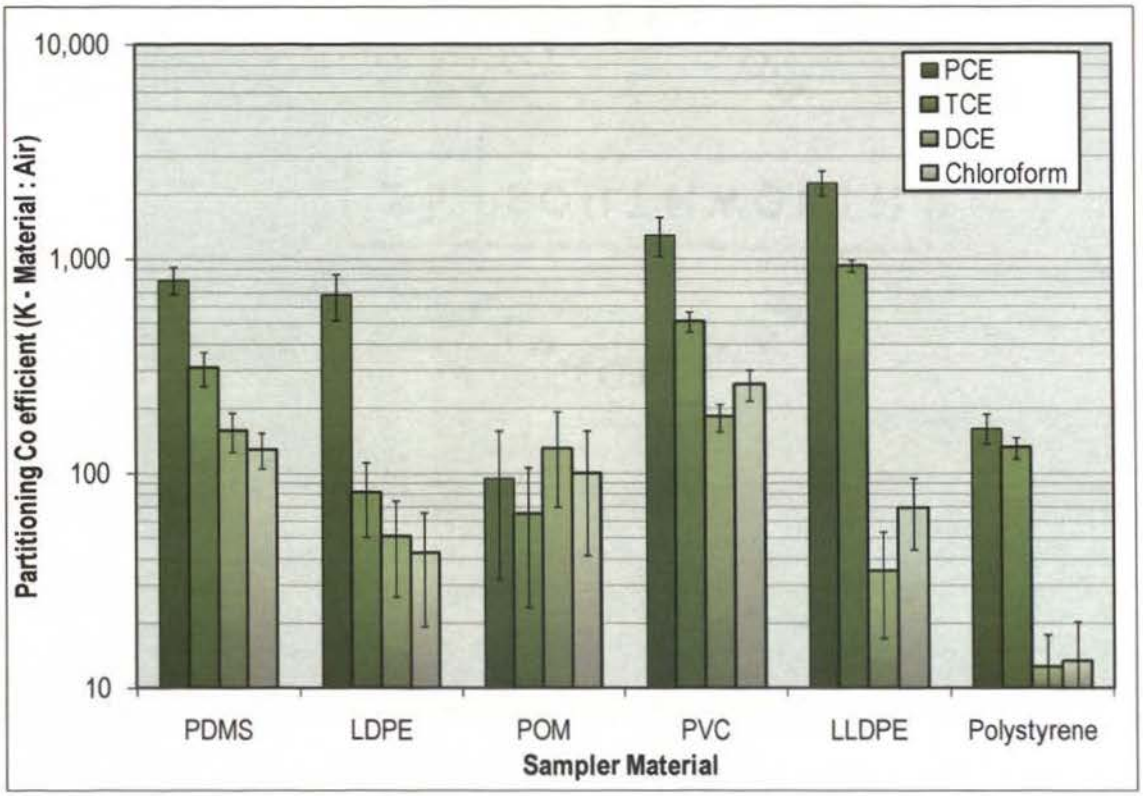

Figure 8 - Graph demonstrating the comparison between the material:air partitioning coefficients for the six sampler materials tested. While LLDPE has the highest partitioning values for PCE and TCE, the PVC sampler has the highest affinity for cDCE and chloroform.

3. GREENHOUSE STUDIES

The comparison of results obtained from tree coring and SPS testing are as demonstrated in Figure 9. Since the PDMS, PVC and the LLDPE sampler appeared to be potentially the best samplers according to the preliminary tests, only these three were used for the greenhouse and Busy Bee laundry site trials.

As can be seen from the graphs in Figure 9 the PDMS sampler had the highest values for log peak area for PCE and TCE, with PVC and tree cores coming in second and third, respectively. The LLDPE sampler had relatively high values for log peak area however it appears to have been mass limited due to the comparatively lower mass of the LLDPE sampler (Refer to Appendix C for sampler characteristics). As for DCE and chloroform, the PVC sampler returns the highest values for log peak area, followed by PDMS, LLDPE and tree cores in that order. The results however appear to be consistent for all chemicals and respective samplers tested. (Refer to Figure 9)

These results clearly show that the values for chlorinated solvent peak areas *in planta* obtained using SPSs are comparable to those obtained from tree coring and that these studies that have been successful in a greenhouse setting can be used at a field site to obtain first hand results at contaminated sites.

4. BUSY BEE LAUNDRY SITE, ROLLA, MO

Sampling of trees at the Busy Bee laundry site was carried out for three trees that previous sampling experiments had shown to be contaminated. The results of tree coring and SPS analysis further validate the fact that the trees were in fact contaminated with chlorinated solvents. As can be observed from the graphs in Figure 10, the contamination in tree 2 is comparatively much higher than in trees 1 and 3. As observed in the

greenhouse study, for PCE and TCE the PDMS sampler showed the highest values for log peak area, while the PVC sampler, the tree cores and LLDPE sampler had comparatively lower values. Since DCE and chloroform were detected only in isolated cases on site, the numbers and graphs have not been included.

