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Phytoforensic tools: directional uptake of chlorinated solvents

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PHYTOFORENSIC TOOLS:
DIRECTIONAL UPTAKE OF CHLORINATED SOLVENTS

by

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A THESIS

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ABSTRACT

Trees have been used to locate contaminated soil and groundwater, augmenting traditional methods, such as well drilling, that are time-consuming and expensive. In the past decade, plant sampling has gained acceptance as a reliable method for site screening. In this new field of phytoforensics, research efforts focus on developing quicker, more accurate and more informative sampling and analysis methods for measuring contaminant concentrations in trees. These phytoforensic tools are a novel approach to site assessments, potentially reducing cost while more effectively locating contaminated groundwater. This thesis evolved from field data suggesting azimuthal concentrations in tree trunks may reflect the corresponding azimuthal concentrations in the groundwater below the tree.

In the lab, large diameter trees were subjected to concentration gradients in the groundwater and analyzed for contaminants and evidence of directional uptake. Upon analysis, concentrations were approximately five times higher on the side of the tree near the highly contaminated groundwater. The conservation of azimuthal PCE and TCE gradients was observed at all levels up the tree. This indicates that advective transport in the xylem exceeds radial or circumferential diffusion of PCE and TCE. Several field sites showed similar data, where concentrations in the tree matched groundwater concentrations in an azimuthal pattern. In practice, each tree sampled directionally can provide compass-like information, pointing investigators towards the most concentrated region of the plume.

ACKNOWLEDGMENTS

First, I need to thank Joel Burken, because despite his love of Hawkeyes, I would never have never known PCE without him. He has been a great source of knowledge, inspiration and any other worthwhile trait I can think of. I need to thank my partner in crime, Micky Shetty. I will always have fond memories of talks about Indian life, trips to Taco Bell and discussing phyto-anything (in no particular order). Amanda Holmes is deserving of thanks for doing all of the work I don't have time to get to. She has been a great source of youthful determination, technical curiosity and cheap labor.

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NOMENCLATURE

SYMBOL	**DESCRIPTION**
BTEX	Benzene, toluene, ethylbenzene and xylenes
CAR	PDMS/carboxen composite fiber
CEC	Cation exchange capacity
cDCE	*cis*-1,2-dichloroethylene
C_{sat}	Contaminant concentration at saturation in water
DNAPL	Dense non-aqueous phase liquid
µECD	Micro electron capture detector
EPA	Environmental Protection Agency
GC	Gas chromatography
HR	Hydraulic redistribution
HS	Headspace
K_{fg}	Fiber-gas partitioning coefficient
K_H	Henry's constant
K_{oa}	Octanol-air partitioning constant
K_{OW}	Octanol-water partitioning constant
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MDL	Method detection limit
NTP	National Toxicology Program
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethylene
PDMS	Polydimethylsiloxane
SPME	Solid-phase microextraction
SPS	Solid phase sampler
TCE	Trichloroethylene
TSCF	Transpiration stream concentration factor
USGS	U.S. Geological Survey
VC	Vinyl chloride

1 BACKGROUND

To efficiently find and measure contaminants in the environment is currently a time-consuming, costly and resource-intensive process. These obstacles are particularly true for chlorinated solvents present in the subsurface. Gaining knowledge regarding the plume concentration and boundaries is critical to remediate a site effectively and efficiently. However, this knowledge often incurs the cost of installing additional sampling wells, which provide only a glimpse into the subsurface conditions. This glimpse also has associated environmental costs, which are becoming more recognized with a recent EPA push for “green” remediation [1].

To address the difficulties stemming from traditional methods, some research has employed trees as a natural monitoring well for detecting chlorinated solvents [2]. Trees are well suited for this application as they naturally extract water and nutrients from the sub-surface. Dissolved non-polar organic contaminants are readily taken up by the tree and translocated towards the leaves. The concept of measuring these contaminants in trees for plume delineation has been termed phytoforensics. Figure 1.1 shows the phytoforensic conceptual model, where many of the critical processes are familiar and passive, such as air-water partitioning. These passive processes allow the tree to function as a natural groundwater well, where solar energy drives the flow of water and some contaminants from the subsurface to above ground.

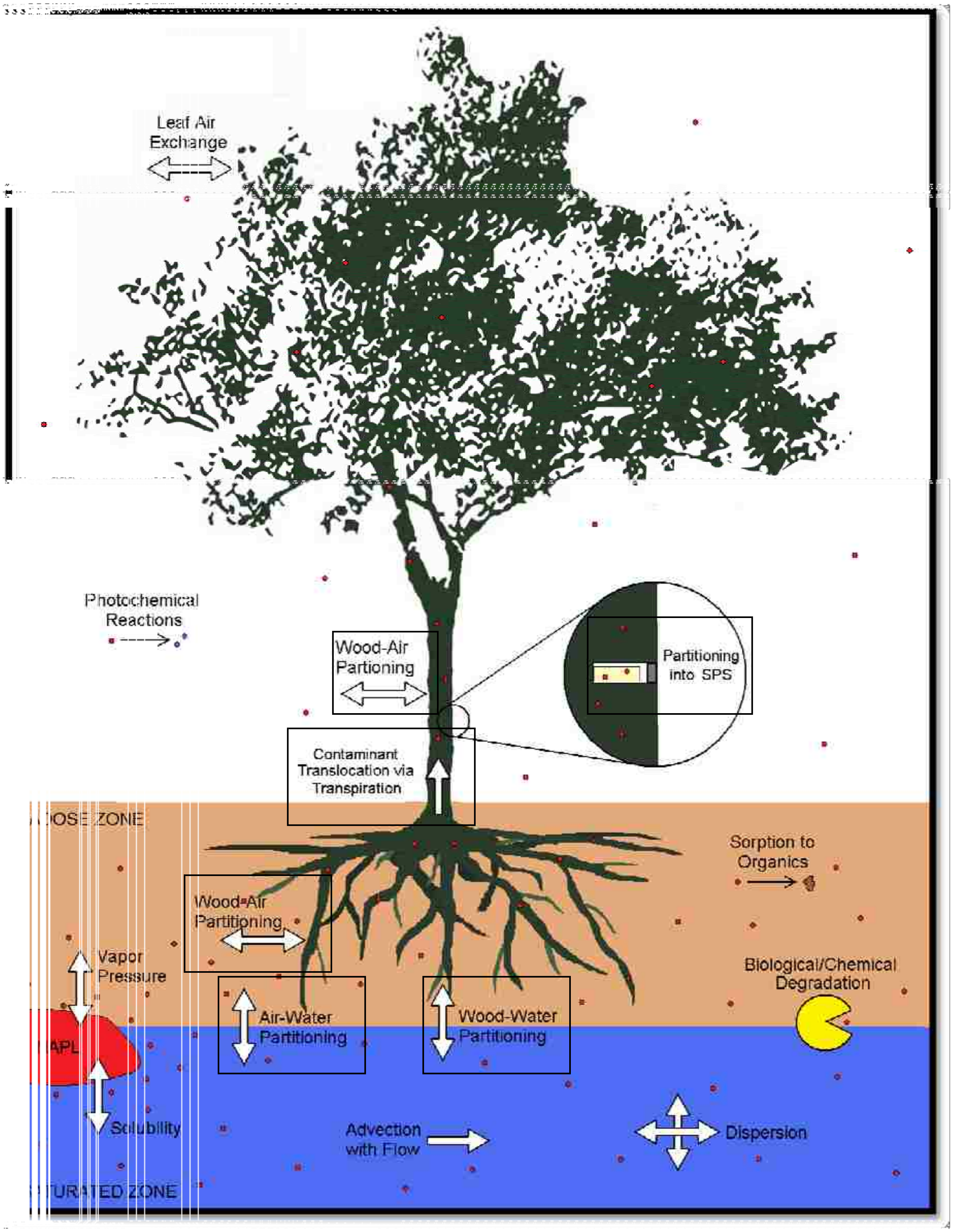


Figure 1.1 – Phytoforensic Conceptual Model, Showing a Variety of Important Processes Related to Measuring Groundwater Contaminants in Trees (Boxed processes indicate directly relevant processes)

The precise relationship between trees and groundwater is difficult to elucidate, as variations between trees such as root depth, trunk diameter, tree species, etc. can complicate correlations. In an effort to obtain a maximum amount of information from each tree sampled, this thesis explores a new phytoforensic tool: directional tree sampling. In general, trees should uptake water in a directional (axial) manner, due to high fluid resistivities associated with non-axial transport. If axial advection and diffusion exceeds radial and circumferential diffusion, azimuthal concentration gradients in the tree will mimic concentration gradients in the underlying groundwater. Sampling on several sides of a tree would yield higher resolution plume delineation, while eliminating the effects of variables related to tree-to-tree differences. Such an advance would improve the resolution and accuracy of phytoforensics, already an efficient and effective screening tool.

2 GOALS AND OBJECTIVES

The overall goal of this work was to investigate directionality and develop directional tree sampling as a reliable tool for delineating groundwater plumes. To accomplish this overarching goal, specific objectives and corresponding hypotheses were formed.

- Objective 1: Develop an experimental laboratory arrangement for dosing large-diameter trees (>5 cm) in a directional manner.

  Hypothesis: Growing large diameter trees in a sufficiently large vessel will allow for observation of directional uptake of tetrachloroethylene (PCE) and trichloroethylene (TCE).
- Objective 2: Create harvesting, sampling and analysis methods for measuring contaminant concentrations in a cross-section of a tree.

  Hypothesis: Sufficient analytical resolution and accuracy must exist to observe directional variation at the lab scale.
- Objective 3: Develop methods for qualifying and quantifying the extent of directional uptake observed in laboratory trees.

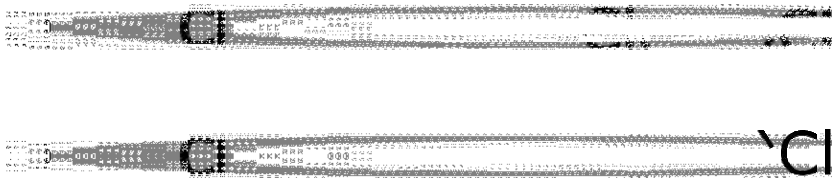
  Hypothesis: Concentrations can be interpolated across the trunk cross-section to develop a qualitative concentration contour map. Calculation of the contaminant centroid will provide a quantitative estimation of directional uptake.
- Objective 4: Test trees for directional uptake of chlorinated solvents at field sites.

  Hypothesis: Trees located near steep concentration gradients will show concentration gradients in their trunk independent of sampling method.

3 LITERATURE REVIEW

3.1 CHLORINATED SOLVENTS

Chlorinated solvents have been used in numerous manufacturing and cleaning operations over the last century, including common processes such as dry-cleaning and degreasing [3]. This widespread use coupled with lax disposal regulation has resulted in a number of sites with contaminated soil and groundwater. Two commonly detected chlorinated solvents, and the focus of this thesis, are tetrachloroethylene, or perchloroethylene, (PCE) and trichloroethylene (TCE), both reasonably anticipated to be carcinogens [4] (see Figure 3.1).



Tetrachloroethylene (PCE)

Trichloroethylene (TCE)

Figure 3.1 – Chlorinated Solvents Used in this Study

Classified as dense non-aqueous phase liquids (DNAPL), PCE and TCE are problematic in the environment for a number of physicochemical-based reasons (see Table 3.1 for properties). These source zones are denser than water, allowing the pure product to sink down until reaching low-permeability media. Geological heterogeneity can lead to spreading of the source zone, as the DNAPL may find cracks and sink to varying depths. Their significant non-polarity makes them sparingly soluble in water; allowing source zones of pure product to exist for decades. The high hydrophobicity also results in significant partitioning to organic carbon and subsequent retardation in the groundwater.

Table 3.1 – Chemical Properties of Selected Contaminants [5]

Contaminant	Log P^0 (atm)	Log C_{sat} (mol/L)	Log K_H (L-atm/mol)	Log K_{OW}
PCE	-1.60	-3.04	1.44	2.88
TCE	-1.01	-2.04	1.03	2.42

PCE and TCE are also heavily oxidized molecules, resulting in limited aerobic biodegradation. Aerobic degradation is rare due to large amount of energy required to circumvent the chlorine atoms to break the carbon-carbon double bond. However, under strong reducing conditions PCE and TCE can be used as electron acceptors [6]. As chlorine atoms are removed, the molecule become less suitable as an electron acceptor, thereby slowing down kinetics [7]. In some respects, reductive dechlorination can be problematic, as degradation products of *cis*-1,2-dichloroethylene (cDCE) and vinyl chloride (VC) are regulated water contaminants (see Table 3.2). For these chlorinated ethenes, maximum contaminant levels (MCL) and MCL goals (MCLG) in drinking water are low. Regulations for VC are particularly strict, as VC is known to be carcinogenic [4].

Table 3.2 – EPA Drinking Water Regulation Limits [8]

Contaminant	MCL (ppb)	MCLG (ppb)
PCE	5	0
TCE	5	0
cDCE	70	70
VC	2	0

3.2 PLANT UPTAKE OF HYDROPHOBIC COMPOUNDS

Plants have long been known to uptake moderately hydrophobic (log K_{ow} 0.5-3) organic compounds [9-10]. While many other variables, like molecular size, are likely involved, hydrophobicity has been the primary variable studied [11]. Uptake is generally measured using the transpiration stream concentration factor (TSCF) as defined below.

$$\text{TSCF} = \frac{C_{\text{transpiration stream}}}{C_{\text{bulk solution}}}$$

Several studies have measured TSCFs for a variety of compounds, although often with only a single plant species. The studies are usually hydroponic and involve young cuttings or seedlings. The collection of these limitations introduces some variability in the data while casting some doubt on applicability in the field. Figure 3.2 illustrates of collection of TSCF curves.

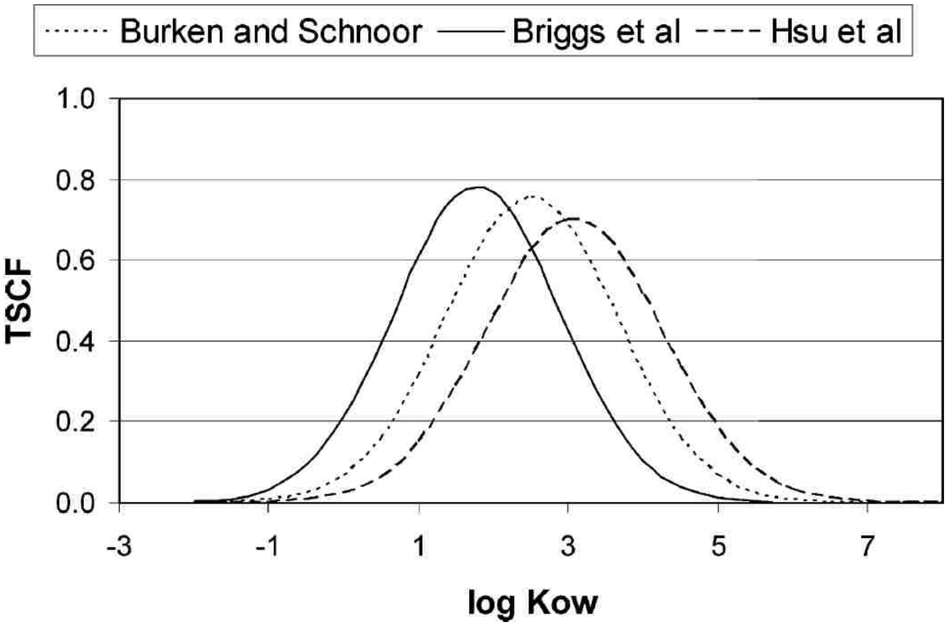


Figure 3.2 – Variability in Observed Uptake of Hydrophobic Compounds [from 11]

As shown in the above figure, compounds with a log K_{ow} in the 1-3 range likely enter the root by absorption to the hydrophobic root tissues [12]. However, a high TSCF requires transport in the water-based xylem, so exceedingly hydrophobic compounds sorb to roots but have reduced mobility. However, some recent studies have observed translocation of tetra- to nonachlorobiphenyls (log K_{ow} of 3-8) in some members of the *Cucurbitaceae* family [13]. Transport of more hydrophilic compounds (log K_{ow} < 0.5) is observed more frequently. Dettenmaier et al. observed transport of numerous hydrophilic compounds when using positive pressure to drive water into the roots [14]. 1,4-Dioxane has a log K_{ow} of -0.27 but has been found to be readily translocated, with TSCFs reported as high as 0.72 ± 0.07 [15]. In general, translocation of contaminants is more complex than simply a relationship based on octanol-water partitioning. While this relationship is adequate for estimating uptake, more research needs to be done to elucidate other critical biological or chemical factors. For example, a model by Trapp showed the presence of root hairs (referred to as “fine roots” by Trapp) had a large impact on translocation of hydrophilic contaminants as shown in Figure 3.3 [16].

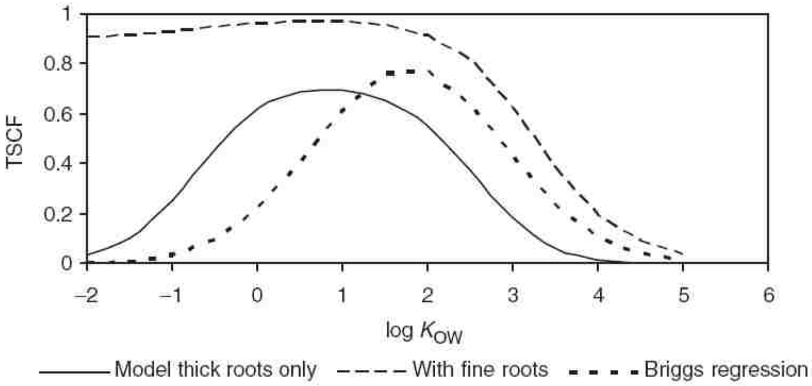


Figure 3.3 – Model Prediction of TSCF with Varying Root Morphologies [from 16]

In addition to translocation, a number of other processes are relevant to a plant’s ability to uptake contaminants from the subsurface. Hydrogeological features such as depth to groundwater and groundwater flow rate clearly affect a plant’s access to contaminants. Plant-soil interactions have a wide range of effects, including root growth, precipitation infiltration, redox conditions and microbial growth. All these factors make robust, precise field-based TSCFs difficult, if not impossible, to determine.

3.3 PLUME DELINEATION USING TREE CORING

Despite inherent geo-chemico-biological limitations on quantifying plant contaminant uptake, Vroblesky et al. first published work indicating that tree coring could be using to identify high-risk areas where wells should be drilled, inferred from tree core concentrations of PCE and TCE [2]. Since this finding, tree coring has been useful numerous times for delineation of shallow groundwater plumes. At New Haven, MO, several contaminated areas were either discovered or delineated using tree coring [17]. Tree concentrations were compared to nearby groundwater and soil concentrations, both being significant with p-values at 0.001 or lower (see Figure 3.4). Note that the correlation was stronger for soil than groundwater, which was shown in lab-scale experiments as well [18].

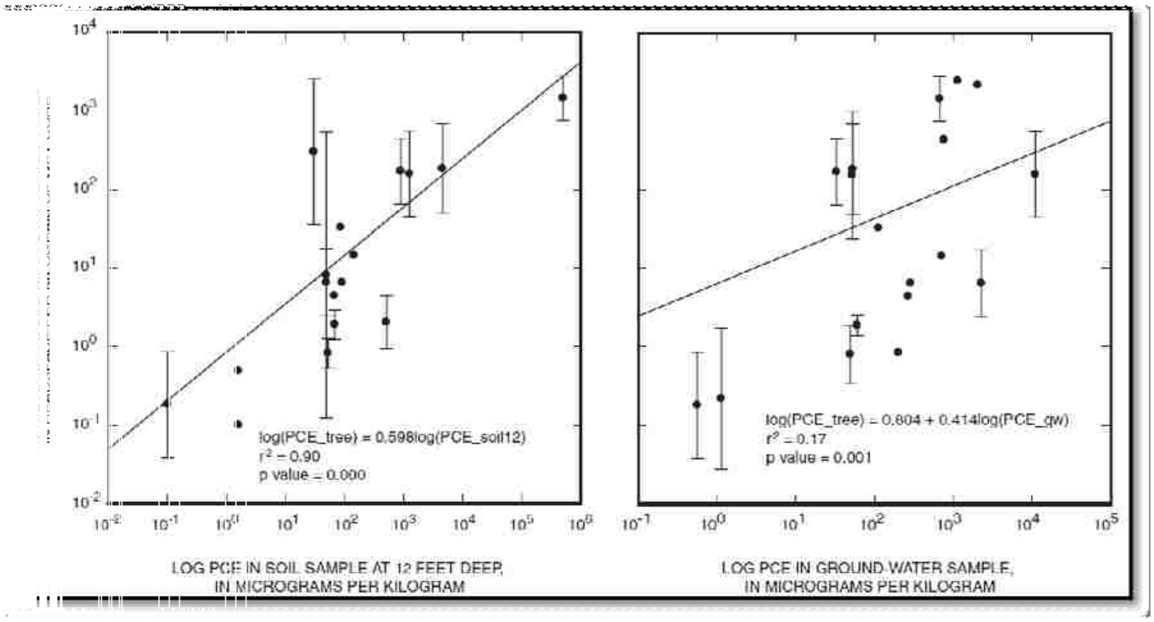


Figure 3.4 – Relationship between PCE Concentrations in Tree Cores and PCE Concentrations in Groundwater and Soil (error bars denote one standard deviation) [from 17]

Although tree cores taken from the trunk are most common, tree branches have also been shown to be useful in delineation of plumes [19]. However, diffusion-based losses to ambient of TCE and PCE up the trunk and the subsequent branch would be expected to limit detection limits [20]. Another group warns of potential limitations, such as false negatives, but still successfully used tree cores to identify areas of contamination [21]. An additional application of this technology is identifying areas of reductive dechlorination, as *cis*-dichloroethylene (cDCE) can be taken up by trees [22] and stored, due to its low Henry's constant of 0.14 at 20 °C [23]. Collectively, these findings have led to the development of a tree coring guide from the U.S. Geological Survey (USGS) and EPA [24].

3.4 MODELING CONTAMINANT TRANSPORT IN TREES

Due to interest in sampling trees for stored contaminants as well as bioaccumulation concerns, several models of contaminant transport have been developed. Many are contaminant or crop specific, such as a recent model for pesticide uptake by potatoes [25]. Trapp presents a more general model that considers 8 different compartments: soil (2), fine roots, thick roots, stem, leaves, fruit, and air [12, 16]. The model considers advection, partitioning to soil and air, and growth dilution. A review by Collins et al. also provides a thorough discussion on uptake pathways for organic contaminants [11]. Other models relevant to this work include the diffusive loss of volatiles from plants [20, 26]. However, these models do not address spatial variability of contaminants in the soil that would result in directional uptake.

3.5 SPME ANALYSIS

To measure the often-low concentrations observed in plants, analytically sensitive methods are required. Solid-phase microextraction (SPME) is a relatively new method for extracting analytes from a matrix without the use of solvents [27], making it advantageous for screening a large number of tree samples. The SPME fiber consists of a thin coating of a sorbent on a fused silica core that is placed into a sample (either immersion or headspace). Upon equilibration or another suitable timescale, the fiber is desorbed into the gas chromatograph (GC) inlet. The inlet is often operated in splitless mode, such that all the absorbed contaminant is directly loaded onto the column without the addition of a fluid. For most matrices, the fiber can be reused numerous times. Several review papers from Pawliszyn's lab provide further background information regarding analytical procedures and use in the field [28-30].

SPME is particularly powerful because the fiber can sorb a wide number of compounds, even for a particular fiber coating. The chemicals used in this study, PCE and TCE are particularly well sorbed by a 100-µm thick polydimethylsiloxane (PDMS) fiber or an 85-µm thick PDMS/Carboxen composite (CAR) fiber [31]. For PCE and TCE, detection limits are very low (less than 0.01 ppb for PDMS) [32]. Due to high fiber-gas partitioning (K_{fg}), experimental K_{fg} values for a PDMS fiber were 780 for TCE and 2,025 for PCE at 22°C [33]. Note that these values are highly temperature sensitive, as K_{fg} for PCE reached 8,685 at 10°C. Other data on PDMS partitioning values can be found in DiFilippo and Eganhouse's review paper [34]. Avila and Breiter observed a linear relationship between log K_{fg} and log K_{oa} for five chlorinated ethenes (R^2=0.77) [33]:

$$\log K_{fg} = 1.35 + 0.49 \log K_{oa}$$

In addition to the high partitioning, the PDMS fiber also exhibits rapid equilibration. Chai and Pawliszyn showed a number of different VOCs reached equilibrium in less than four minutes [35]. Another study from the Pawliszyn lab showed desorption of *o*-xylene took approximately one minute at 25°C [36]. In general, research supports equilibration times of 1-2 minutes for most short chlorinated aliphatic hydrocarbons (< C2).

There are few limitations of SPME, such as the aforementioned kinetics which becomes more significant with larger molecules. Some fibers can swell in some solvents or potentially become saturated at high concentrations of analytes. Like all passive samplers, another limitation is depletion of the sample if a sufficient volume is not available. Furthermore, PDMS fiber-gas partitioning can be reduced by approximately 10% at a relative humidity higher than 90% [35]. This condition is likely encountered when sampling tree cores, as woody biomass typically contains 50% water by mass. Despite these limitations, SPME is valuable because it can result in lower detection limits than traditional headspace sampling at room temperature. SPME also is much quicker and requires no solvents like comparable methods such as liquid-extraction or solid-phase extraction.

Few studies have used SPME to sample compounds in plants. Vuckovic et al. provides a recent review of *in-vivo* sampling, including plant sampling [30]. Some of these studies have measured pesticide transport in plants [37-38], while others have focused on plant compounds such as secondary metabolites or hormones [39-43]. Measurement of chlorinated solvents in trees by SPME has not previously been reported outside of this lab, although SPME has been used to measure chlorinated solvents in a number of other media, such as urine and blood [44-45].

3.6 TREE MORPHOLOGY AND PHYSIOLOGY

Understanding contaminant transport in trees requires detailed knowledge of tree morphology and physiology. Trees are woody species that exhibit secondary growth (i.e., lateral growth of the vascular tissues), which differentiates them from many plants. Two divisions of trees are common in North America: angiosperms (“hardwoods”) and gymnosperms (“softwoods”).

A tree trunk is largely vascular tissue, consisting of xylem and phloem tissues. The majority of the trunk is secondary xylem, the water-conducting portion of the trunk, with a new layer added each growing season. The innermost xylem tissue, called heartwood, has been shown by dye tests to prevent radial transport of water [46]. The heartwood is the darker xylem tissue in Figure 3.5.

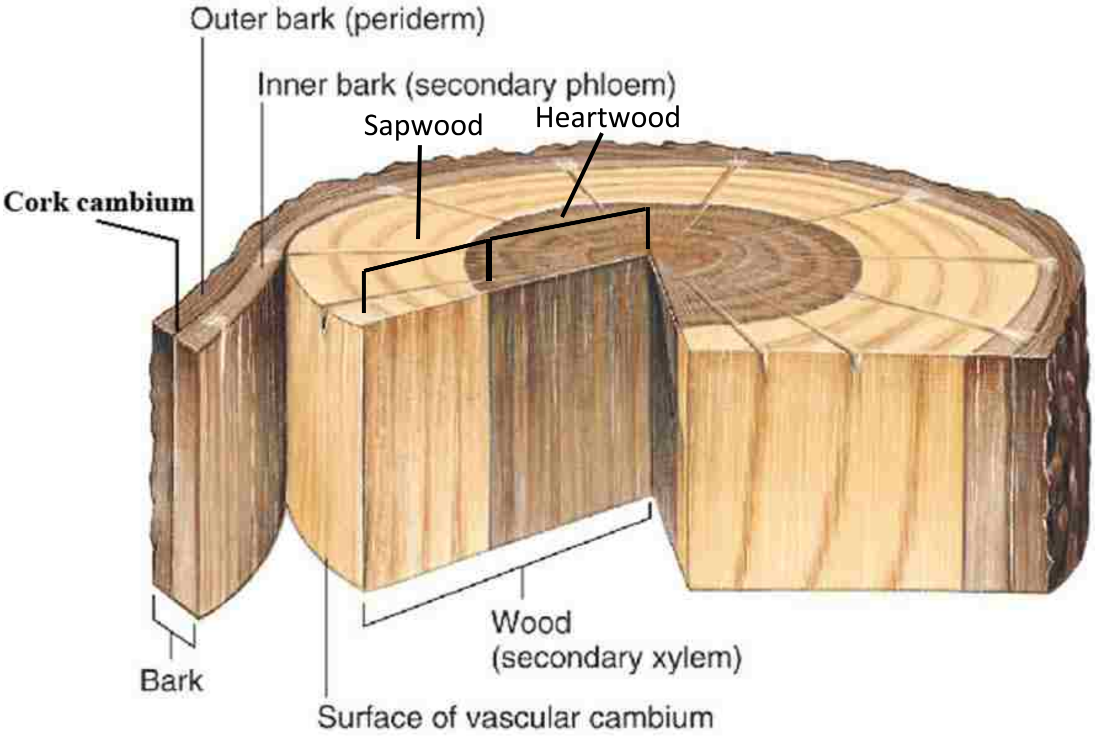


Figure 3.5 – Morphology of Tree Trunk [adapted from 47]

One important difference between angiosperms and gymnosperms is in the structure of the xylem tissue, specifically the tracheary elements conducting water and contaminants. Figure 3.6 shows a cross section of an oak tree, where the vessels are the water conducting elements. These vessels are highly lignified dead cells, thereby functioning as simple pipes.

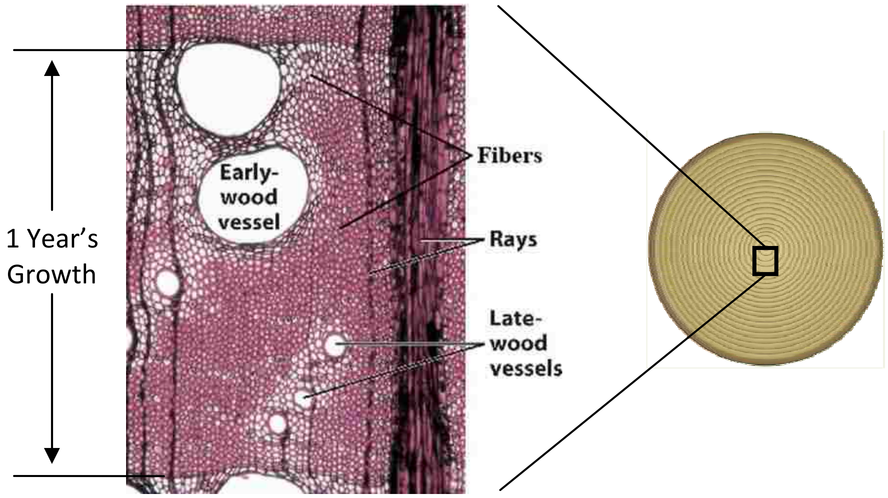


Figure 3.6 – Cross Section of Oak Tree Showing Vascular Tissue [adapted from 47]

Gymnosperms conduct water through tracheids, which are much smaller in diameter. In angiosperm trees, the size of vessels can change throughout the season. Such trees are called ring-porous, where vessels early in the season (earlywood) are much larger than vessels later in the season (latewood). Some angiosperms do not exhibit differences in vessel size during the growing season and are terms diffuse-porous. Figure 3.6 shows an example of an oak tree, which is an exemplary example of a ring-porous species. Such differences in morphology are anticipated to affect contaminant uptake and diffusion.

In addition to axial transport, vessels also allow for lateral transport to neighboring vessels. This function is critical in the event a vessel become blocked by an air embolism. This non-axial transport is accomplished through small pits on the walls of the vessels (see Figure 3.7). This pathway is much more resistive than the axial pathway, thus being rarely used under normal circumstances [47-48].

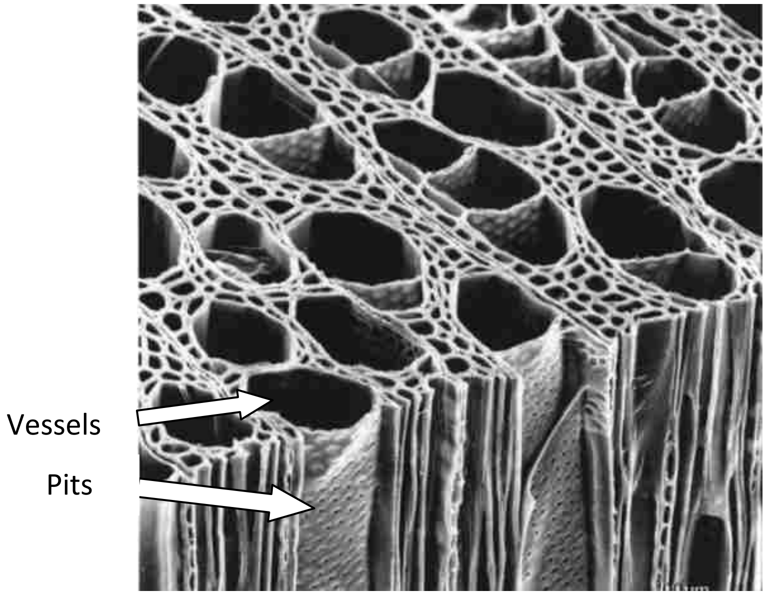


Figure 3.7 – Wood from *Populus grandidentata* Showing Pits Connecting Vessels [from 48]

3.7 TREE UPTAKE OF WATER

Transport of water through the soil via trees has been extensively studied due the desire to develop effective irrigation practices. While water transport is clearly site and climate specific, there have been numerous attempts to characterize this swath of variables. Green et al. provides a thorough review of various water transport models [49]. Models generally treat the tree trunk as a simple pipe linking extraction of water by the roots to the evaporation of water by the leaves. Water flux is usually characterized by either soil to root transfer or leaf to air transfer. For example, the Gardener and Darcy-Richards' equation uses soil properties, such as hydraulic conductivity and soil-water matrix potential to calculate the quantity of water moved. Other models such as the Penman-Monteith equation use canopy characteristics, such as stomatal resistance and leaf area to calculate total transpiration rates. However, neither of these model types explains the directional uptake of water (and associated contaminants) that would be relevant to this study.

More relevant to directional uptake of water is the concept of hydraulic redistribution (HR), also sometimes called hydraulic lift. During dry weather and at night, groundwater is carried by the deep roots up to the drier surface soils and redeposited for uptake during the day [50-51]. HR has been demonstrated in more than 50 different plant species [52]. The process has been shown to be passive, where water flows through the roots according to potential differences, hence hydraulic redistribution [53]. Figure 3.8 shows a typical example of hydraulic lift, where lateral roots show a negative sap velocity (i.e., away from the tree).

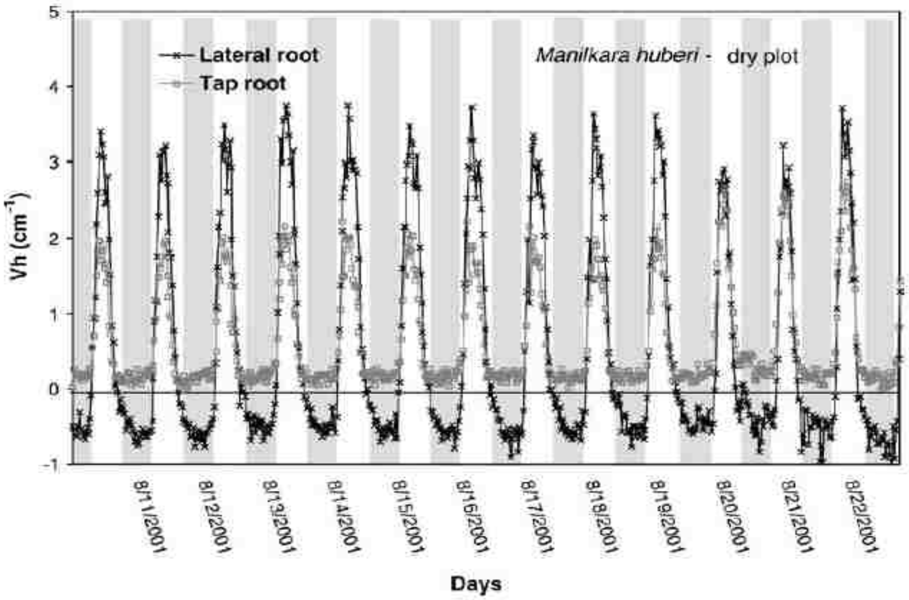


Figure 3.8 – Sap velocity (Vh) Showing Strong Hydraulic Lift at Nighttime (water transported from tap root through lateral roots to soil) [54]

Hydraulic distribution gives strong evidence towards the passive transport of water throughout the tree, as the trunk is no more active than the roots. Passive transport flows towards areas of lower potential, as evidenced by the relatively rare cases of lateral HR. Thus, under typical conditions water is transported through the tree with its directionality conserved (azimuthally), due to the absence of an active mechanism for redistributing water in the xylem. Any contaminants are expected to move with the xylem sap, although retarded due to partitioning into the woody tissue.