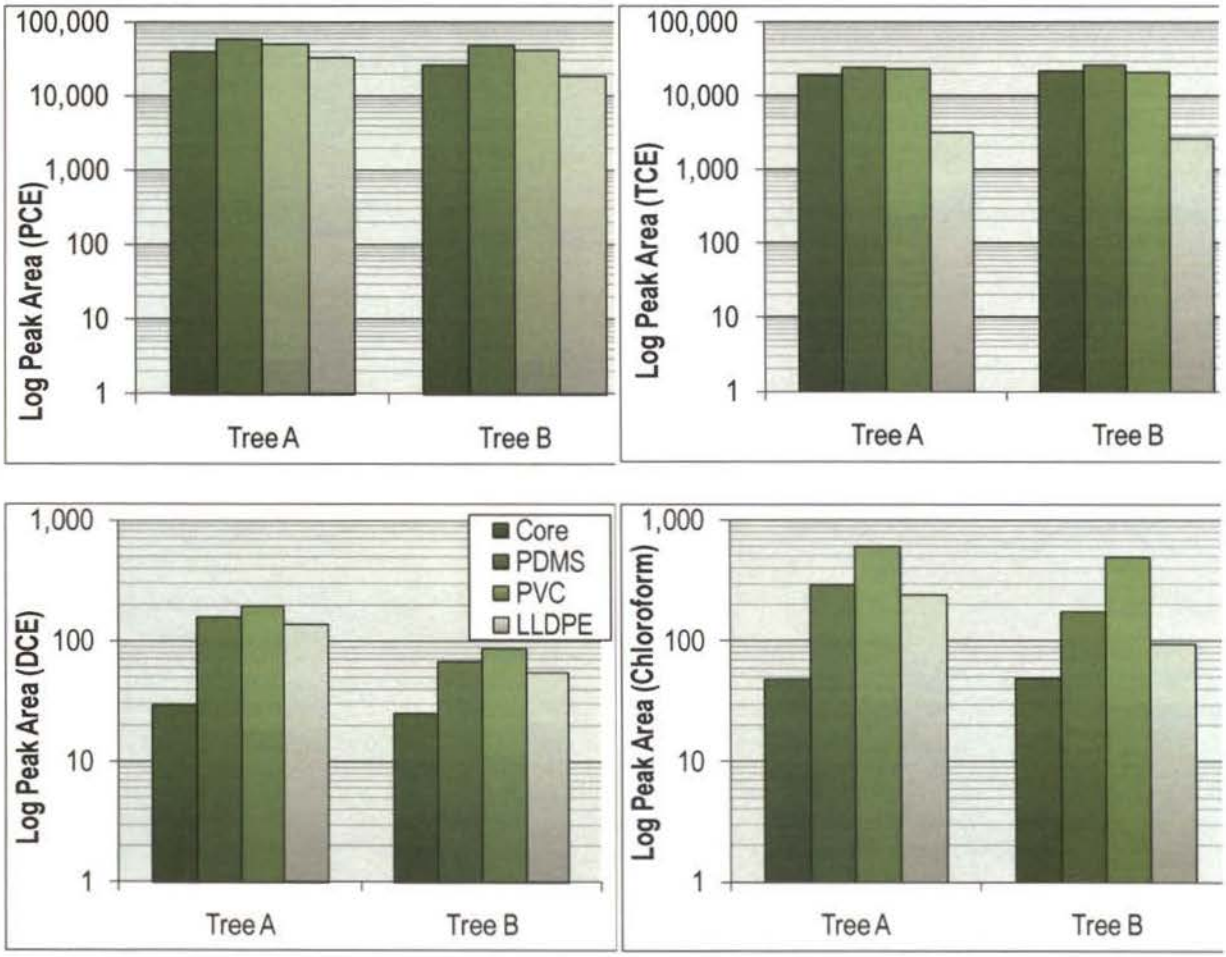

Figure 9 - Graphs showing the relative sensitivities of the sampler materials for PCE (top left) and TCE (top right). Sensitivities for cDCE (bottom left) and chloroform (bottom right) when tested *in planta* during the greenhouse study are also shown. The legend for materials is the same for all graphs displayed.

These results clearly indicate that SPSs have excellent potential at improving method detection limits for *in planta* sampling and that the variability observed in tree coring results are mirrored in the results from the analysis of SPSs.

5. DOW CHEMICALS SITE, SARNIA, ON, CANADA

During each trip to the Dow Chemicals site in Sarnia, ON, approximately 30 tree cores were collected and the cores were replaced by SPSs. Once the tree cores and SPSs were analyzed in the laboratory the concentration in the tree core were compared to the concentration in the SPS.

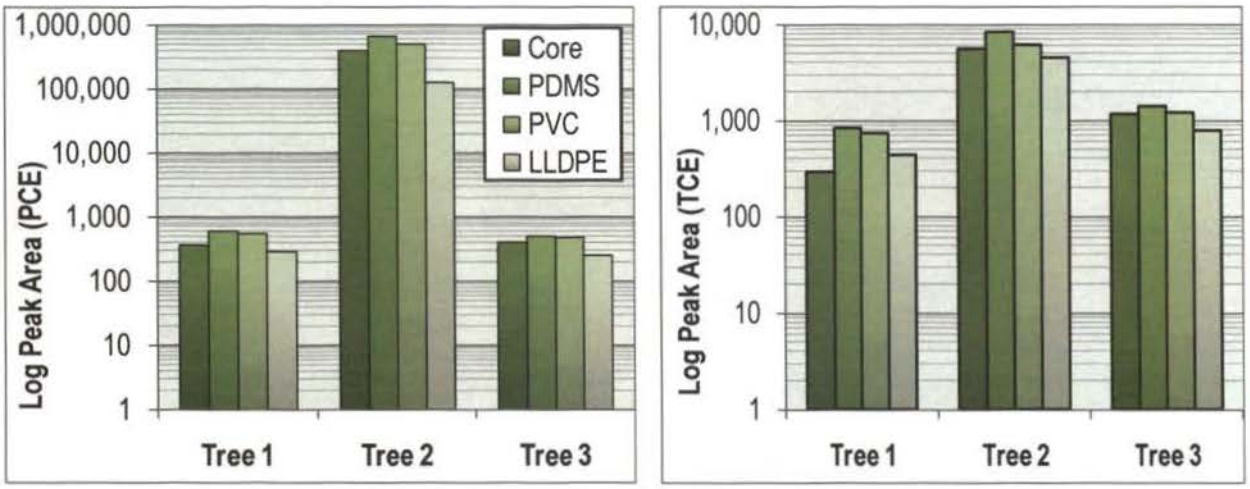

Figure 10 – A graph showing the relative sensitivities of the sampler materials for PCE and TCE when tested *in planta* during the on-site study at the Busy Bee Laundry site, Rolla, MO. Trees 1 & 2 were Bald Cypresses *(Taxodium distichum (L.) Rich)* while tree 3 was an Oak *(Quercus robur (L.))*. The legend for materials is the same for all graphs displayed.

A key assumption made during this study is that once the SPS is placed *in planta*, there is no change in tree contaminant concentration over the three or four week equilibration time. This is analogous to the concentration in the dosing chamber experiment where the headspace concentration may be controlled suitably. However, since this is difficult to replicate in the field, this major yet necessary assumption was required to be made. Since all trees sampled on site were hybrid poplars of nearly similar age, the variability in tree cores may be assumed to be negligible. The SPS and tree core data were plotted for both trips as can be seen in Figure 11.

In these figures each data point represents a single bore in the tree where the *in planta* concentration was estimated using data from both the core and the SPS. Since one tree core or SPS often contained more than just a single chlorinated solvent, each core or SPS is represented by multiple points on the graph in Figure 11. Cases where the cores or SPSs were unable to detect any contamination were omitted in order to enhance clarity.

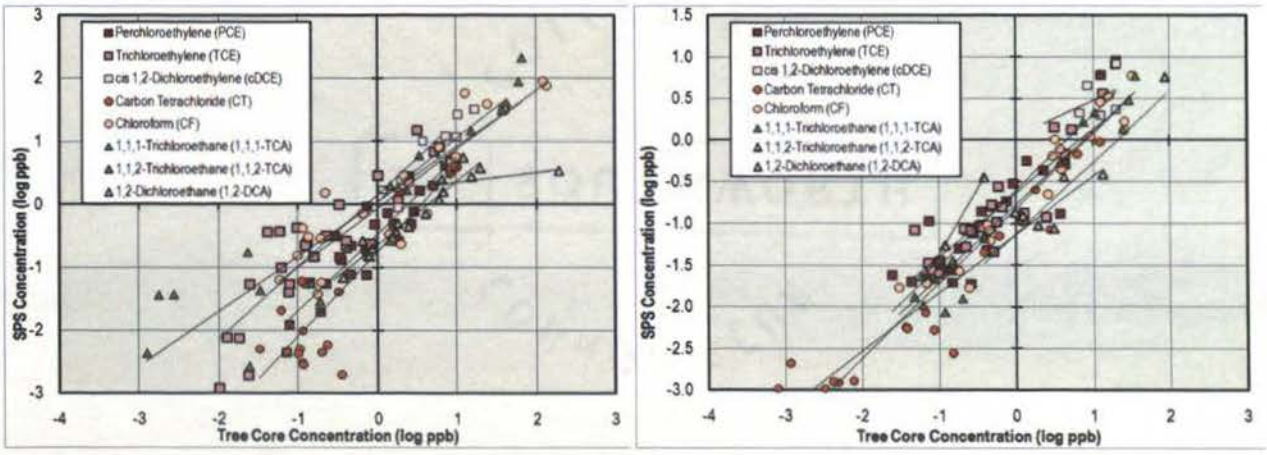

Figure 11 - Graph comparing tree core data and SPS data from separate sampling trips in August (left) and October (right) 2010 for a variety of chlorinated solvents found at the Dow Chemicals site in Sarnia, ON, Canada. Overall there was good linearity observed.