A critical aspect of directional uptake of water and contaminants are the comparative resistances between axial and radial or circumferential transport. The less similar, the more likely axial transport of contaminants will dominate. Brooks et al. spiked an area of soil with deuterated water and observed a strong resistance to water transport across the tree compared to roots on the same side of the tree [53]. James et al. also demonstrated limited radial transport of deuterated water in four different tree species [55]. Another study measured sap flow on 8 sides of a tree and the corresponding roots after a rainfall event [46]. They found a good match between lateral root sap velocities and stem sap velocity in the azimuthal direction (Figure 3.9). Their conceptual model of water transport in Figure 3.10 shows high circumferential and radial resistance restricts flow across the trunk. This is because flow across the trunk (non-axially) must travel through pits. Both of these pathways have smaller openings than xylem vessels in the axial direction, leading to greater fluid resistances.

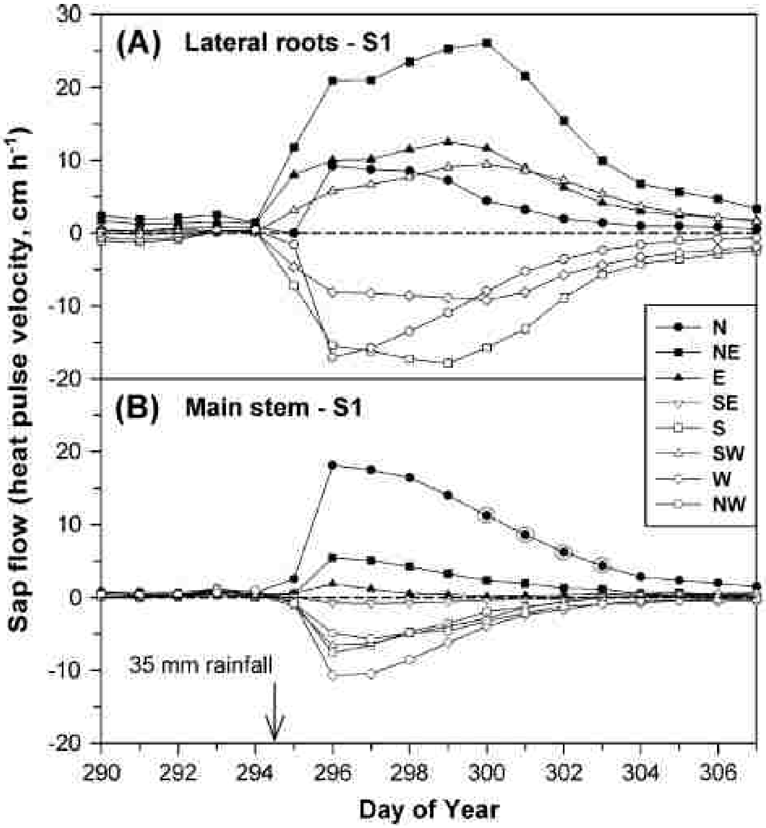


Figure 3.9 – Nighttime Sap Flow Measured at 8 Different Azimuthal Locations [from 46]

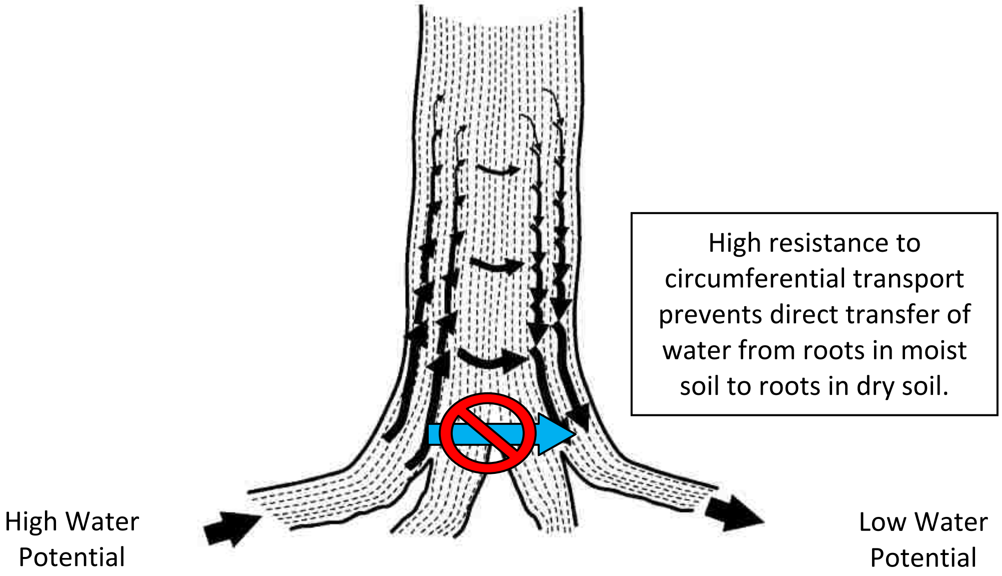

High resistance to circumferential transport prevents direct transfer of water from roots in moist soil to roots in dry soil.

Figure 3.10 – Conceptual Model of Water Transport in Trees [adapted from 46]

However, one study by Fernandez et al. was unable to correlate local irrigation events to sap flows on the corresponding side of the tree [56]. This may be able to be explained by the smaller diameter of the tree (18 cm), whereas the trees in the Burgess and Bleby study were 40-60 cm in diameter. A smaller diameter tree may limit azimuthal conservation, as circumferential and axial transport likely scale as a function of diameter.

The overall result is that axial transport of contaminants is expected to be the dominant form of advective transport. Other forms of contaminant transport would include diffusive transport in the axial, radial and circumferential directions. To observe azimuthal conservation of contaminants, axial transport must exceed radial or circumferential transport.

3.8 DIRECTIONAL UPTAKE OF CONTAMINANTS

Very few observations have been made regarding directional uptake of contaminants. Some evidence for directional uptake of contaminants comes from fertilizer studies. Radio labeled phosphorous has been used to show phosphorous applied to particular lateral roots travels to certain leaves or branches [57].

With regard to contaminants, Vroblesky found directional variation of TCE in a tree at a site in Charleston, SC [58]. In tree SC1, concentrations on the southeastern and southwestern sides were approximately three times larger than concentrations on the northeastern and northwestern sides. This agrees well with the plume, as shown below in Figure 3.11. Note that this was the only tree sampled on four sides, so limited additional directional data is available. Tree SC101 was cored on the northwest side (291 ppb) and southwest side (31 ppb). These data indicate directionality, but were taken two years apart, making the measurements difficult to compare.

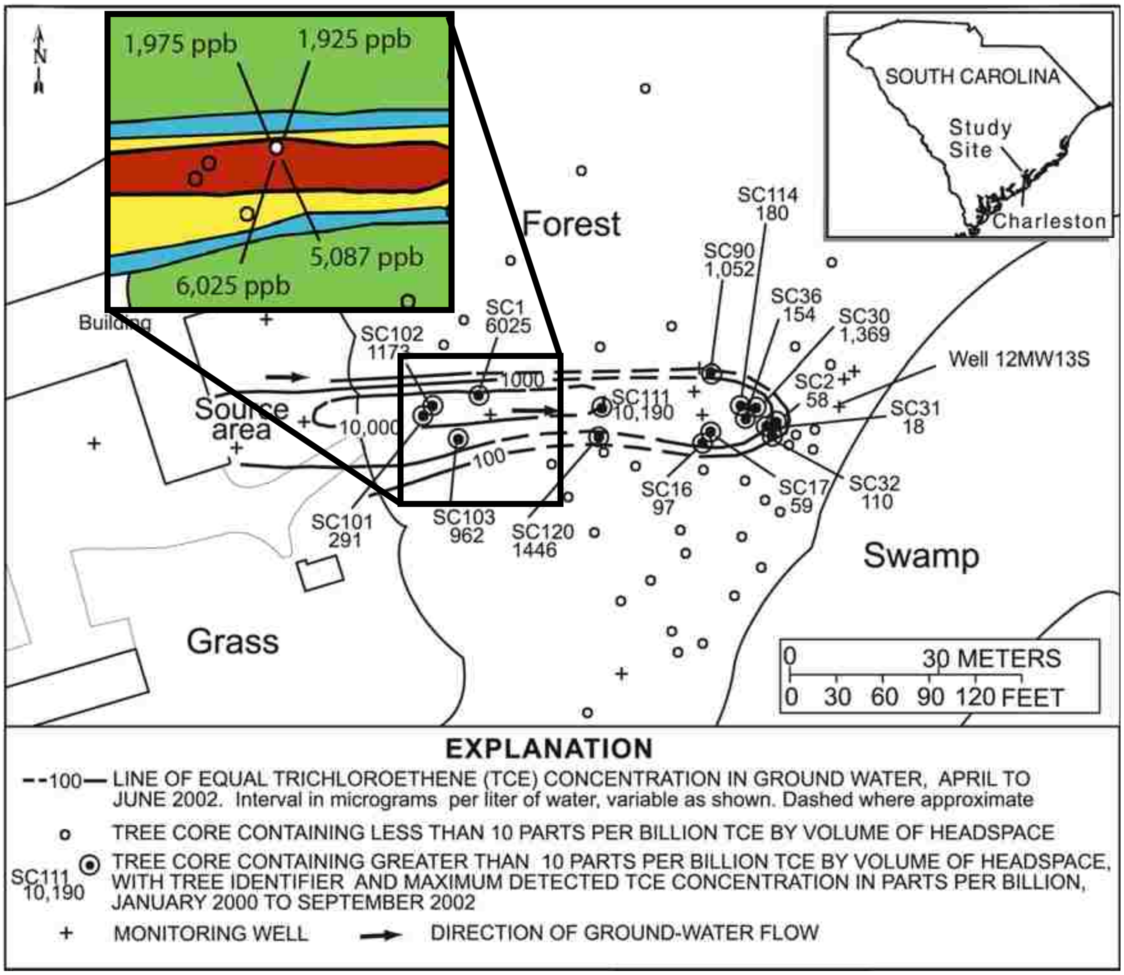


Figure 3.11 – Plume Map at Charleston, SC Site [from 58]

Schumacher et al. also observed directional variation in two trees cored at the New Haven, MO site. For both trees, the concentrations were found to vary by a factor of 3-5 around the tree. Tree TW02, a 25 cm diameter eastern red cedar, was cored 25 times at 6 different heights. The side of the tree exhibiting the highest concentrations on PCE shifted slightly with height, a phenomenon attributed to spiraling xylem tissue [17]. The data for tree TW02 is shown below in Figure 3.12.

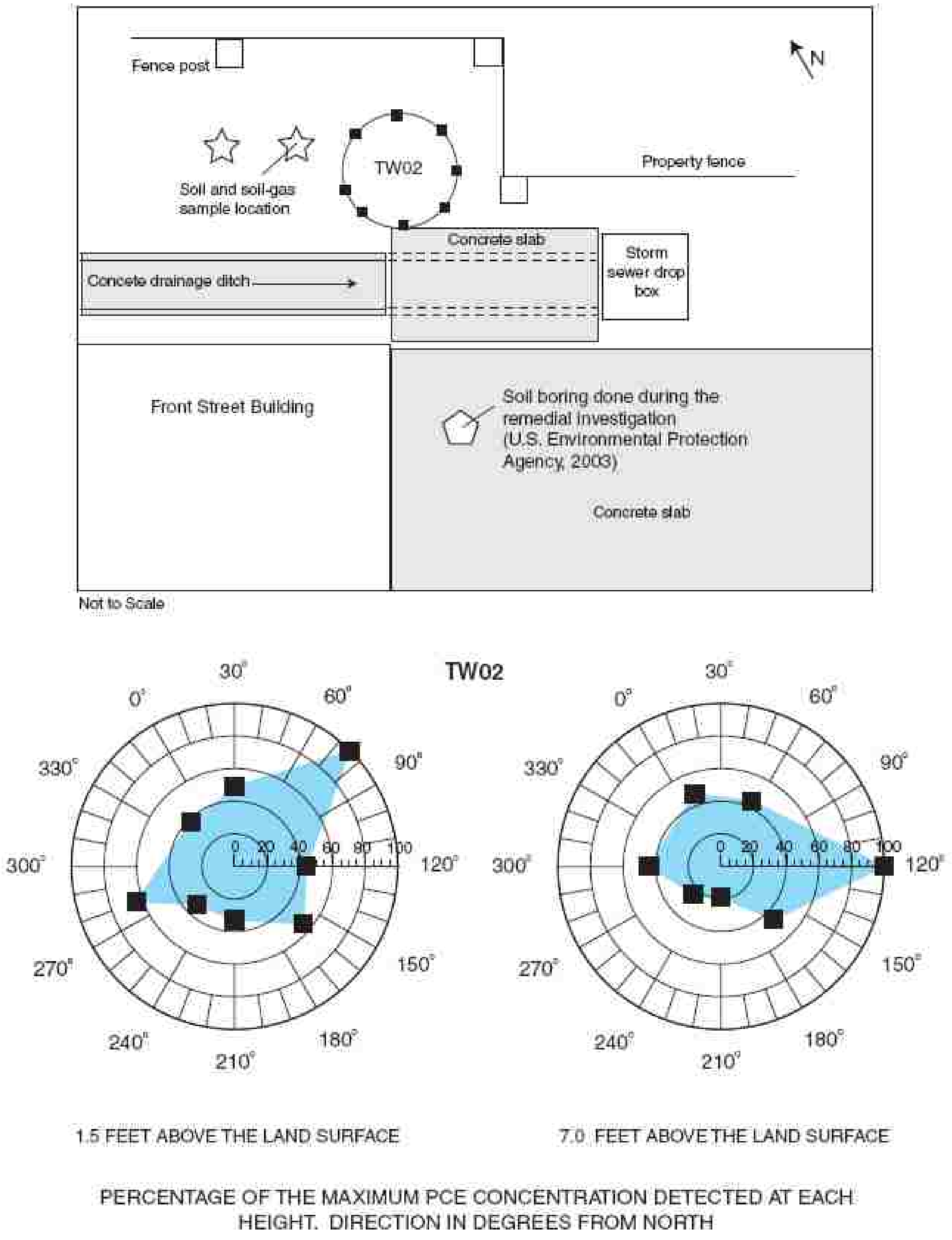


Figure 3.12—Directional Variation in PCE Concentrations in a Red Cedar [from 17]

In both trees, relating the directional concentrations in the trees to the corresponding groundwater or soil vapor concentrations was difficult. The trees were located near physical obstructions or modifications, such as drainage ditches, concrete slabs, or buildings. These disturbances undoubtedly affected contaminant transport as well as root growth, making it difficult to draw any conclusions.

Large diameter trees on well-documented plumes with steep concentration gradients are rare. To gather additional data, a laboratory setting will be required so trees can be subjected to such conditions while being closely monitored.

PAPER

Directional Uptake of Chlorinated Solvents for Phytoscreening

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ABSTRACT

Trees have been used to locate contaminated soil and groundwater, augmenting traditional methods, such as well drilling, that are time-consuming and expensive. In the past decade, plant sampling has gained acceptance as a reliable method for site screening. These phytoforensic tools are a novel approach to site assessments, potentially reducing cost while more effectively locating contaminated groundwater. This paper investigates a new tool: directional tree coring, a concept originating from field data suggesting azimuthal concentrations in tree trunks may reflect the corresponding azimuthal concentrations in the groundwater below the tree.

To test this in the lab, large diameter trees were subjected to concentration gradients in the groundwater. These trees were analyzed for contaminants and evidence of directional uptake. Upon analysis, concentrations were approximately 5 times higher on the side of the tree near the highly contaminated groundwater. The conservation of azimuthal PCE and TCE gradients was observed at all levels up the tree and overall

concentrations decreased with increasing height above ground. Several field sites showed similar data, where concentrations in the tree matched groundwater concentrations in an azimuthal pattern. In practice, each tree sampled directionally can provide compass-like information, pointing investigators towards the most concentrated region of the plume.

BACKGROUND

Widespread use and lax disposal standards of various chlorinated solvents in the past decades has resulted in contamination of soil and groundwater a number of sites [1]. Additionally, the hydrophobic, recalcitrant nature of these compounds makes them long-lived in the environment. It is estimated that thousands of sites across the United States have soil and groundwater contaminated with chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE) [2]. Due to carcinogenicity concerns, drinking water limits are low [3-4]. High volatility also makes vapor intrusion a concern in residential areas [5-6].

Detecting and monitoring these compounds is time-consuming and resource-intensive. Measuring concentrations in trees has been proposed as a low-impact alternative [7-8]. However, some challenges exist such as depth to groundwater and uptake of surface water [9-11]. Often, these challenges can be overcome by sampling numerous trees. This paper focuses on an approach to obtain several data points from a single tree: directional sampling.

Water movement in trees is largely passive, flowing from regions of high potential in the roots to regions of low potential in the leaves. The transport is through vessels and tracheids, small pipe-like elements in xylem tissue. Passive transport of water has been recently shown in the concept of hydraulic redistribution (HR), where water is transported from wet soil to dry soil via root xylem [12-13]. The majority of the flow is often axially through the vessels, as non-axial flow is through small pits (i.e., more resistive) in the vessels. Much like the water transport, the chemical transport of chlorinated solvents is passive. It is hypothesized that compounds from the subsurface on one side of the tree will be found in the trunk on the same side, as axial transport is expected to exceed circumferential or radial transport.

Directional uptake of contaminants has been reported previously at a field site studied by Vroblesky et al. [9]. One tree was located along a steep subsurface contamination gradient, where TCE concentrations ranged from 10 ppm (north) to less than 100 ppb (south) across 10 meters. The southwest and southeast sides of the trunk contained 5,087 and 6,025 ppb respectively, while the northwest and northeast sides contained 1,975 and 1,925 ppb respectively. Schumacher et al. also observed directional variation in two trees at a field site in New Haven, MO, but were unable to relate these concentrations to groundwater concentrations due to the nearby buildings [14]. This paper seeks to reproduce these findings in the laboratory and field. If the hypothesis is confirmed, additional information may be gathered from a single tree, providing a compass-like indication of where the plume is most concentrated.

EXPERIMENTAL METHODOLOGY

EXPERIMENTAL SETUP

To create a realistic field scenario, large-diameter (> 5 cm) sandbar willow cuttings (*Salix exigua* subsp. *interior*) were grown in reactors designed to create a directional concentration gradient in the subsurface. The experiment was carried out in two separate stages: a small-scale preliminary experiment and a larger-scale experiment. In the preliminary experiment, one 10-cm diameter cutting (Tree A1) was grown in a 20-L reactor containing commercially-available potting soil. Tree A1 was allowed to grow for approximately 4 months prior to being harvested. In the large-scale experiment, four 5 to 10-cm diameter cuttings were grown in a 200-L reactors filled with a loam mix (Trees B1-B4). The loam mix was 40% sand, 45% silt, 15% clay and contained 5.8% organic matter. The salt pH was measured at 6.8 and the cation exchange capacity (CEC) was 13.3 meq/100g. The University of Missouri Extension Soil Testing Laboratory (Portageville, MO) determined all soil characteristics. The four trees were allowed to grow for 5 months prior to harvest, with the exception of tree B3, which grew for only 3 months, as the original tree did not survive. In both experiments, the willow cuttings were approximately 2-3 m in length.

Water was fed into the bottom of all reactors through a perforated tube to ensure uniform distribution (see Figure 1). 40 solid polymer samplers (SPSs, described below) were placed in each of the 200-L reactors, 8 at 5 different levels.

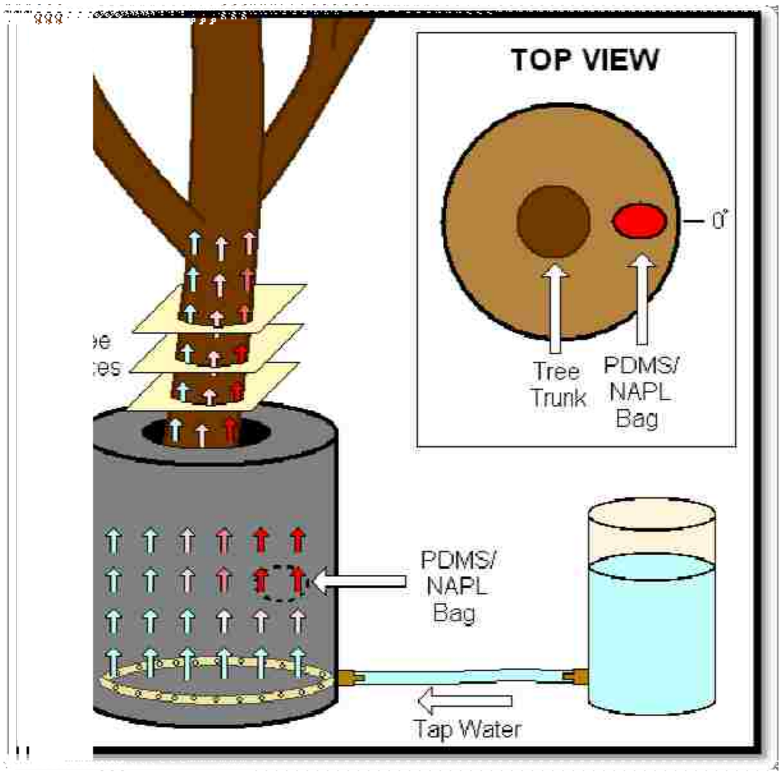


Figure 1 – Schematic of Reactor Setup

The contaminant source was placed as polydimethylsiloxane (PDMS) oil spiked with PCE and TCE. A zip-top plastic bag containing 4 mL of PCE and 6 mL of TCE in 400 mL of PDMS oil was placed at 1/3 the depth of the reactor near the drum wall. The high partitioning (i.e., low specific activity coefficient) of the contaminants in the PDMS oil limits solubility in the aqueous phase by generating a dilute plume near the bag. Using approximate PDMS-air partitioning values of 2,000 for PCE and 1,200 for TCE, Henry's constants of 0.58 for PCE and 0.34 for TCE (at 20°C), the approximate aqueous concentration were 14 ppm PCE and 54 ppm TCE [15-16].

The trees were sampled using a destructive method, where sections were taken across the trunk as shown in Figure 1. The thickness of each section was approximately 4 cm. Each slice was then split radially to obtain eight azimuthal segments. Each segment was further split to gather radial information. Figure 2 shows a picture of a harvested tree.

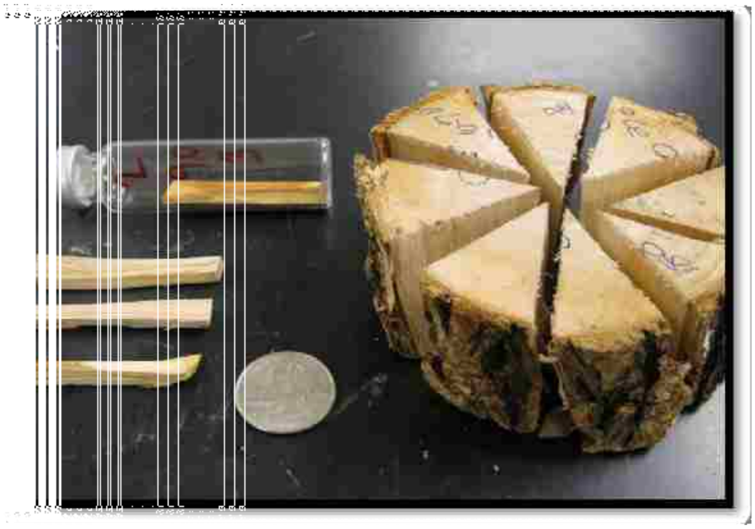


Figure 2 – Destructive Sampling of Willow Trees

PCE and TCE concentrations in the trees were mapped in Surfer® 9 using standard kriging. The coordinates were obtained by assuming a uniform thickness per radial slice at the corresponding azimuthal angle. No outer boundary conditions were imposed when kriging the data.

ANALYTICS

All samples were analyzed using solid-phase microextraction (SPME) of the vial headspace (HS) (Supelco, Bellefonte, PA). Using a CombiPAL SPME auto sampler (CTC Analytics, Zwingen, Switzerland) the SPME fibers were desorbed into an Agilent 7890 gas chromatograph (GC) equipped with a micro electron-capture detector (µECD).

The woody samples were analyzed with a 100-µm PDMS SPME fiber using a 5-minute extraction time, followed by a desorption time of 3 minutes at an injector temperature of 230^{o}C. Purge flow occurred after 0.75 minutes and was 60 mL/min. Average column velocity was 33 cm/s using nitrogen as the carrier gas. The column was a VOCOL® column with dimensions of 10m x 200µm x 1.2µm (Supelco, Bellefonte, PA). The temperature was held at 40^{o}C for 0.75min and then ramped at 20^{o}C/min until 160^{o}C was reached, which was the termination of the run. The µECD detector was set at 250^{o}C.

Calibration was obtained using 10 mL of water in a 20-mL vial spiked with, PCE, TCE, and the degradation product *cis*-dichloroethylene (cDCE). The headspace of the five different standards was sampled and a linear calibration plot was obtained from three standard sets. The concentrations and peak areas were log transformed to ensure homoscedasticity for least squares regressions. Check-standards were placed every 10-15 samples to ensure the calibration remained valid (±10%). Method detection limits (MDLs) were calculated for equilibrated PCE and TCE water concentrations using EPA methods [17]. Because the tree core matrix is inherently variable and difficult to mimic in the laboratory setting, water standards were used to determine the method detection limit (MDL). For PCE, the MDL was 0.5 ppt (part per trillion) at an estimated signal-to-noise ratio ($^{S}/_{N} = \frac{\bar{x}}{s}$) of 11. For TCE, the MDL was 8 ppt while the MDL for cDCE was 1.2 ppb due to lower fiber partitioning, volatility, and fewer chlorine atoms.

Wet and dry wood masses were taken using a Metler Toledo XS 205 Dual Range balance, operated at a resolution of 0.01 mg. The wet mass of the core was used to correct for sample depletion as contaminants partition to the headspace. This mass-balance approach is shown in Ma and Burken [18], using wood-air partitioning values from literature [5, 18].

FIELD SITES

Directional samples were collected from trees at two field sites in Canada. One field site was a research site at the Canadian Forces Base Borden in Borden, ON while the other was a closed manufacturing plant in Kitchener, ON [19-22]. Both sites have well documented chlorinated solvent plumes. The sites were sampled during June 2009, September 2009, and May 2010 using tree coring and solid phase samplers (SPSs) as the trees could not be destructively sampled.

Tree cores were obtained using a 0.5-cm increment borer (Forestry Services Inc., Pawleys Island, SC) at the two sites. Methods are described in detail in Vroblesky [8] and are briefly summarized here. The cores were approximately 8 cm in length and were taken at breast height (approximately 1.5 m). Upon extraction, the core was transferred immediately to a 20-mL vial with a screw-top cap and Teflon/silicone septa (Supelco, Bellefonte, PA). Field blanks were taken every 10 to 15 samples. After the sampling was completed, the vials were stored on ice and then refrigerated until analyzed. Prior to extraction, the samples were warmed to room temperature.

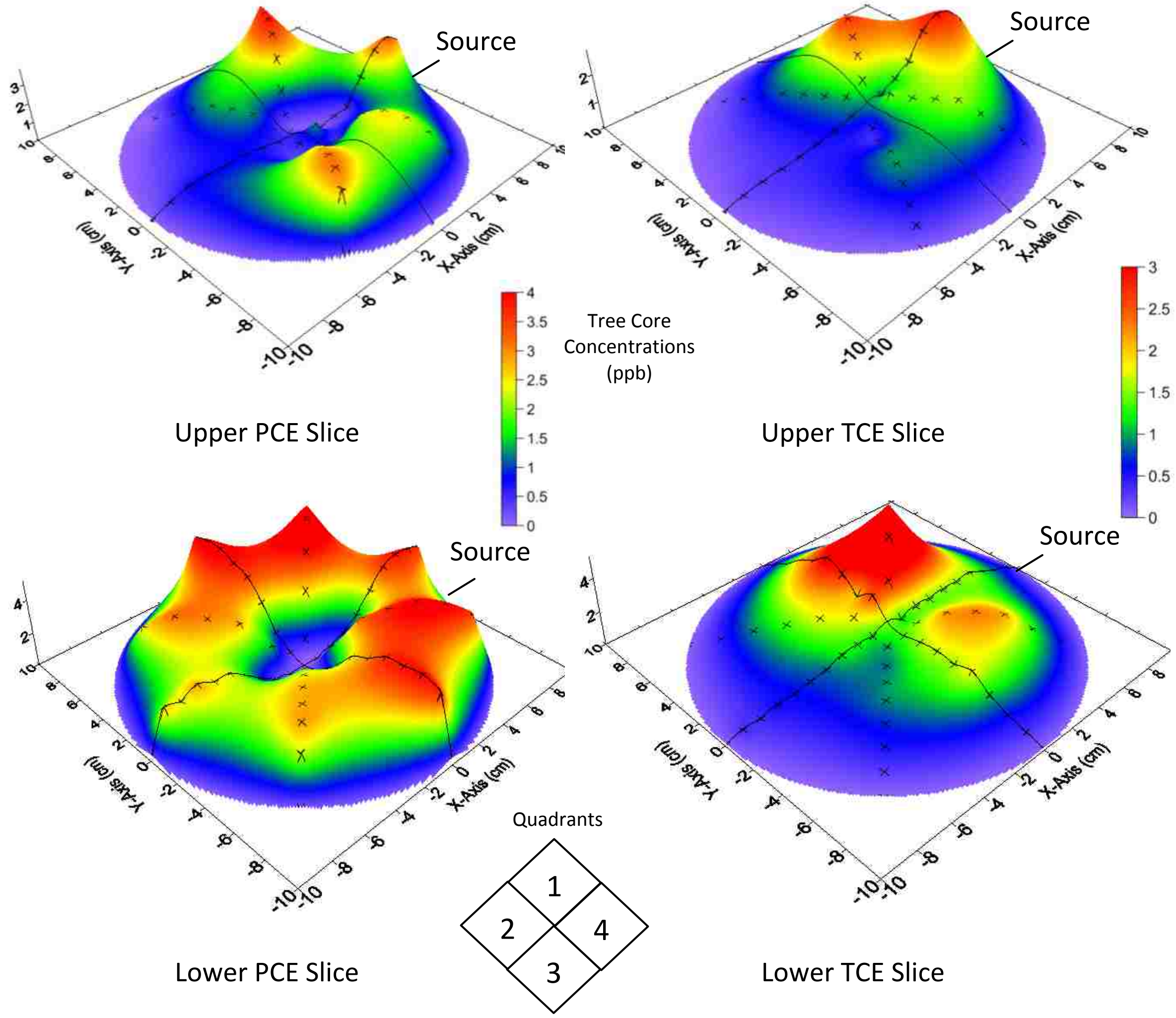
Solid Phase Samplers (SPSs) were employed as a passive sampling technique for measuring contaminant concentrations in the trees. SPSs were constructed from 0.5 g ± 2% of Tygon® Tubing (Formulation R-3603, ID: 1.6 mm, OD: 4.8 mm). Stainless steel wire was looped through the tubing to aid insertion and removal of the SPS from the tree. The SPSs were cleaned in methanol for 2 days, dried in a 100^{o}C oven for 3 days and then wrapped in aluminum foil until used onsite. Trip blanks were regularly vialed on-site.

The SPSs were placed into the vacated core-space in the tree and a #10-32 x ½-inch machine screw was used to seal the bore-hole. Following 10-14 days of equilibration, the SPSs were removed and placed into 20-mL vials with a screw-top cap and Teflon®/silicone septa. These vials were refrigerated until analysis by SPME-GC as described previously.

RESULTS AND DISCUSSION

LABORATORY RESULTS

The laboratory arrangement was effective at generating a subsurface gradient and corresponding directionality was observed in trees. The directional data for Tree A1 are shown in Figure 3, where '+' indicates a measured data point. The location of the source zone is at zero degrees, which corresponds to a maximum x value and a y value of zero.



Upper PCE Slice

Upper TCE Slice

Lower PCE Slice

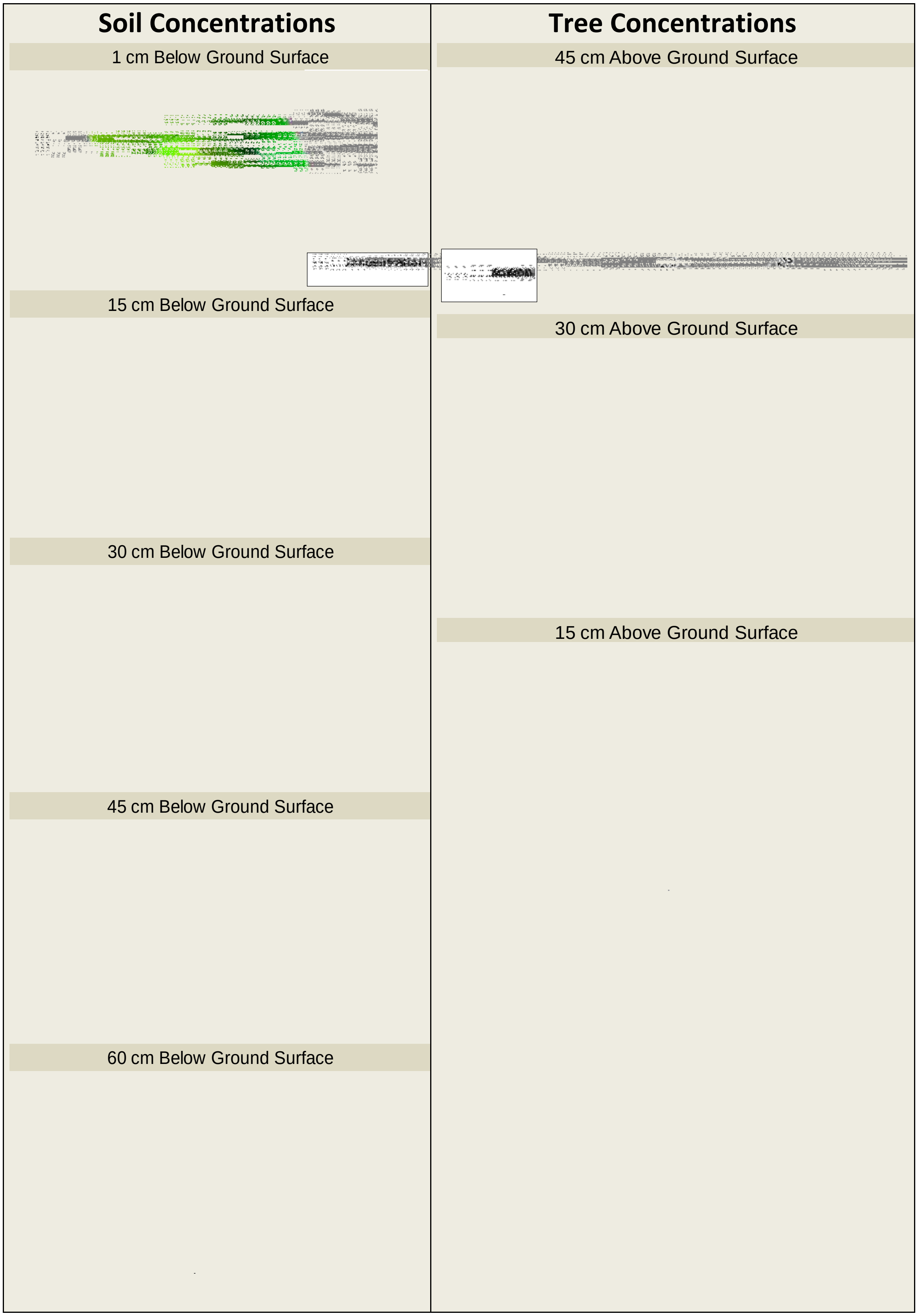
Lower TCE Slice

Figure 3 – Directional Profile of Tree A1 (all concentrations in ppb)

Both the PCE and TCE showed azimuthal variation favoring the first and fourth quadrants. The variation appeared least noticeable for PCE for the lower slice, perhaps due high circumferential diffusion relative to radial diffusion. An alternate explanation is radial variation in the wood-air partitioning coefficient for PCE.