Overall, cores and SPSs demonstrated good linearity across a wide range of contaminants. It is also interesting to note that the graphs have been plotted on a log- log scale because the concentrations represented cover several orders of magnitude. Some points on the graph have been extrapolated off the calibration curve and these are also represented on the figure. For example, 1, 2 - DCA and cDCE show poor linearity in the figure. This may however be attributed to the poor sensitivity for these compounds. Another possibility for these discrepancies may be the competitive sorption for some chemicals with a higher affinity for the SPS than others. For example, since PCE has a higher affinity for the SPS it may competitively sorb onto sites on the sampler that may have otherwise been taken up by a chemical with a comparatively lower affinity for the SPS.

For the tree concentrations to be proportional to the SPS concentrations for the chemicals of interest, the fitted line for that chemical must represent a slope close to 1 with an intercept close to zero. The appears to be truer in the case of the samples collected from the August sampling trip relative to those taken during October as can be observed in Figure 11. This may be attributed to the seasonal changes in the tree concentrations during October that resulted in lower SPS concentrations during that particular sampling trip. It was observed that less than half of the leaves on the trees sampled were green during the October sampling trip, since it was the beginning of the onset of fall. Due to leaves being lost, evapotranspiration may be hypothesized to slow down or cease completely, which means that there is minimal possibility of the contaminants being resupplied to the tree trunk to compensate for diffusive losses through the trunk. Another possibly valid hypothesis is that the SPSs had not yet reached

equilibrium when they were retrieved from the trees in early December, due to the much lower ambient temperatures. All lab scale experiments were carried out at room temperature and hence although the SPSs appear to reach equilibrium in 10 days for most samplers tested, the impacts of ambient temperature need to be evaluated. As is demonstrated from the above results, 8 compounds were simultaneously analyzed at the Sarnia site and this validates the application of SPSs to monitored natural attenuation studies at sites that are contaminated with multiple contaminants.

IV. FUTURE IMPLICATIONS

The use of SPSs may serve as a tool in the quick and accurate delineation of shallow groundwater plumes of PCE and TCE, thus having potential as an aid during Phase I site assessments. The quick turnaround time, simple procedures in sampler preparation and deployment, low cost and time requirements, minimally invasive green approach to sampling, as well as accurate and repeatable results ensure that these methods hold a lot of promise for the future. The ideal SPS for *in planta* applications to detect chlorinated solvents must possibly possess the key characteristics of very high partitioning for chlorinated solvents as well as a degree of reproducibility. Although a short equilibration time is also a desirable characteristic, in - field deployment is a time intensive exercise when compared to the time required for analysis. Thus sampling should allow the SPSs adequate time to equilibrate within the tree. The prospect of allowing a SPS to sit within the trees for a few extra days is a safer approach to sample accuracy, than is the chance of the samplers not reaching equilibrium. Ambient temperature is a major concern when these SPSs are deployed in the field and although it is difficult to measure the variations in temperature within the tree, laboratory studies to

better understand the effects of these temperature variations are recommended. As for the most suited of the sampler materials for PCE and TCE, a large diameter LLDPE sampler appears to be the best at being able to detect *in planta* and the resultant subsurface contamination. There is also potential for the study of contamination by other compounds *in planta* using the SPS approach. However it must be noted here that the dosing chamber experimental setup used in these studies is an attempt to mimic conditions *in planta*, and the two scenarios are different in many respects. The conditions inside of a tree are extremely hard to mimic in the laboratory and there is a need to improve the experimental setup used in such experiments so that a system more closely resembling the inside of a tree maybe used to enhance the understanding of the plant - sampler - contaminant interactions taking place therein.

V. RECOMMENDATIONS FOR FUTURE WORK

There is definite potential for improvement with regards to these SPSs and the experimental methodology that is employed in their use. While this particular study looked specifically at optimizing the "best" sampler material for chlorinated solvents, a similar thought process and concept can also be employed for other contaminants such as BTEX compounds and other volatile and semi – volatile organics. There is also obvious scope for the study of other sampler materials that may be suitable for *in planta* applications. Neoprene and tenax may prove to be viable options in this regard.

In terms of methodology, the chlorinated solvents studied appear to be extremely sensitive to changes in ambient temperature and hence it is important to incorporate a mechanism whereby a better understanding of the ambient temperature variations maybe incorporated in the analysis post sample collection. Temperature corrections also need to

be incorporated during analysis of samples to account for the changes in the transpiration stream of the tree itself. As was evident from the long term sampling of some tree species during this study, there is a substantial difference in the uptake of water and in- turn contaminants during the different months of the year and hence a long term study using a standard set of trees in the field may prove to be a good idea, to better understand these seasonal effects and the variations in concentration thereof. While this study used a screw to plug in the SPS *in planta*, there is a need to develop a method or apparatus that is better able to ensure the seal between the SPS and the tree borehole headspace. This will ensure that true equilibrium is established and it is not hampered by the loss of contaminant to the ambient atmosphere due to a poor seal by the head screw.

Another aspect of the SPSs that needs to be explored further is the absorption mechanism that these samplers use to collect the contaminants. In order to better understand the mechanistic properties of the sampler, surface transport studies need to be carried out and a mass transport model for a tree with an SPS inserted *in planta* needs to be established in the future. However, this task is complicated by the fact that it is difficult to replicate the internal environment of a tree in the laboratory. Hence, the first step in this direction would be to establish a less complex model using a simpler laboratory apparatus.

APPENDIX A.
UPTAKE KINETICS EXPERIMENTS GRAPHS

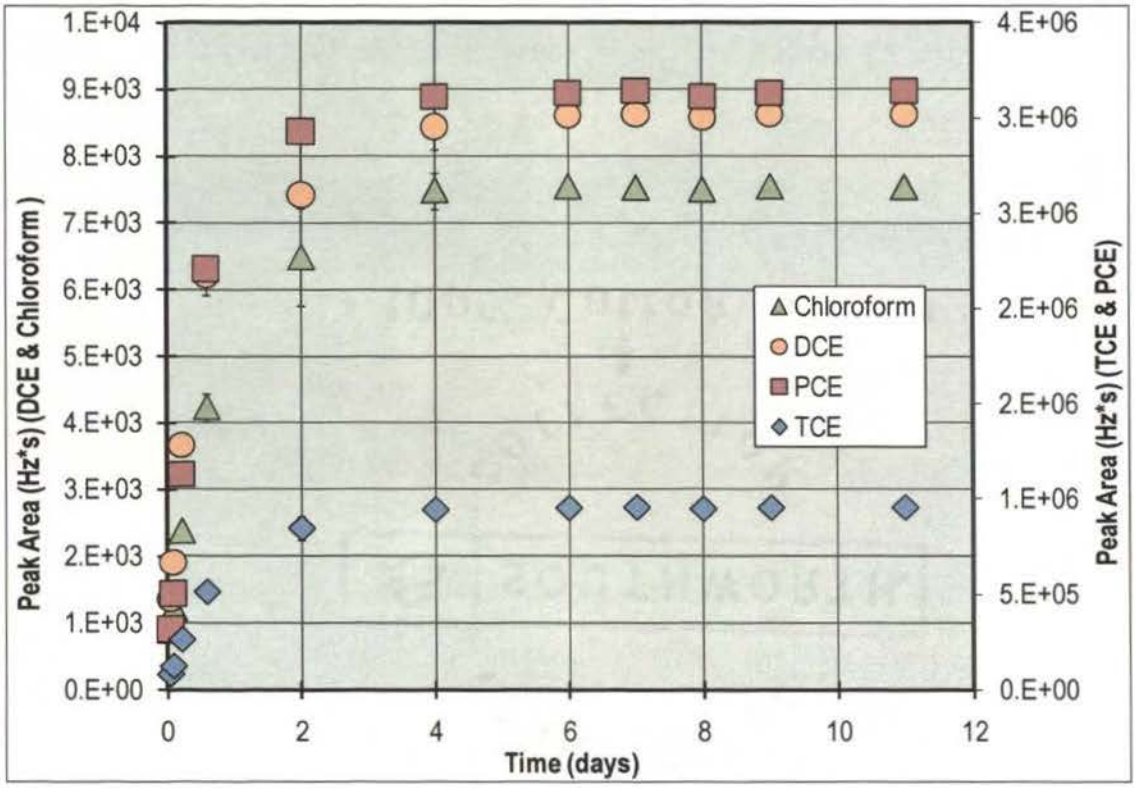

Figure A.1 A graph demonstrating the transient uptake curve for the LDPE sampler.

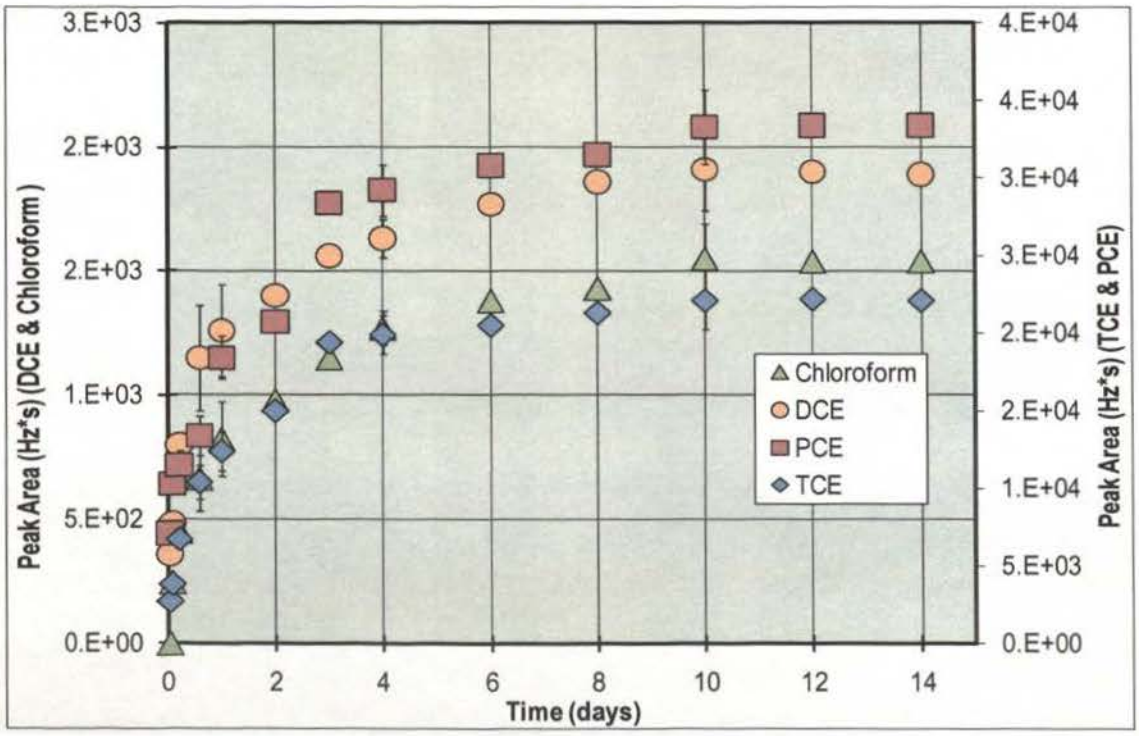

Figure A. 2 A graph demonstrating the transient uptake curve for the POM sampler.

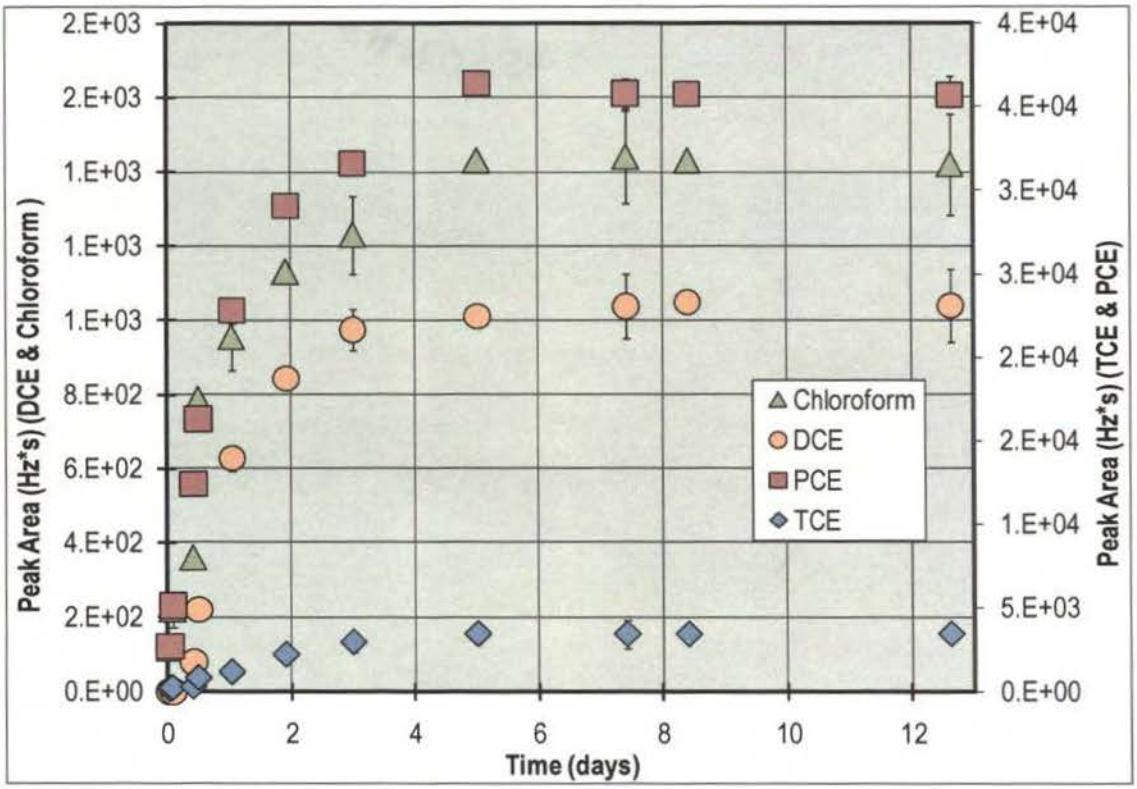

Figure A. 3 A graph demonstrating the transient uptake curve for the LLDPE sampler.