In the large-scale experiment, trees B1, B3 and B4 showed vigorous growth. Tree B2 exhibited severe leaf curl throughout the experiment, which limited its growth. This can be seen in the flattening of the cumulative water usage curve (see APPENDIX B). For this reason, tree B2 was not harvested for data.

The cross-sectional PCE data for Tree B3 are shown in Figure 4. The left side shows SPS soil concentrations in log ppb while the tree concentrations are not log transformed for clarity. The data for the tree exhibit lower concentrations with height, which is consistent with the diffusional loss to the atmosphere through the lenticels [14, 23].



Soil Concentrations

1 cm Below Ground Surface

15 cm Below Ground Surface

30 cm Below Ground Surface

45 cm Below Ground Surface

60 cm Below Ground Surface

Tree Concentrations

45 cm Above Ground Surface

30 cm Above Ground Surface

15 cm Above Ground Surface

Figure 4 – Directional Profile for Tree B3 (Left: Soil, Right: Tree)

The directionality in this tree was biased towards quadrants I and IV as in Tree A1; however, the gradient was not as strong. In addition, there appeared to be less circumferential diffusion, perhaps due to slightly different growth morphologies.

Trees B1 and B4 however, did not show strong directional variation. Instead, the contaminant mass was largely located at the center of the tree, with a slight bias towards the source zone. Figure 5 shows a typical concentration profile observed in these trees.

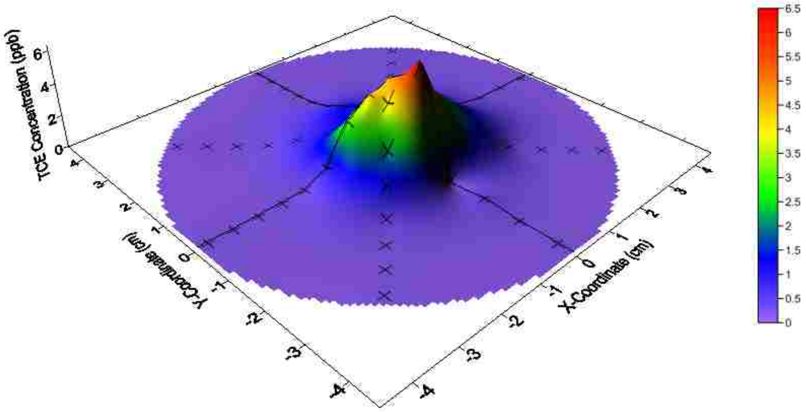


Figure 5 – Tree B1 TCE Concentration in Lower Slice (ppb)

This observation is hypothesized to be a result of contaminant exhaustion in the soil. Figure 6 shows the average and maximum soil concentration for trees B1, B3 and B4. Note that tree B3 soil shows higher concentrations of PCE and TCE in excess of an order of magnitude. Contaminant kinetics can be envisioned in the tree as a loading phase, where contaminant is translocated into the shoots. The contaminants in the transpiration stream experience retardation until a pseudo-steady state is reached. While contaminants are partitioning to the tree biomass, the NAPL reservoir in the soil is being depleted of contaminant, so less contaminant is translocated to the shoots. As a result, concentrations in the trunk decrease as the compounds diffuse out of the bark. The middle of the tree, being farthest from the bark will have the highest concentrations during this "unloading" phase, leaving a peak as shown in Figure 5.

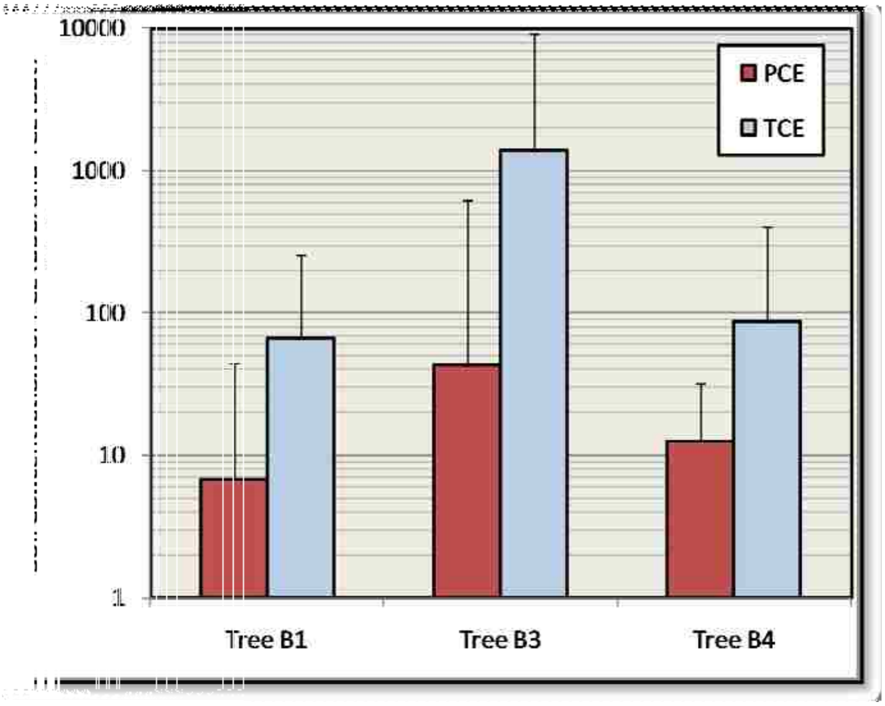


Figure 6 – Average Soil Concentrations (Positive error bars denote maximum)

The hypothesis of soil depletion and "unloading" in the tree is also supported by comparing the maximum tree concentration as a percentage of the maximum soil concentration (Figure 7). This idea is similar to the transpiration stream concentration factor (TSCF), but only considers maximum concentration, which should be less than 100% as PCE and TCE passively enter the plant [24-25]. While inherent heterogeneities in the soil concentrations prevent accurate determination of a TSCF, TSCF's greater than 100% indicate contaminant depletion in the soil relative to the tree, as tree concentrations exceed soil concentrations.

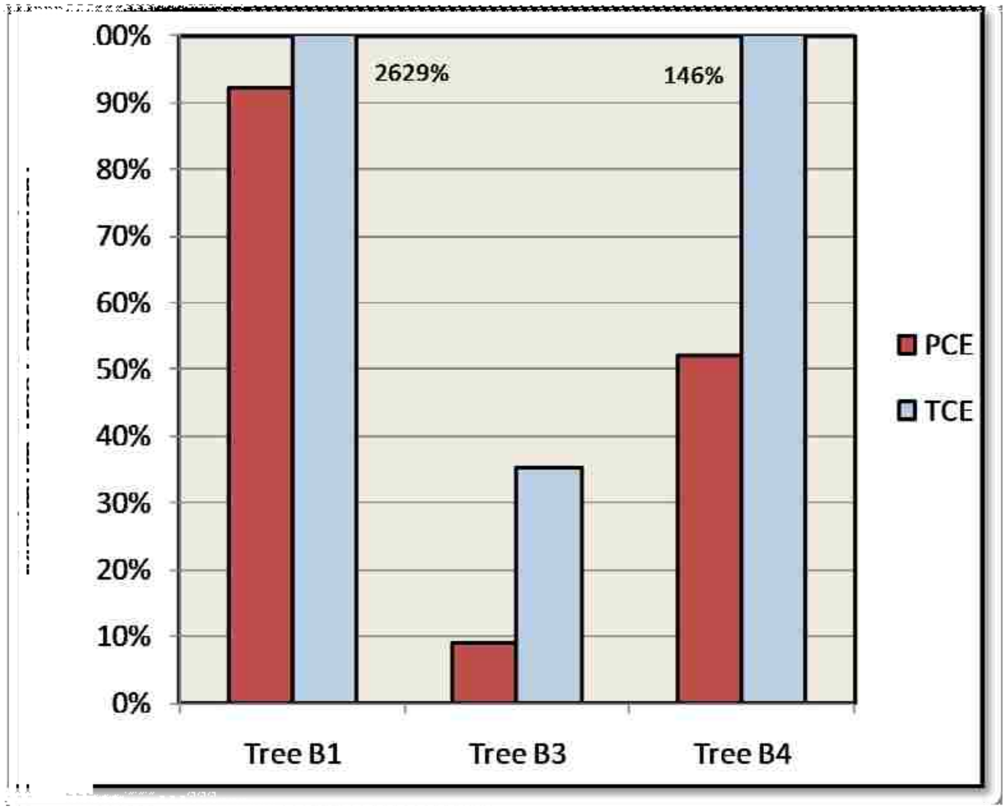


Figure 7 – Maximum Tree Concentrations Relative to Maximum Soil Concentrations

Despite apparent depletion of the soil, clear trends can be gleaned from the dataset. Calculating the centroid of the cross-sectional concentration can be used to estimate the directionality. The below equation shows the calculation of the directionality in the x-direction, x_C.

$$x_C = \frac{\sum x_i \cdot C_i}{\sum C_i}$$

For a particular slice, this value can be normalized by the radius:

$$x\% = \frac{x_C}{r}$$

Plotting these centroid values for all slices of the three trees yields Figure 8.

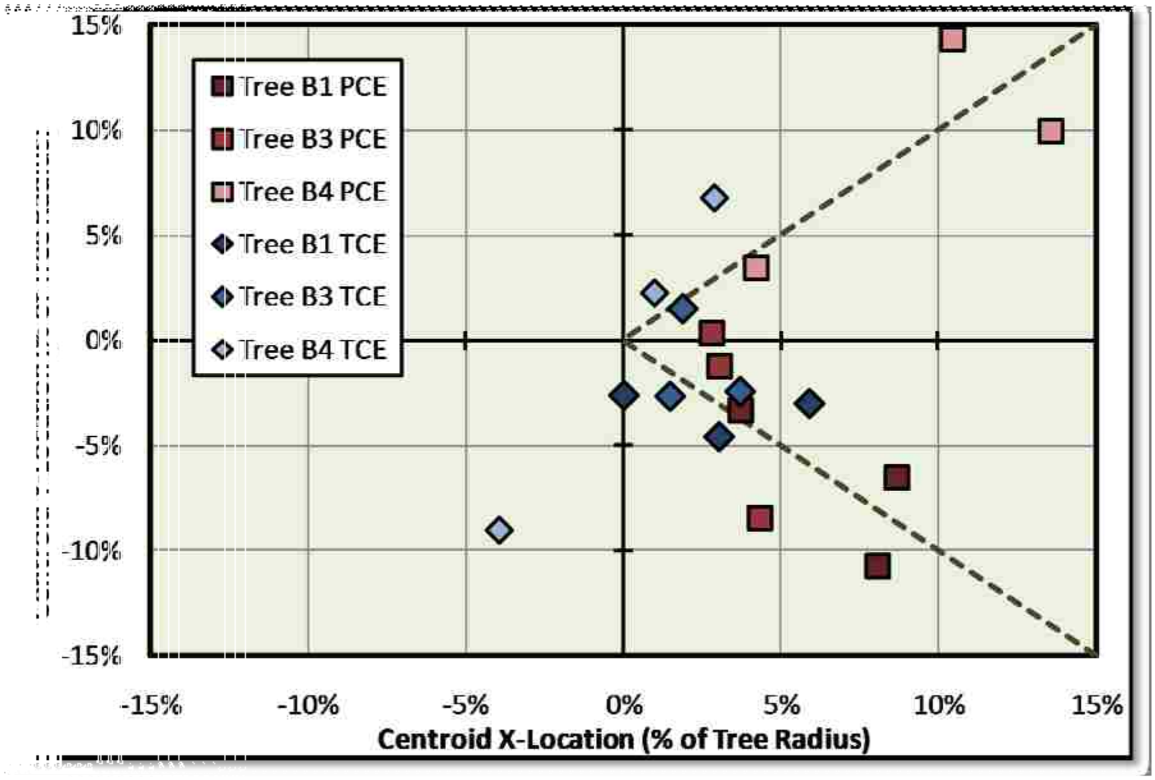


Figure 8 – Radius-Normalized Centroid for Trees B1, B3 and B4

Seventeen of eighteen centroids have positive x-coordinates, with no clear pattern of y-coordinates, providing further evidence of directional uptake of contaminants. The average centroid for PCE was (7%, 0%) and for TCE was (2%, -2%). Figure 9 shows the same calculation for all levels of the soil from trees B1, B3 and B4.

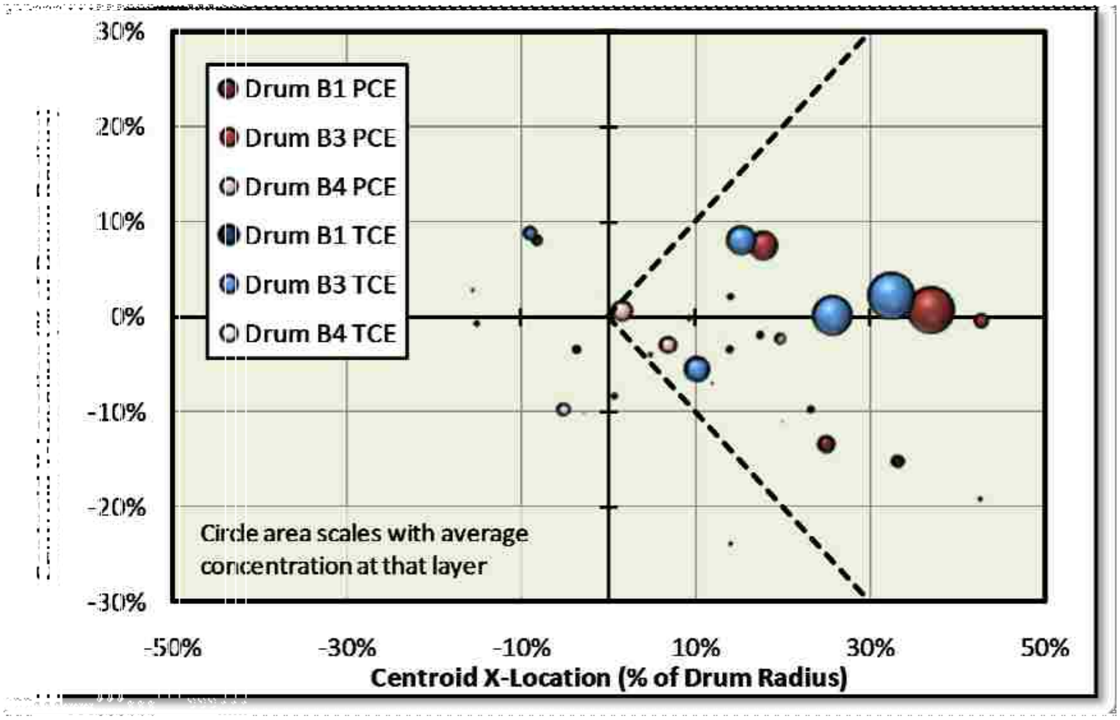
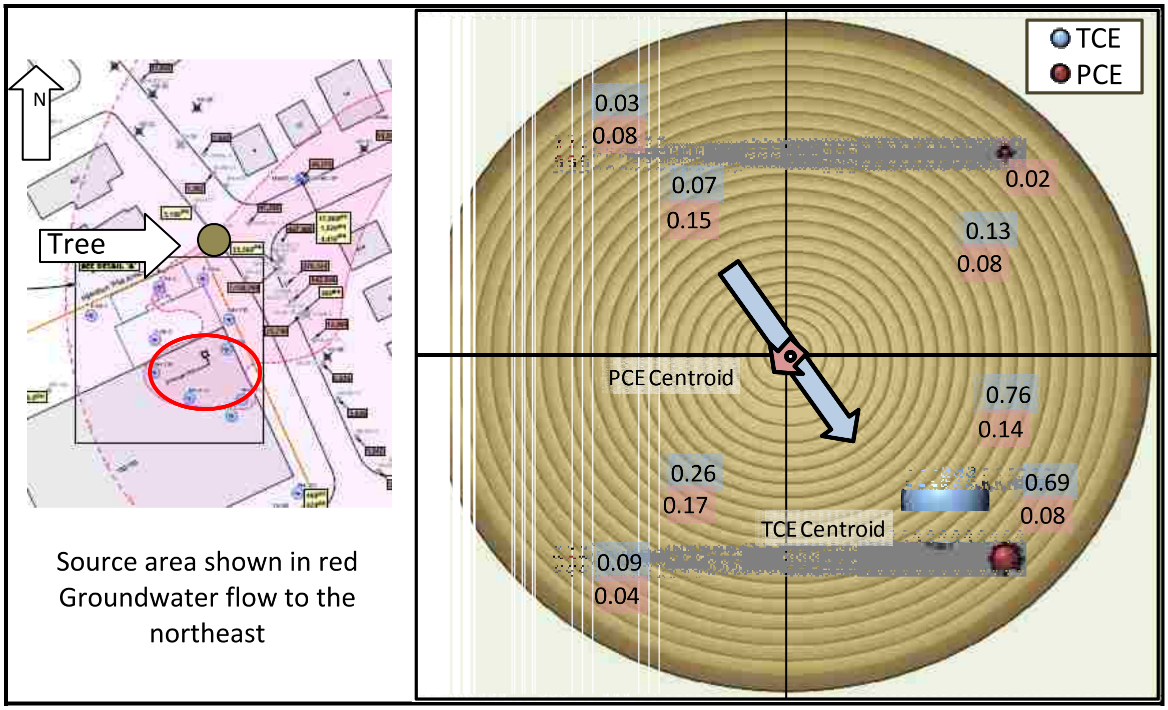


Figure 9 – Radius-Normalized Centroid for Soil

The soil data show more scatter, which is expected given the large variation in depth. Regardless, the soil centroids generally have positive x-coordinates. One large difference is that the soil centroids have a stronger directional bias, as the centroid x-location reaches as high as 40% of the drum radius, indicating a much steeper gradient in the drum than in the tree.

FIELD STUDIES

At the Shanley site, tree 16 was cored on four sides and at two different depths. This tree was chosen for proximity to the source zone and large diameter (57 cm). Figure 10 shows the concentrations observed in the tree cores, where a missing data point indicates the contaminant was not detected. The highest concentrations of TCE were found in the southeast side of the trunk, which matches well with the plume map. PCE concentrations in the tree show much less directional variability, suggesting that the PCE plume gradient is less steep in this location. However, PCE well data was highly variable at the site, making evaluation of this statement difficult. The location of the contaminant centroid is also shown in the figure for PCE and TCE. For TCE, the centroid is clearly on the side of the tree towards the more concentrated region of the plume.



Source area shown in red
Groundwater flow to the northeast

Figure 10 – Left: TCE Plume Map Showing Location of Directional Tree, Right: Directional Concentrations Found in Tree Cores (ppb), Shanley Site, Tree 16, May 2010

At the Borden site, Tree 22 was cored on four different sides, each at two different depths. Figure 11 and Figure 12 show the resulting tree core data from two different trips. The southwest data show very high concentrations in the inner cores. The less obvious repeated detection of contaminants in the southwest outer core also implies the most concentrated region of the plume lies to the southwest. Figure 13 shows the plume maps for the Borden site. While the groundwater data do not extend completely to Tree 22, it appears that high concentrations to the southwest of Tree 22 are more likely than any other direction.

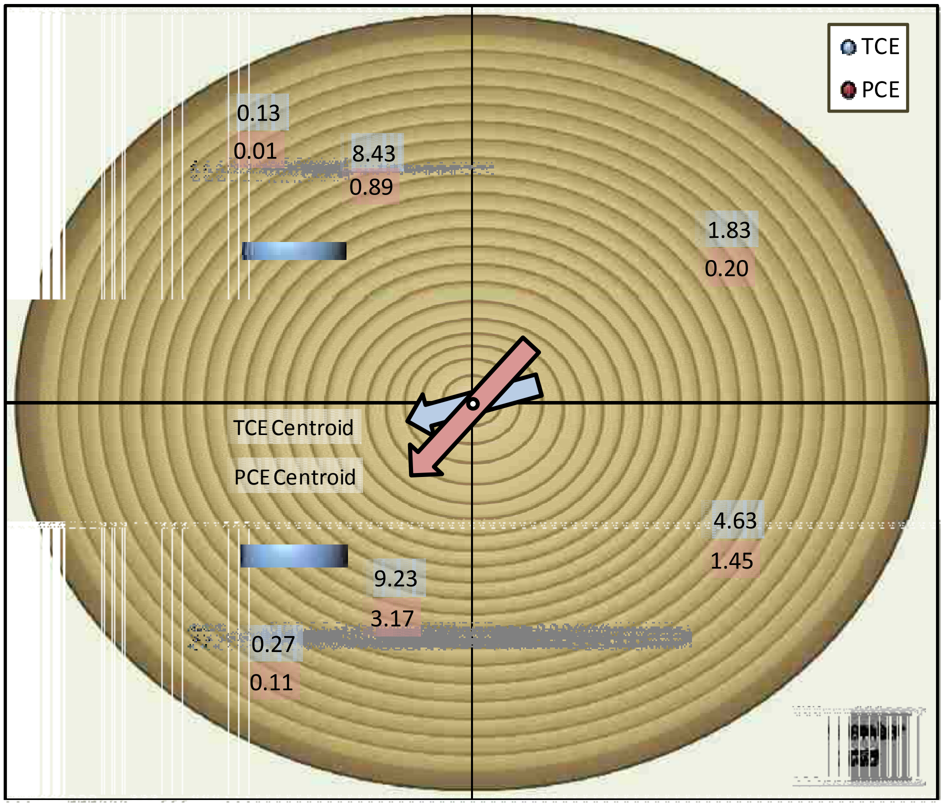


Figure 11 – Tree Core Concentrations (ppb) in Tree 22 at Borden Site (Sept 2009)

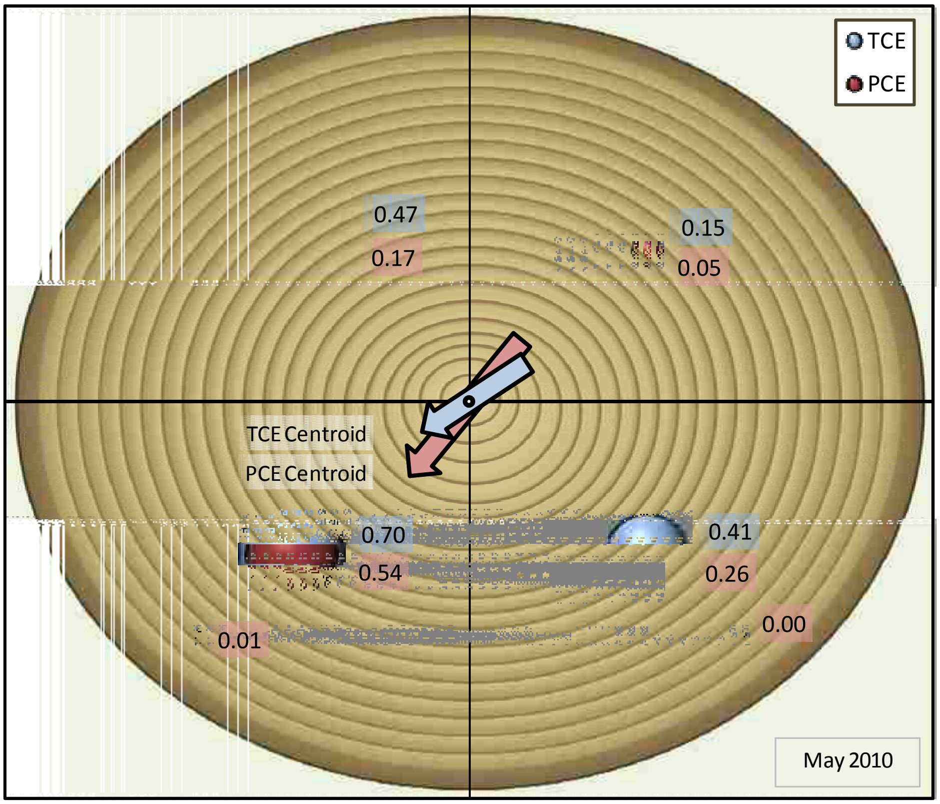


Figure 12 – Tree Core Concentrations (ppb) in Tree 22 at Borden Site (May 2010)

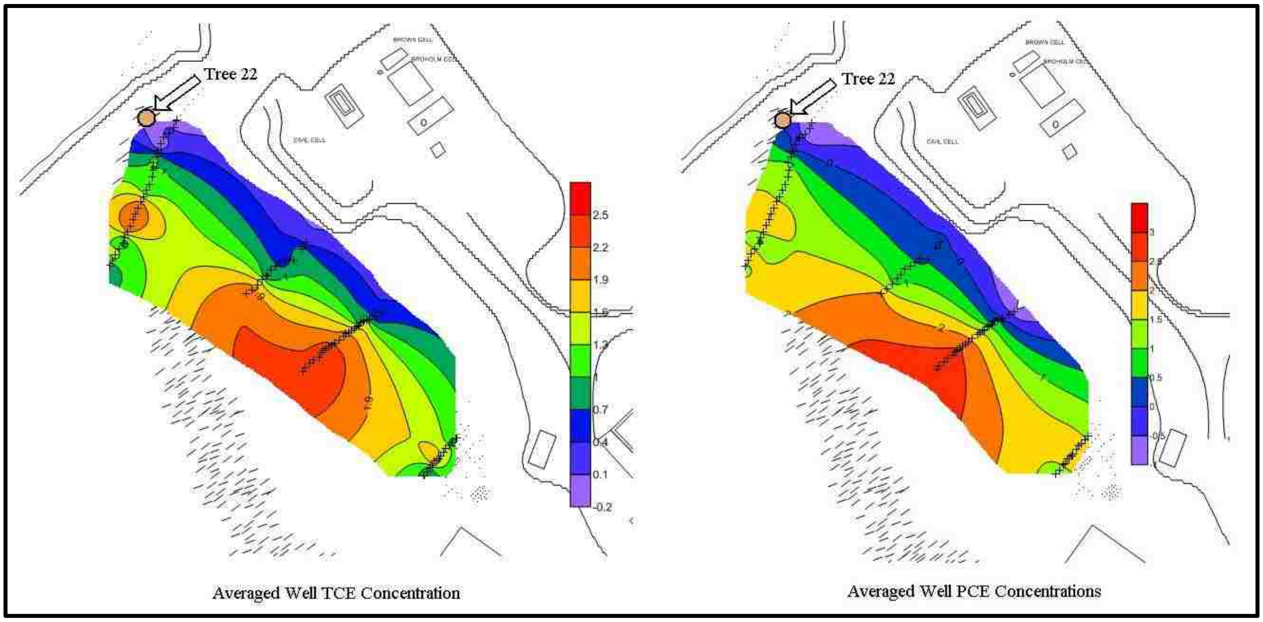


Figure 13 – Borden Site Plumes Showing Tree 22

Data from both trips have similar PCE and TCE centroids, despite differences in absolute concentrations between the two trips. Variations in plant PCE and TCE concentrations have been shown to vary seasonally [26] and be affected by recent rainfall [9], which is likely reflected by these data. However, the robustness of the directional data is evident, making directional tree coring a valuable site assessment tool. Such a tool can be used to provide compass-like information, pointing phytoscreening investigators towards more concentrated regions of the plume.

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SECTION

4 CONCLUSIONS

This evidence of directional uptake is a promising tool for future investigations. In the greenhouse and in the field, directional patterns of subsurface contamination were observed in tree cross-sections. This was observed for a number of methods, including tree coring, solid phase samplers, and destructive sampling. Sampling large trees on multiple sides increases directional resolution, without the need for coring additional trees. This helps to eliminate noise created by tree-based variables such as transpiration rate and type of wood. Directional tree coring is likely to become a useful phytoforensic tool for rapid plume delineation.

5 RECOMMENDATIONS FOR FUTURE WORK

5.1 DIRECTIONAL SAMPLING

Modeling directional transport in trees will be helpful to gain additional fundamental understanding of the process and sensitive variables. Two critical variables, diameter and tree species are expected to affect directional transport, but are difficult to easily reproduce in the lab or field. As the tree decreases in diameter, non-axial transport becomes more important, because distances are smaller and sampling precision is independent of tree size. Tree species affects the wood structure, thereby altering contaminant diffusivities. These can be measured much more easily than directional uptake and are much more useful to the general phyto community. However, developing such a model is not trivial, as the three-dimensional advection-diffusion equation must be solved. An approach is detailed in APPENDIX C.

An area of future research relevant to field tree coring is determining wood-water and/or wood-air partitioning coefficients for a number of tree species. These data are critical when correcting for sample depletion in the vial. Currently, all trees are assumed to have the same partitioning. In addition, variations in partitioning with depth should be investigated, as heartwood likely has very different partitioning than sapwood. One suggested experiment would be to take a long cross-section of a trunk and split it into small segments (see Figure 5.1).

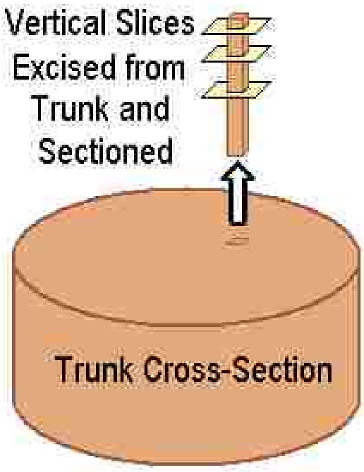

Figure 5.1 – Removing Wood Samples for Prospective Partitioning Experiment

Multiple vertical slices could be excised and placed in a chamber containing PCE and TCE. Following equilibration, the portioning coefficient could be determined using the methodology of Legind et al. [60].

5.2 PHYTOFORENSICS

The used of solid polymer samplers (SPSs) *in-planta* is promising, but additional parameters should be determined to ensure robust data collection. SPS equilibration time should be determined at field-relevant temperatures. In addition, partitioning coefficients are temperature dependent and should be corrected for temperature at the time of removal. This is particularly important for long-term sampling applications.

SPS materials should be selected for BTEX compounds. BTEX have properties similar to many chlorinated solvents, so appropriate materials may be similar to ones selected for chlorinated solvents. One concern for BTEX compounds is aerobic degradation of the compounds. A biofilm may develop on the surface of the SPS, degrading BTEX prior to analysis. One approach may be ultra-smooth tubing intended to prevent microbial growth. Another option is integrating or coating the SPS with an anti-microbial material, such as copper.

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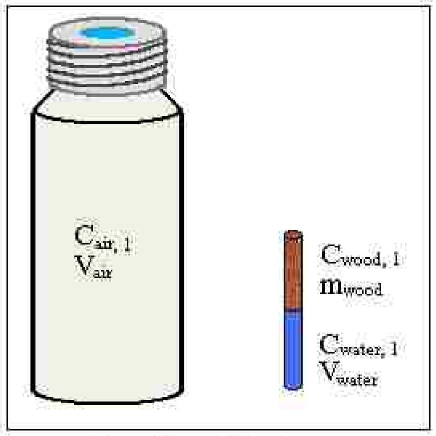
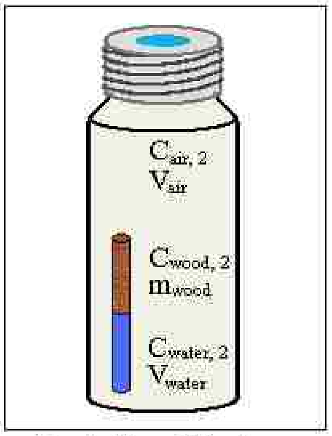
APPENDIX A

EFFECT OF TREE CORE MASS

Previous studies in the area of phytomonitoring have reported concentrations of contaminant in tree cores relative to the sample mass. To develop a more meaningful measurement of core concentration, it is desirable to determine the concentration in the xylem water. This does require a calculation of the loss of contaminant mass to the headspace. The problem is a simple mass balance, shown in the below figure and following equations, where the core is considered to be composed of a mass of dry wood mass and a volume of water (to match typical units).



Pre-Equilibrium



Post-Equilibrium

Terms used in Partitioning Model

$$C_{air,1} \cdot V_{air} + C_{wood,1} \cdot m_{wood} + C_{water,1} \cdot V_{water} = C_{air,2} \cdot V_{air} + C_{wood,2} \cdot m_{wood} + C_{water,2} \cdot V_{water}$$

It is assumed that the initial concentration of contaminant in the vial is negligible, allowing that term to be neglected. It is also assumed that negligible loss of water occurs (due to humidification of headspace air) as well as negligible fluctuations in vial air pressure. Using Henry's constant for air-water partitioning, the wood-water partitioning value, K_{lw}, and the densities of water and wet wood, the resulting change in water concentration due to headspace partitioning can be calculated using the following equation.

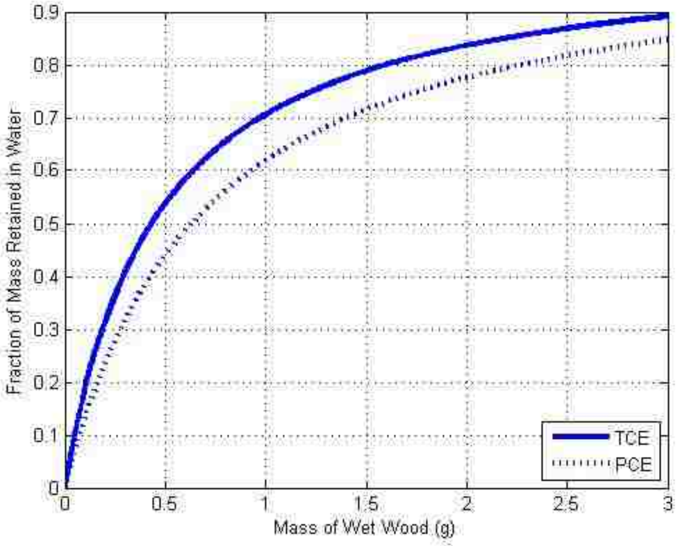
$$\frac{C_{water,2}}{C_{water,1}} = \frac{m_{wood} + \frac{m_{water}}{\rho_{water} \cdot K_{lw}}}{m_{wood} + \frac{m_{water}}{\rho_{water} \cdot K_{lw}} + \frac{K_H \cdot V_{air}}{K_{lw}}}$$

In this equation, the mass of water in the core and the dry weight of the core were measured using a Metler Toledo XS 205 Dual Range Balance, operated at a resolution of 0.01 mg. The density of wet wood was used to calculate the volume of air in the vial. The constants used in the calculation are shown in the below table. Note that the wood-water partitioning value was determined for Poplar trees, and likely varies for other tree species.