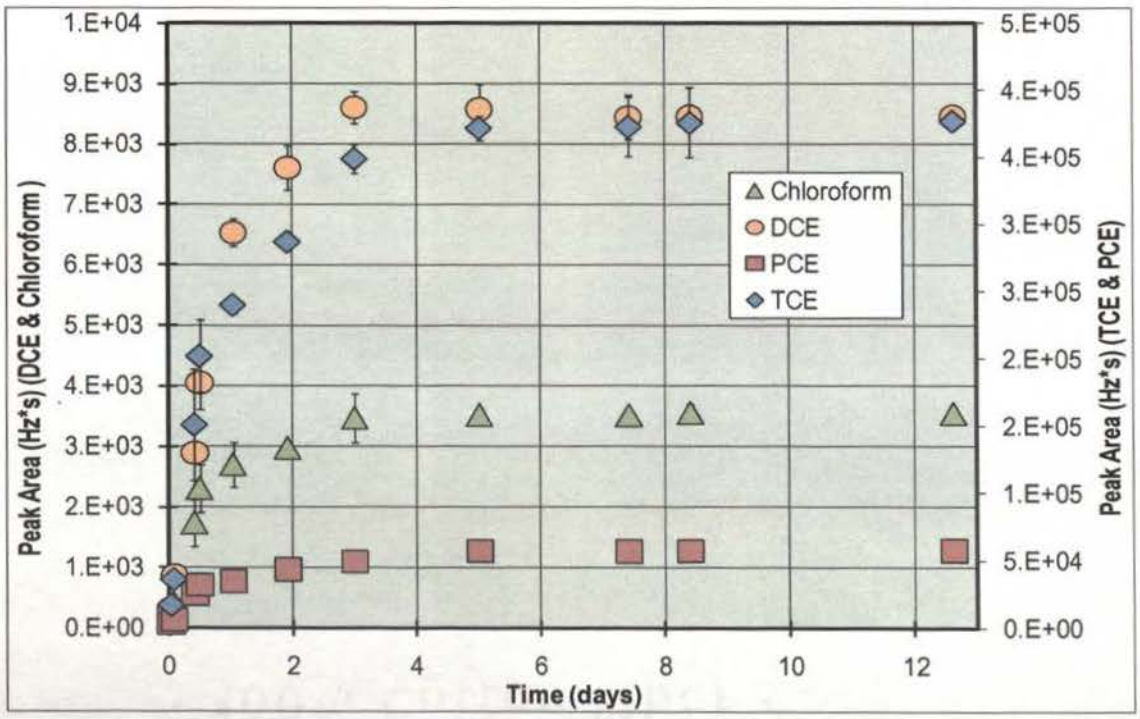

Figure A. 4 A graph demonstrating the transient uptake curve for the polystyrene sampler.

APPENDIX B
PARTITIONING COEFFICIENT GRAPHS

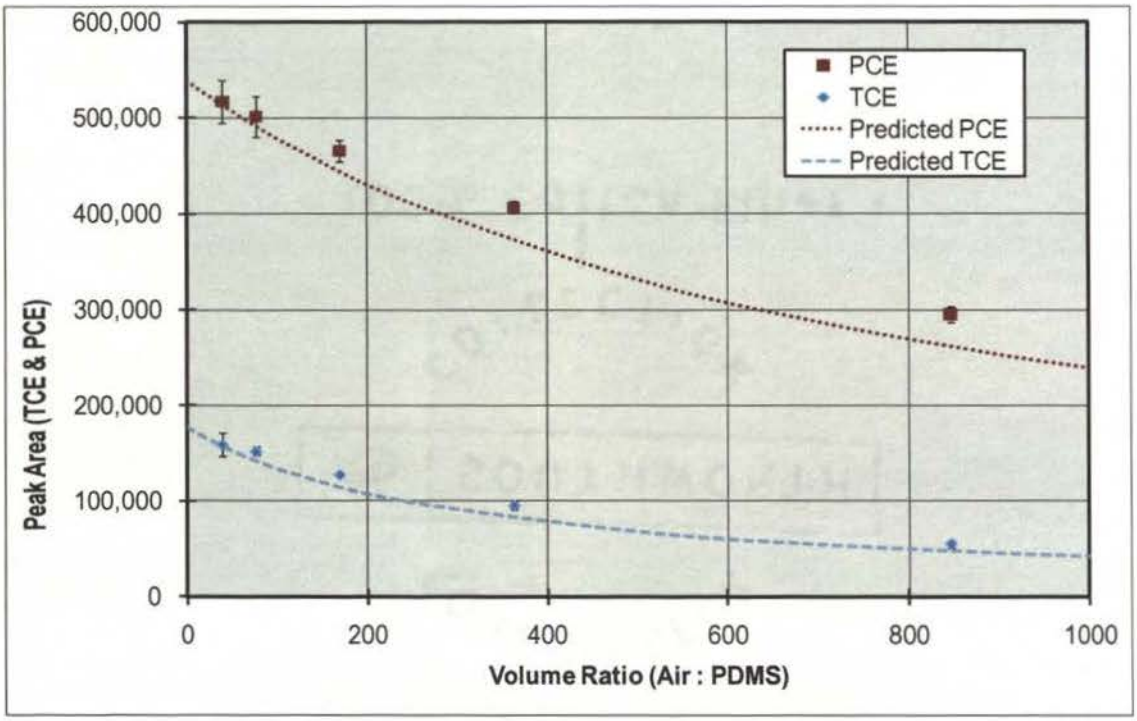

Figure B. 1 A graph demonstrating the partitioning coefficient data for the PDMS sampler. Data is plotted for PCE and TCE.

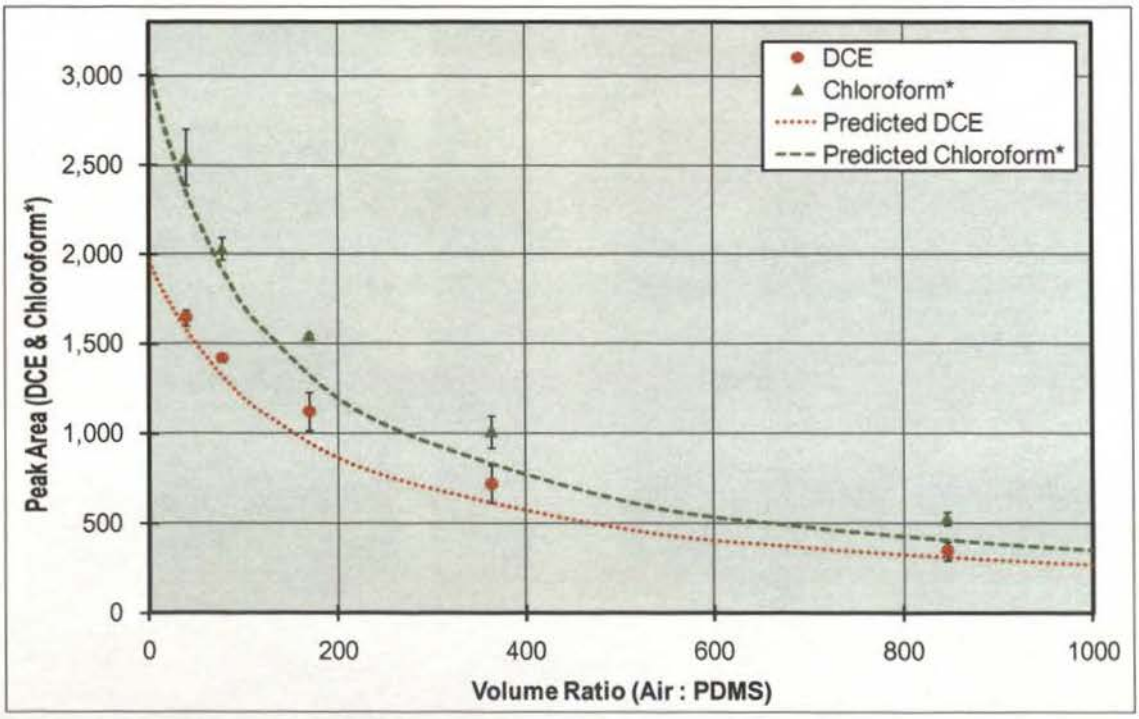

Figure B. 2 A graph demonstrating the partitioning coefficient data for the PDMS sampler. Data is plotted for cDCE and chloroform.