Constants Used in Calculations

Contaminant	**ρ_{water}**	**$\rho_{wood, wet}$**	**$K_{H\ (28.5°C)}$ (v/v) [23]**	**K_{lw} (g/L)**
TCE	1,000 g/L	850 g/L	0.437	0.0385 [62]
PCE			0.852	0.051 [18]

Plotting the above equation for a range of sample masses shows the importance of a sufficient sample size. While concentrations found in small sample sizes can be compensated in theory, any error in the partitioning values is amplified. It is therefore advisable to obtain a mass of a tree core exceeding the steeply sloped region of the curve (i.e., 1 g.).



Effect of Sample Mass of Measured Concentration

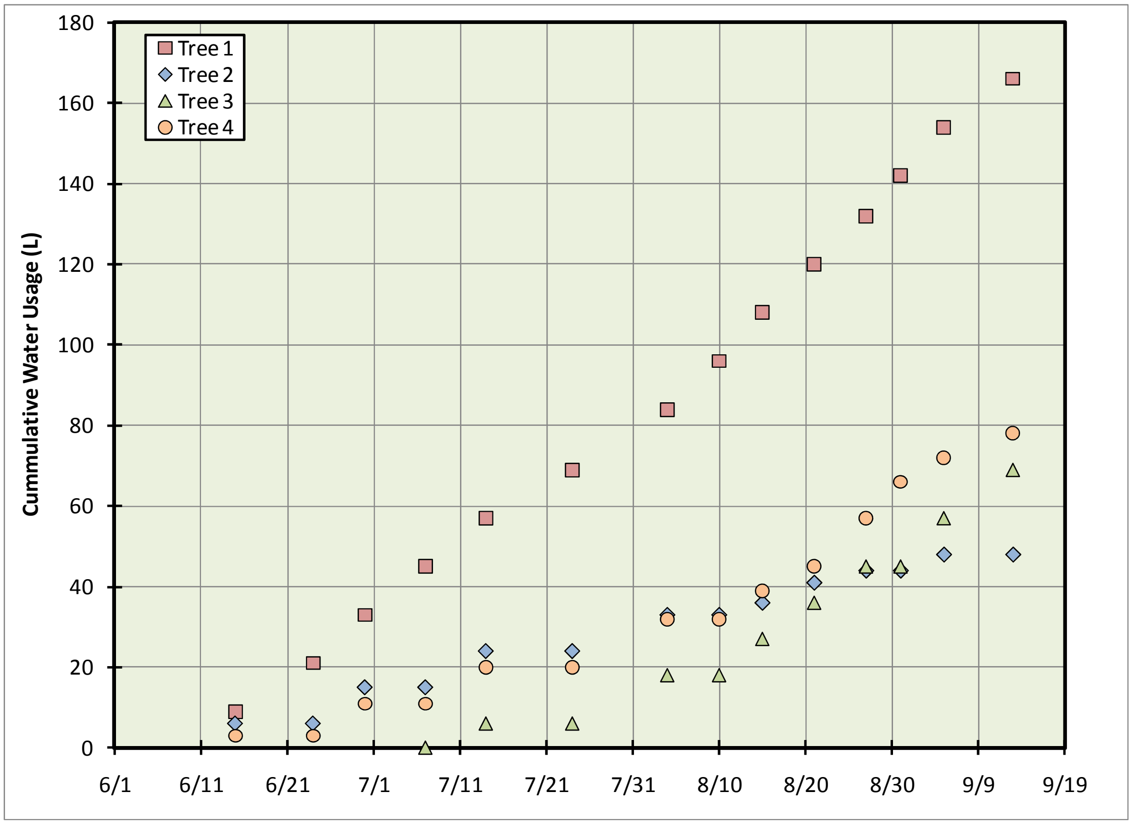
MATLAB Code

```
%~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
% Matt Limmer
% Partitioning in vial calculations
% 6/3/10
%~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

clear
clc
%% Three Compartment Model

%Constants
rho_wood=850; %density of wet wood g/L
rho_water=1000; %g/L
Vvial=20/1000; %L

%water to dry wood ratio
ratio=.5;
mwoodwet=0:.01:3; %g
mwater=mwoodwet*ratio;
mwood=mwoodwet-mwater;

%PCE
Kww=.051; %L/g
Kh=0.852; %at 28.5 deg C

Vair=Vvial-mwoodwet/rho_wood;

A=mwood+mwater/(rho_water*Kww);
```

```
B=mwood+Kh*Vair/Kww+mwater/(Kww*rho_water);

Cwood_frac=A./B;

figure('Name','3 Compartment Model')
hold on
plot(mwoodwet,Cwood_frac,'-k', 'LineWidth', 1.5)
xlabel('Mass of Wet Wood (g)')
ylabel('Fraction of Mass Retained in Water')

%TCE
Kww=.0385; %L/g
Kh=.437; %at 28.5 deg C

A=mwood+mwater/(rho_water*Kww);
B=mwood+Kh*Vair/Kww+mwater/(Kww*rho_water);

Cwood_frac=A./B;

plot(mwoodwet,Cwood_frac, '--k', 'LineWidth', 3)

%cDCE
logKow=1.86;
Kww=10^(-.28+0.668*logKow);
Kww=Kww/1000; %L/g
Kh=0.166; %at 28.5 deg C

A=mwood+mwater/(rho_water*Kww);
B=mwood+Kh*Vair/Kww+mwater/(Kww*rho_water);

Cwood_frac=A./B;

hold on
plot(mwoodwet,Cwood_frac, ':k', 'LineWidth', 3)
legend('PCE', 'TCE', 'cDCE', 'Location', 'SouthEast')
grid on
%
```

APPENDIX B

TREE WATER USE



Cumulative Water Usage of Trees

APPENDIX C

MODELLING APPROACH

To model the system, the tree was considered a cylinder of uniform diameter. Beginning with the three-dimensional advection-diffusion equation in radial coordinates [61]:

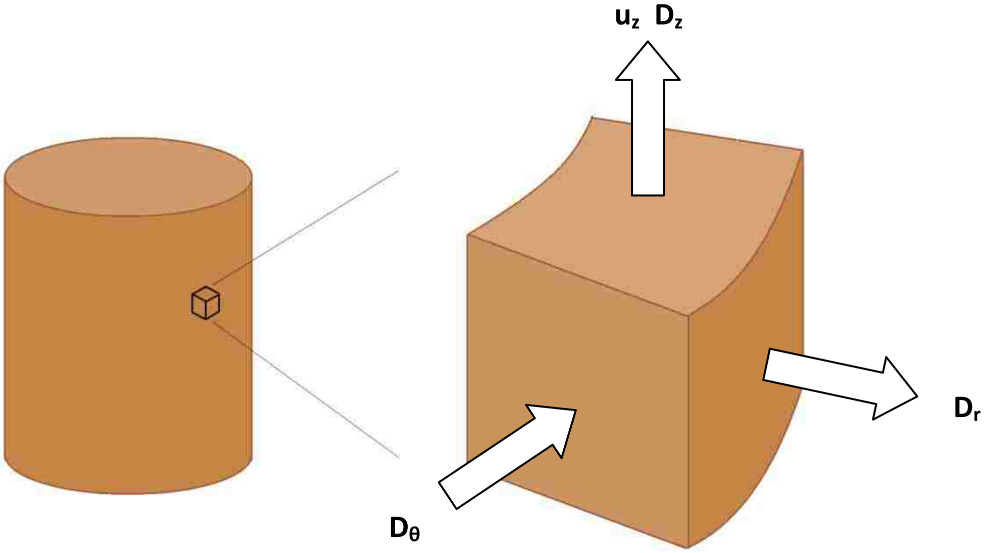
$$\frac{\partial C}{\partial t} + \left[u_r \frac{\partial C}{\partial r} + u_\theta \frac{1}{r}\frac{\partial C}{\partial \theta} + u_z \frac{\partial C}{\partial z}\right] = \left[D_r \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + D_\theta \frac{1}{r^2}\frac{\partial^2 C}{\partial \theta^2} + D_z \frac{\partial^2 C}{\partial z^2}\right] + R$$

Where:
C = contaminant concentration in xylem water [mg/m^3]
u_i = contaminant velocity in i direction [m/s]
D_i = diffusivity in i direction [m^2/s]
R = reaction term

Transport of the contaminant through the tree trunk was examined at steady state, and allowed for a number of transport pathways. Axial, radial and circumferential diffusion were considered. Although diffusivities were assumed isotropic within a particular direction, they were allowed to vary between the three coordinate directions due to the morphology of the tree xylem. In the axial direction, flow is through xylem vessels or tracheids, which function as narrow pipes. In this case, the diffusivity was assumed to be the same as in water. Circumferential and radial diffusivities are taken from the literature. These diffusivities are anticipated to be species-dependent, especially in cases of varying wood morphologies. Several distinct wood morphologies exist, including ring-porous and diffuse-porous. In ring-porous species, the wood differs greatly in the radial direction, giving rise to visible rings. These rings represent regions of dense fibers, which would likely decrease diffusivity in the radial direction. In diffuse-porous woods, the structure is largely homogenous on a macro-scale. This leads one to believe that radial and circumferential diffusivities would be similar in these species.

Advective transport was considered only in the axial direction, as this is the dominant flow direction in trees. Some circumferential flow is possible through pits connecting xylem vessels, but this path involves additional fluid resistance. It is thought to be used only in cases where air embolisms block the less restrictive axial path. Axial flow rates and distributions were taken from literature.

For the contaminants investigated in this model, very little degradation has been observed in tree species. The limited amount of reactions that do occur are likely enzymatic, occurring only in living cells. With the exception of the phloem tissue, a tree trunk consists of mostly dead cells. Therefore, any degradation was neglected. The below figure illustrates the transport phenomenon considered.



Tree unit element illustrating advective and diffusive fluxes

The general advection-diffusion equation then reduces to the following:

$$u_z \frac{\partial C}{\partial z} = D_r \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + D_\theta \frac{1}{r^2}\frac{\partial^2 C}{\partial \theta^2} + D_z \frac{\partial^2 C}{\partial z^2}$$

To solve this equation, six boundary conditions were required. At the outside edge of the trunk, *R*, the concentration was assumed to be zero, due to volatilization and subsequent dilution to ambient.

$$C(r = R, \theta, z) = 0$$

Losses to the atmosphere in this "leaky pipe" type problem result in the concentration approaching zero at infinite axial distance.

$$C(r, \theta, z = \infty) = 0$$

Another boundary condition is at the base of the tree, where the input concentration is known. This input concentration was non-uniform across the cross-section, in an effort to study directional uptake of contaminants. The below figure shows the concentration at the base of the tree, assumed constant. This figure also shows the anticipated water velocity, which was considered parabolic in this model.

$$C(r, \theta, z = 0) = \text{Given}$$

The contaminant shape facilitates symmetric boundary conditions:

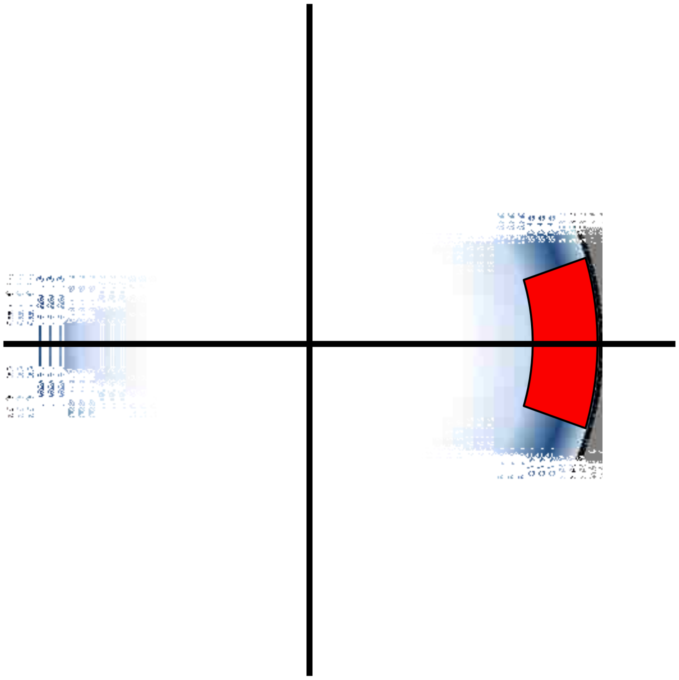
$$\left.\frac{\partial C(r, \theta, z)}{\partial \theta}\right]_{\theta = 0} = 0$$

$$\left.\frac{\partial C(r,\theta,z)}{\partial \theta}\right]_{\theta=\pi} = 0$$

The input contaminant shape is also centered radially on the area of greatest water flux. This yields another boundary condition:

$$\left.\frac{\partial C(r,\theta,z)}{\partial \theta}\right]_{r=R} = 0$$

Where: R = radius of greatest water flux



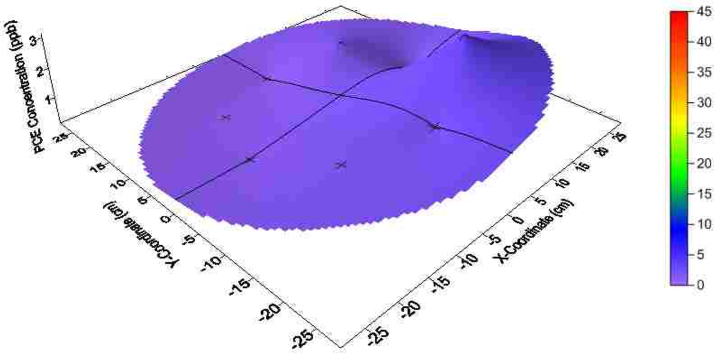
Water velocity profile (in blue) showing concentration boundary condition at base of tree

Such a model does not lend itself to an analytical solution and must be solved numerically.