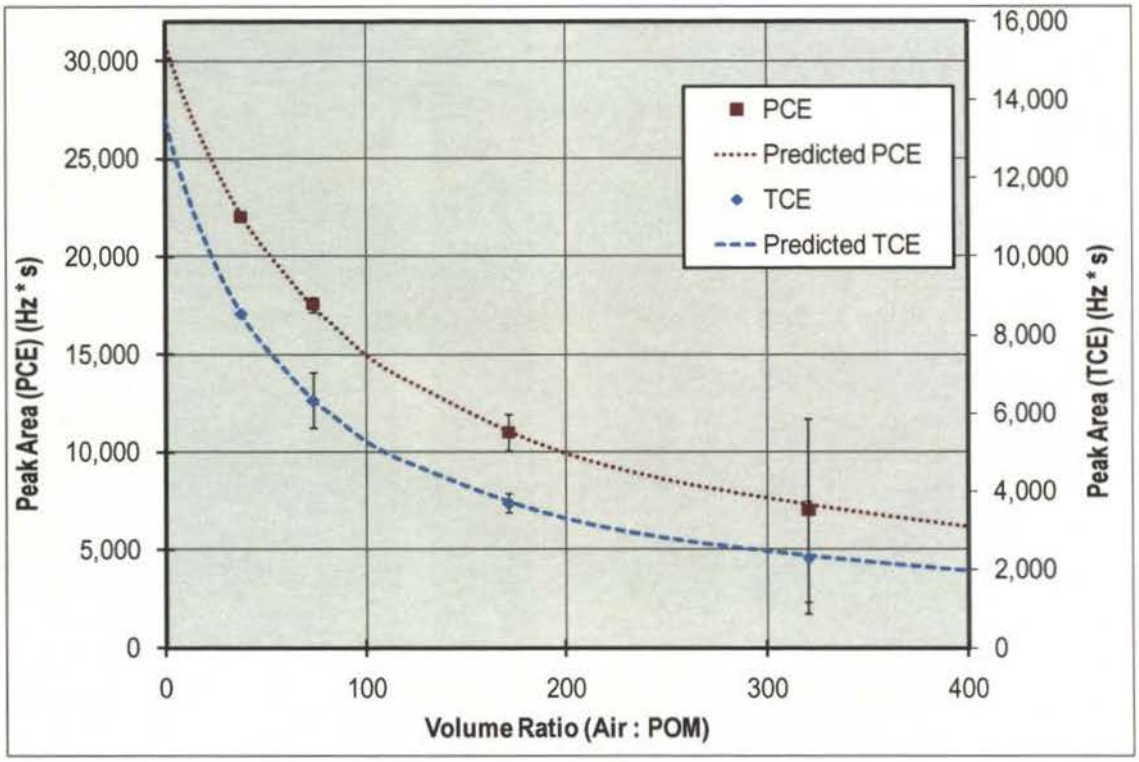

Figure B. 3 A graph demonstrating the partitioning coefficient data for the POM sampler. Data is plotted for PCE and TCE.

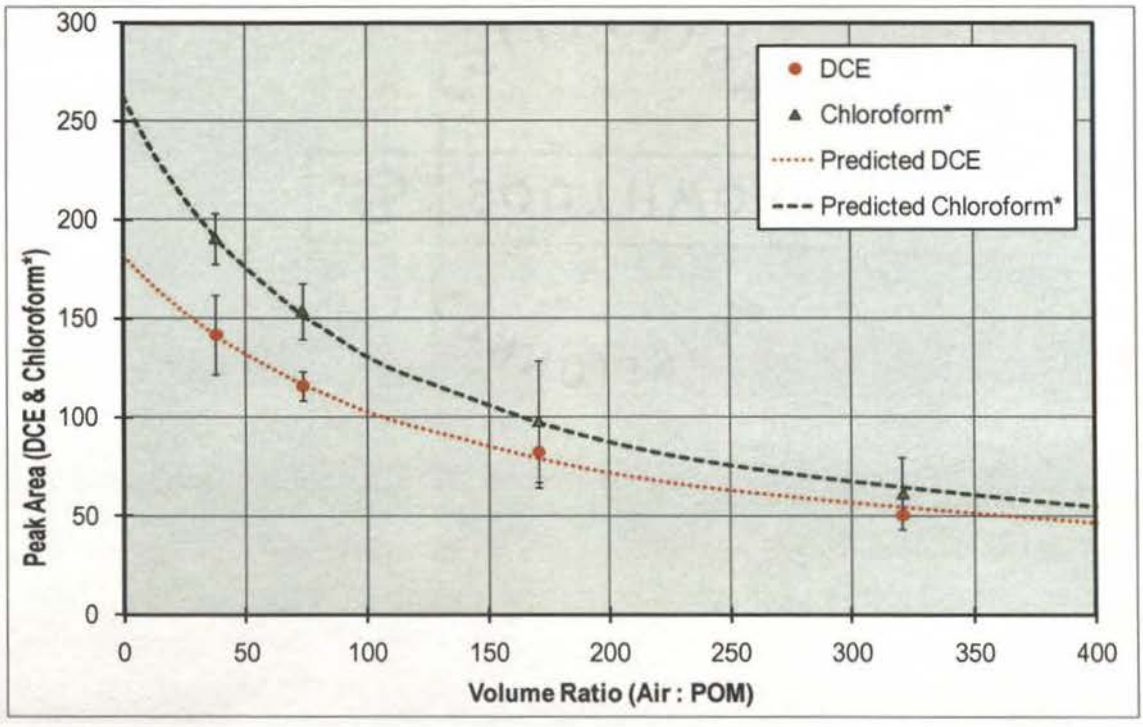

Figure B. 4 A graph demonstrating the partitioning coefficient data for the POM sampler. Data is plotted for cDCE and chloroform.

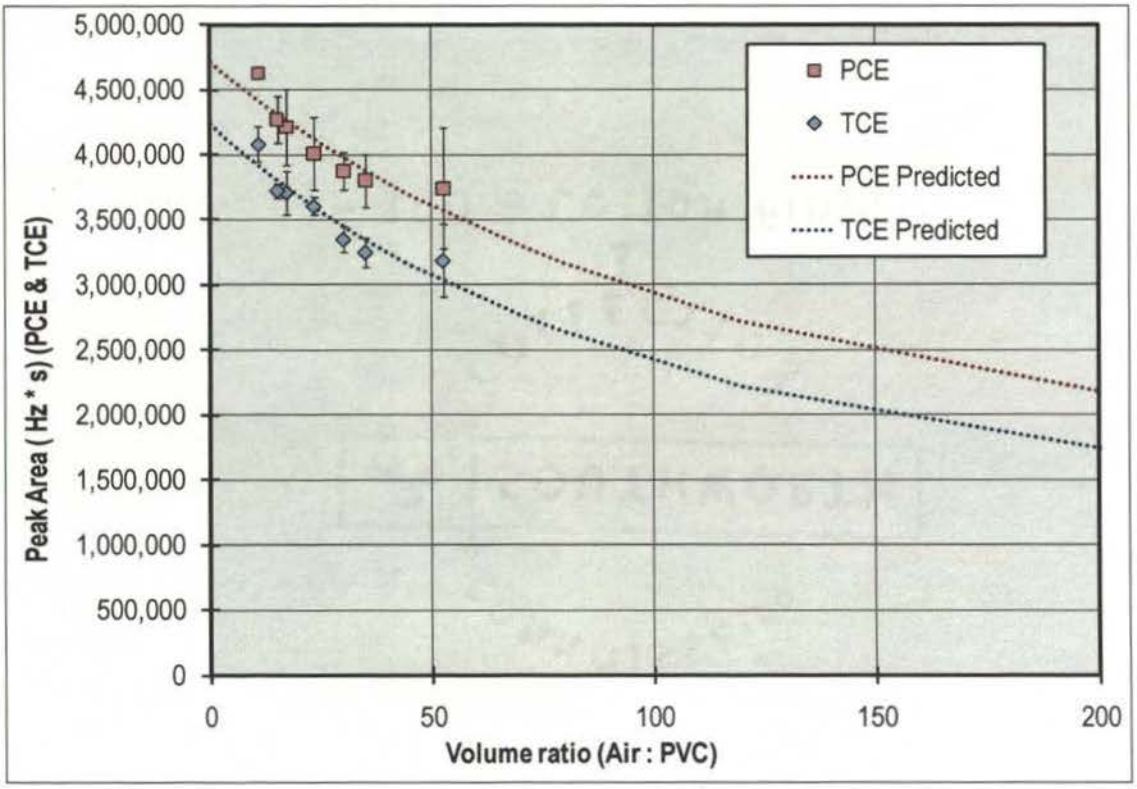

Figure B. 5 A graph demonstrating the partitioning coefficient data for the PVC sampler. Data is plotted for PCE and TCE.

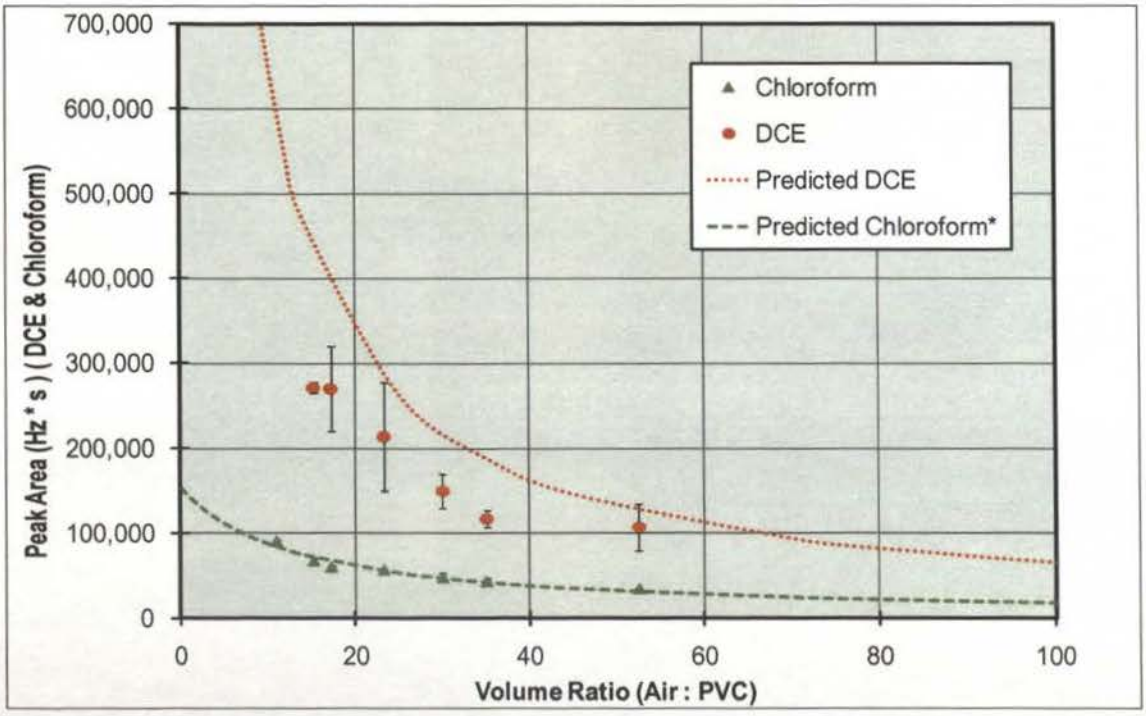

Figure B. 6 A graph demonstrating the partitioning coefficient data for the PVC sampler. Data is plotted for cDCE and chloroform.

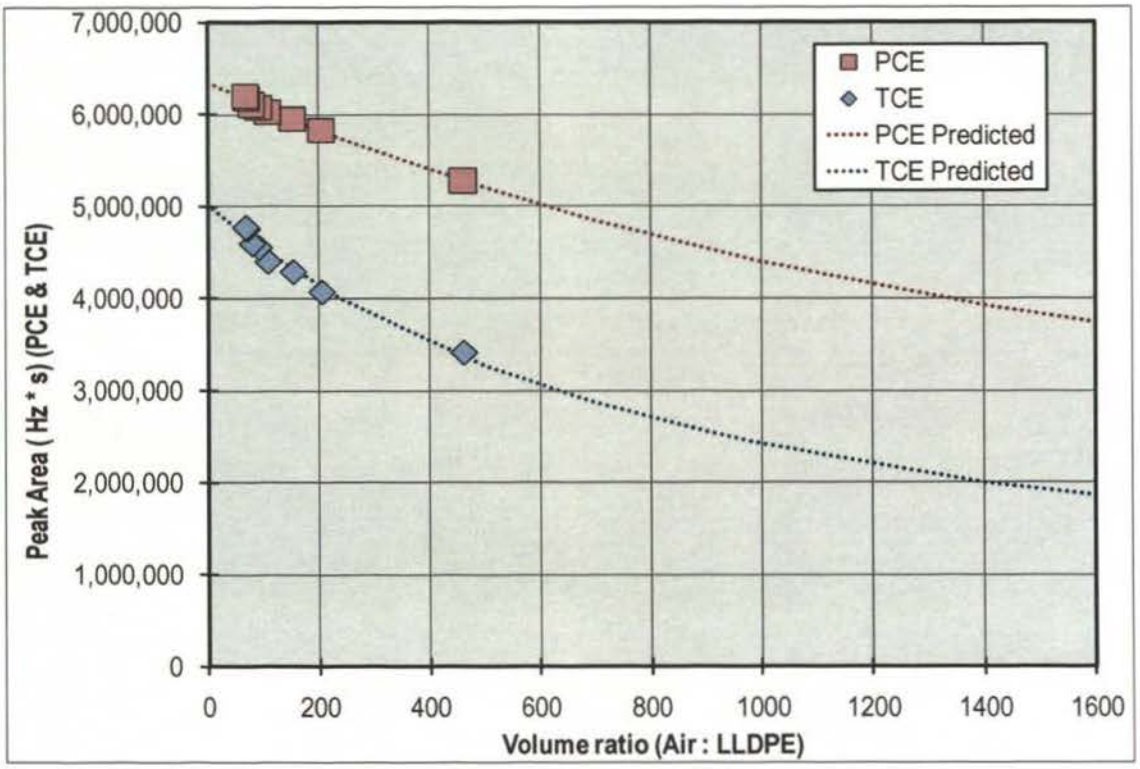

Figure B. 7 A graph demonstrating the partitioning coefficient data for the LLDPE sampler. Data is plotted for PCE and TCE.

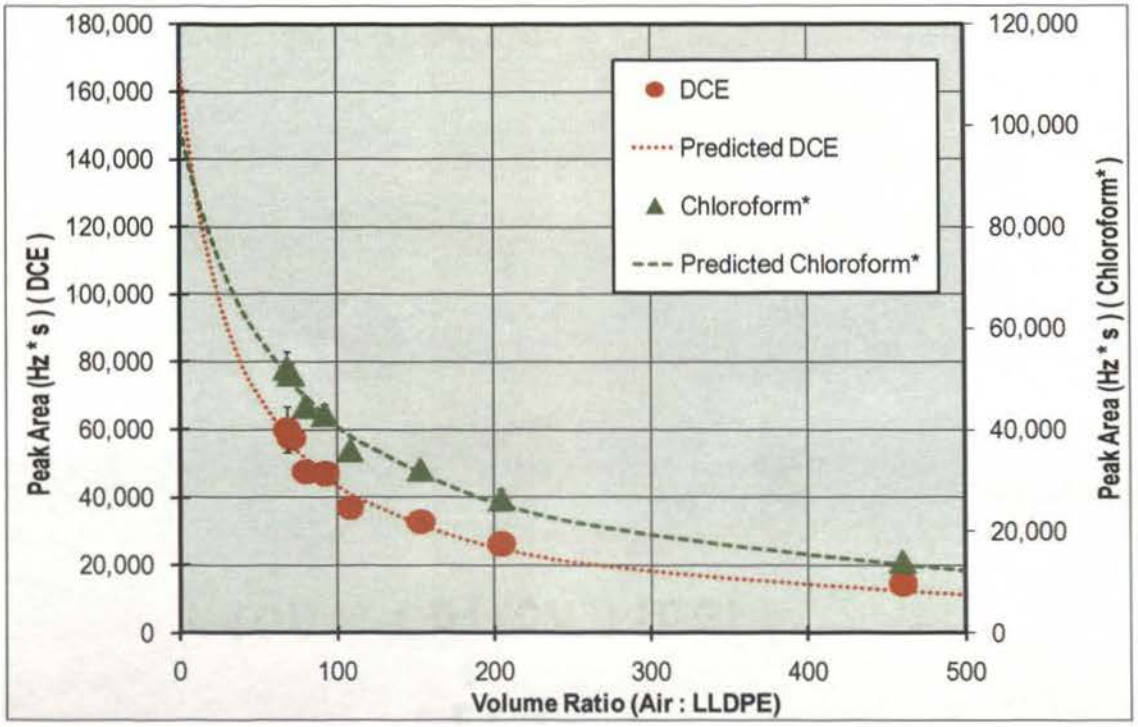

Figure B. 8 A graph demonstrating the partitioning coefficient data for the LLDPE sampler. Data is plotted for cDCE and chloroform.

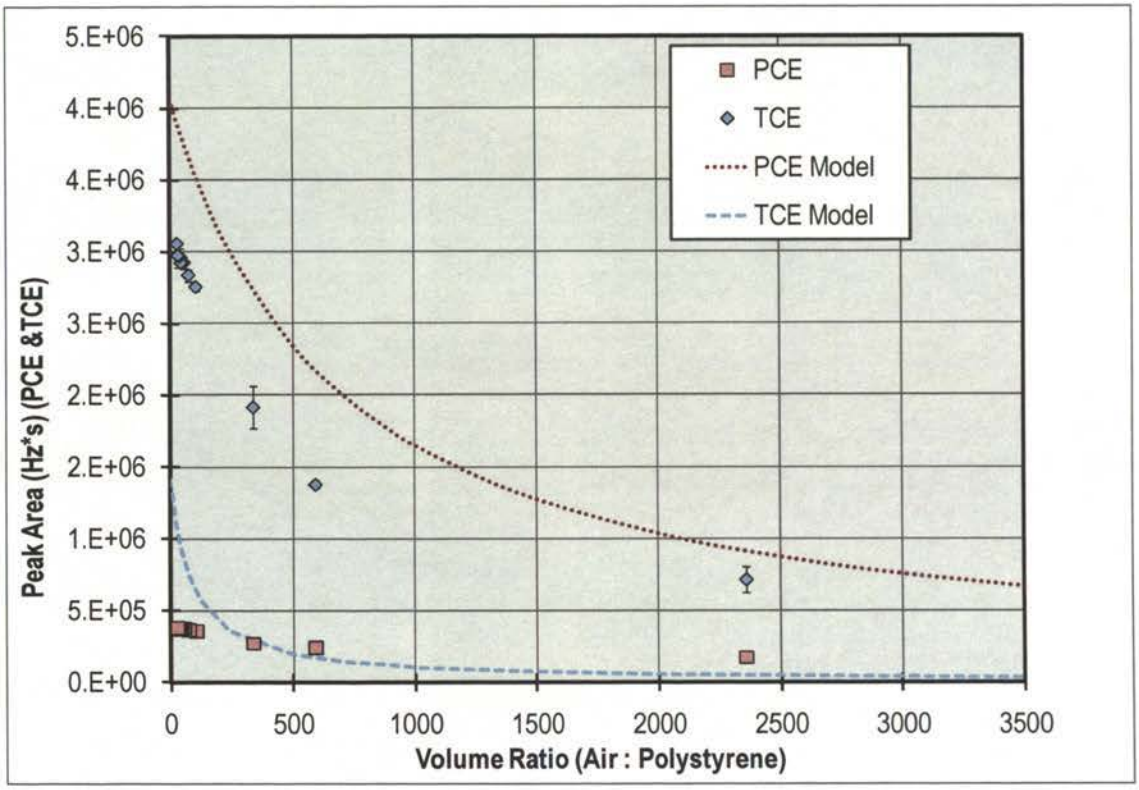

Figure B. 9 A graph demonstrating the partitioning coefficient data for the polystyrene sampler. Data is plotted for PCE and TCE.

APPENDIX C
SAMPLER CHARACTERISTICS FOR ALL MATERIALS

Table 2 Table listing the physical properties and configurations of the six sampler materials tested.

SAMPLER	CONFIG.	I. D (INCH)	O. D (INCH)	WALL THICKNESS (INCH)	MASS OF SAMPLER PIECE (GM)	DENSITY (G/CC)
LLDPE	TUBING	1/16	1/8	0.031	0.15	0.92
PDMS	TUBING	3/32	7/32	1/16	0.65	1.26
PVC	TUBING	1/16	3/16	1/16	0.60	1.18
LDPE	TUBING	1/8	1/16	1/32	0.18	0.93
POM	ROD	-	3/16	-	0.65	1.28
PS	ROD	-	1/4	-	0.45	1.05

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6. VITA

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