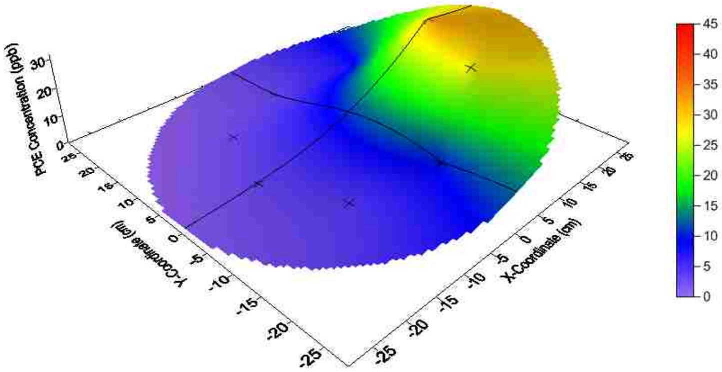
APPENDIX D

ADDITIONAL DIRECTIONAL TREE PLOTS

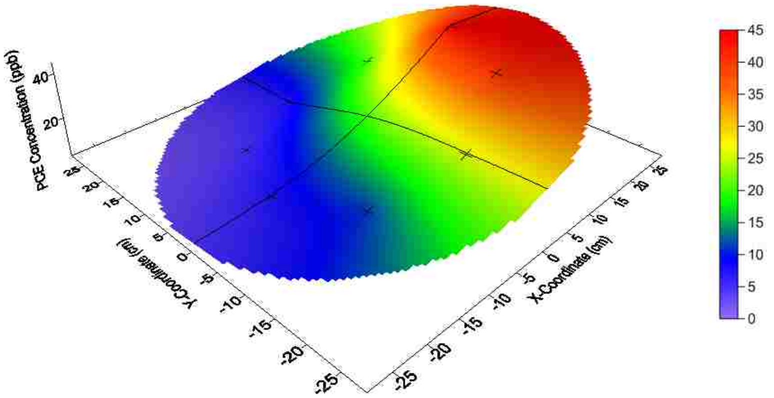
Tree B1 Soil PCE Profiles



1 cm below ground surface

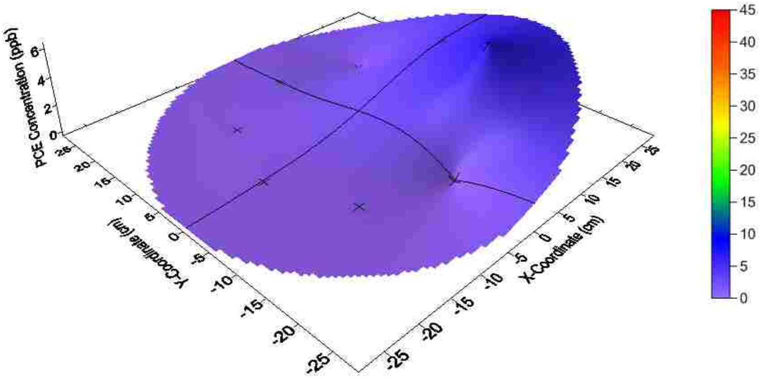


15 cm below ground surface

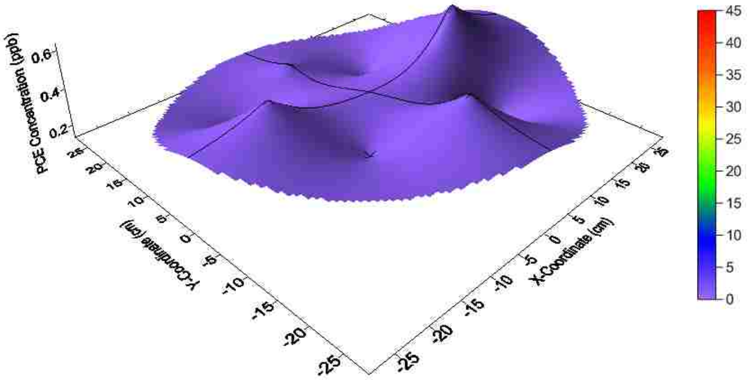


30 cm below ground surface

45 cm below ground surface

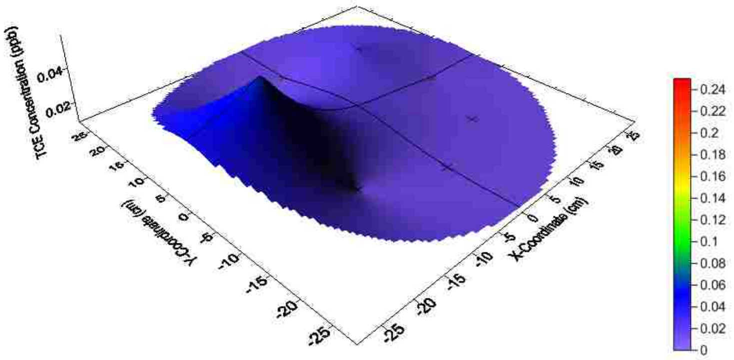


60 cm below ground surface

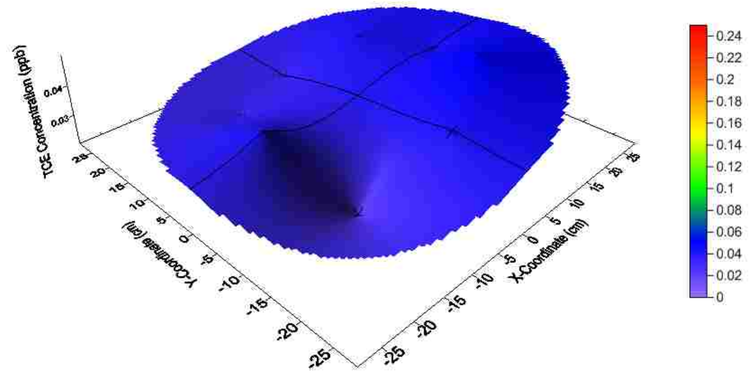


Tree B1 Soil TCE Profiles

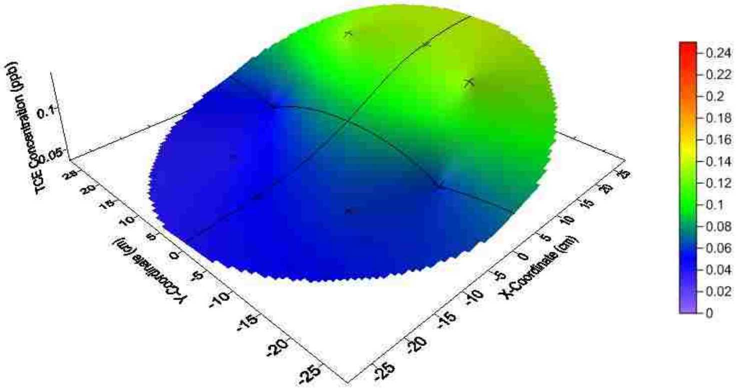
1 cm below ground surface



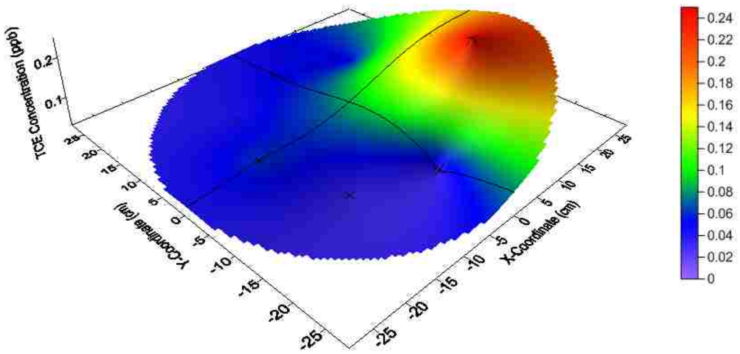
15 cm below
ground surface



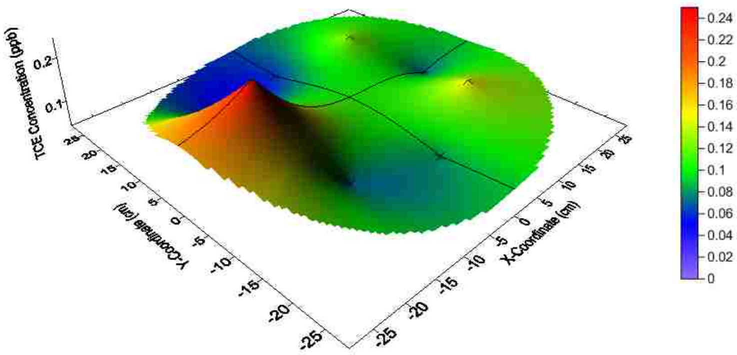
30 cm below
ground surface



45 cm below
ground surface

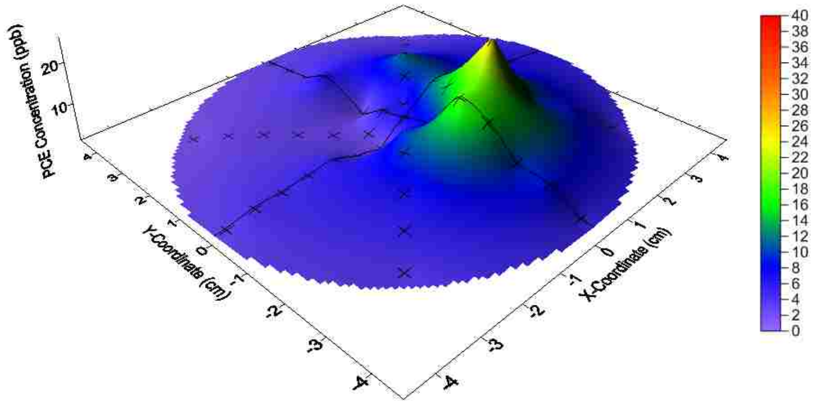


60 cm below
ground surface

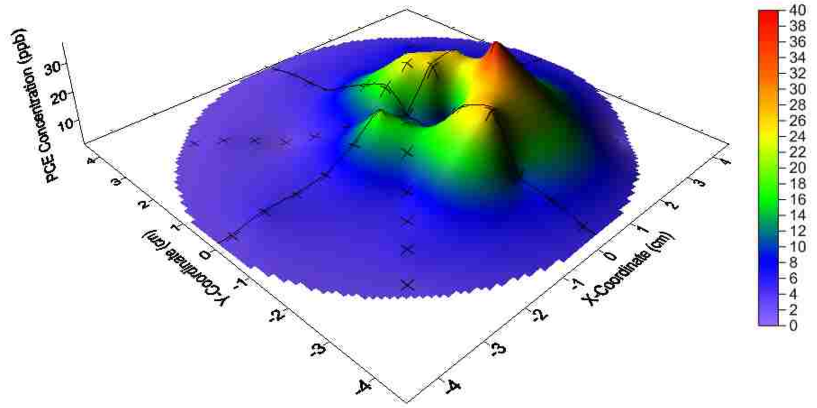


Tree B1 PCE Profile

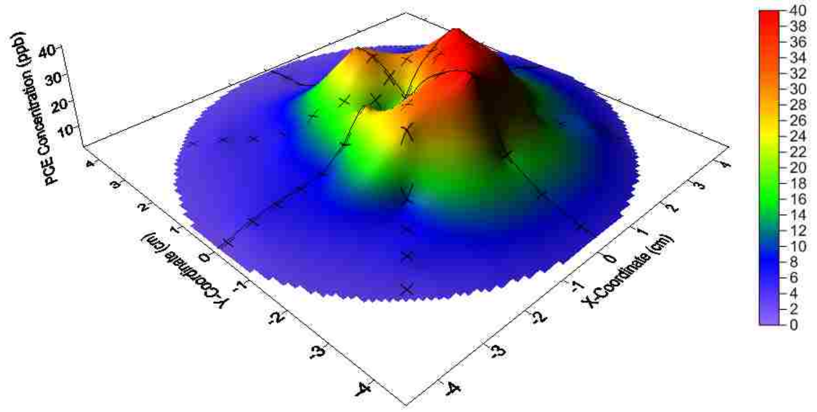
45 cm above
ground surface



30 cm above
ground surface

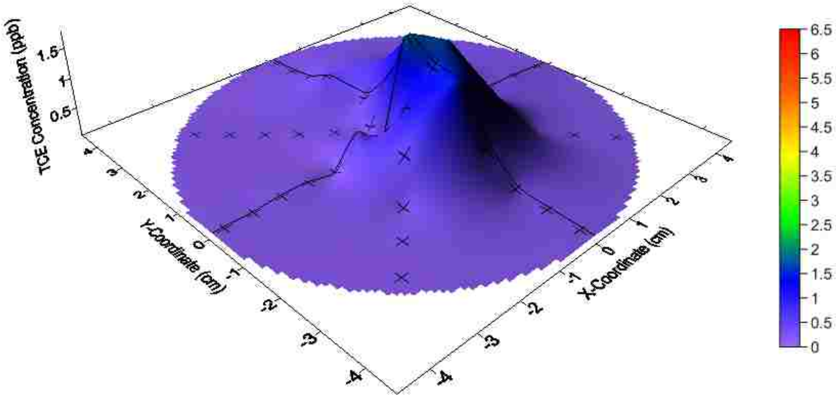


15 cm above
ground surface

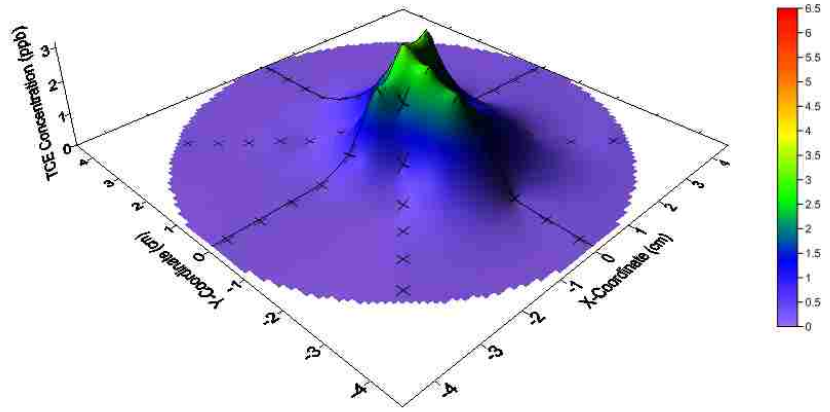


Tree B1 TCE Profile

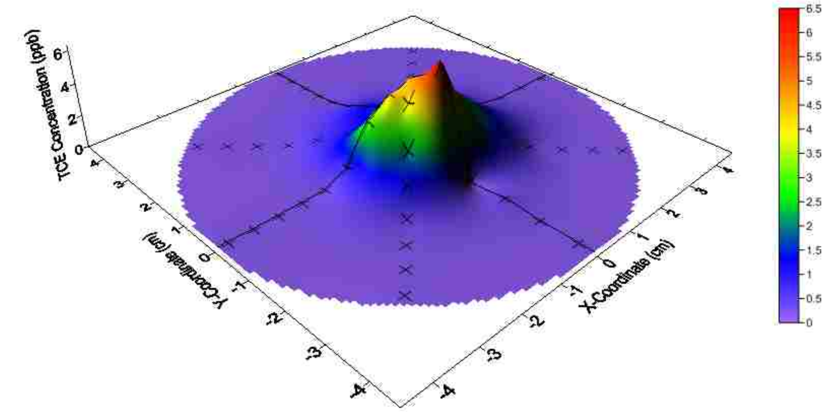
45 cm above
ground surface



30 cm above
ground surface

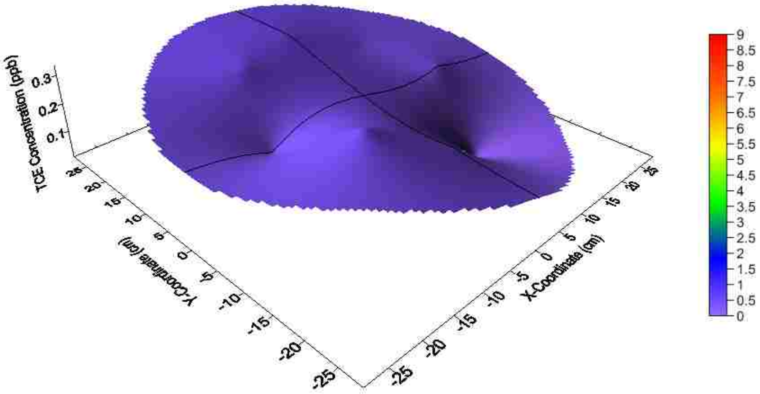


15 cm above
ground surface

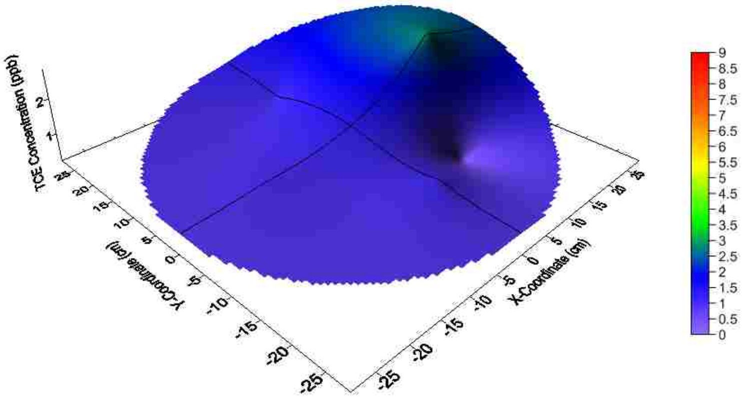


Tree B3 Soil TCE Profiles

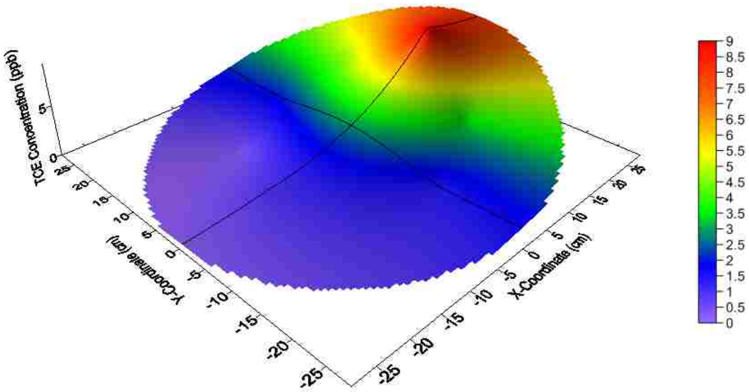
1 cm below ground surface



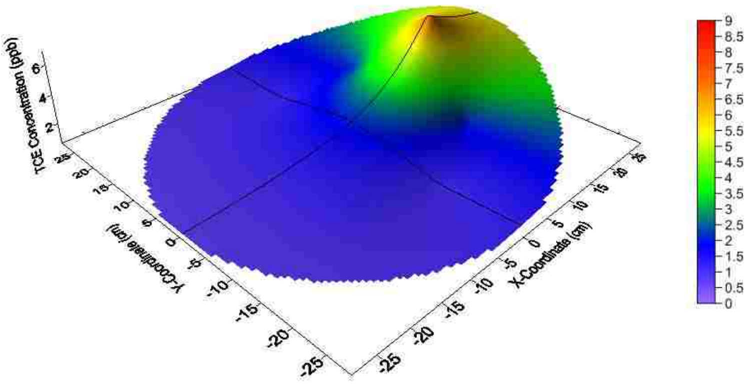
15 cm below ground surface



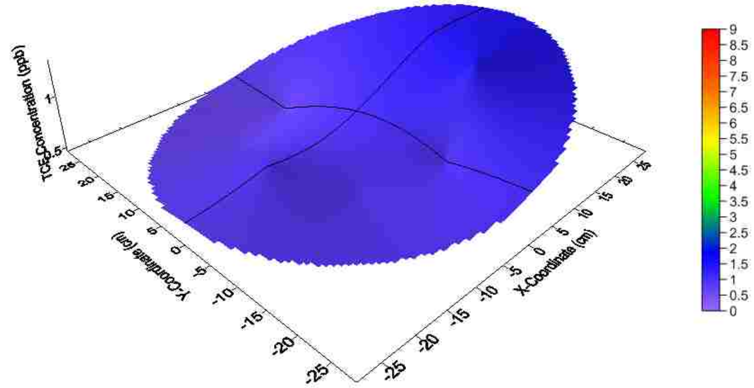
30 cm below ground surface



45 cm below
ground surface

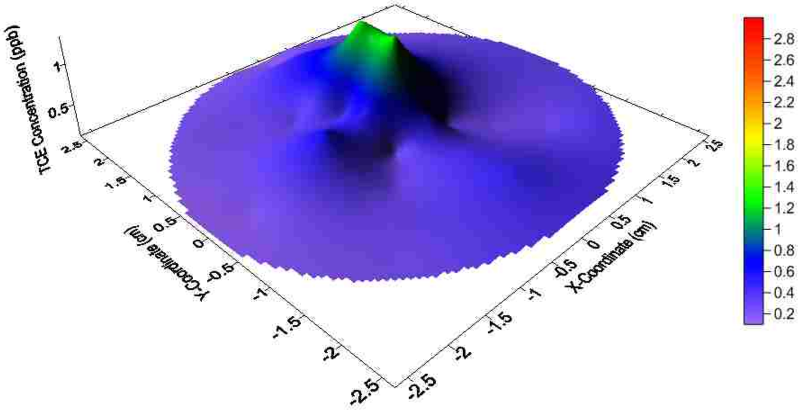


60 cm below
ground surface

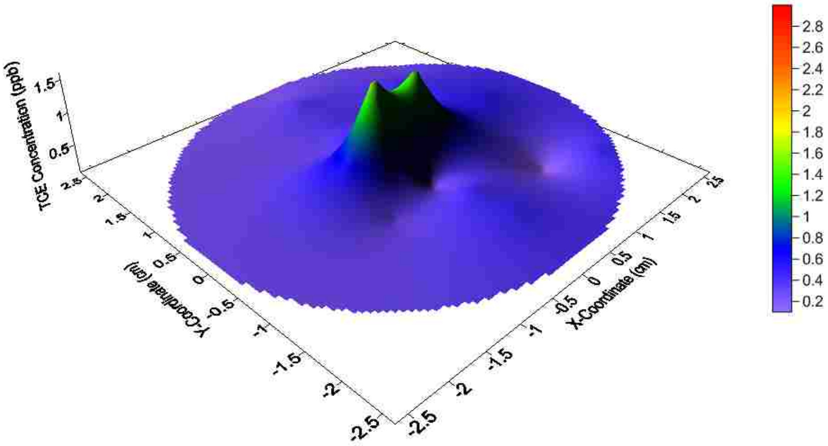


Tree B3 TCE Profiles

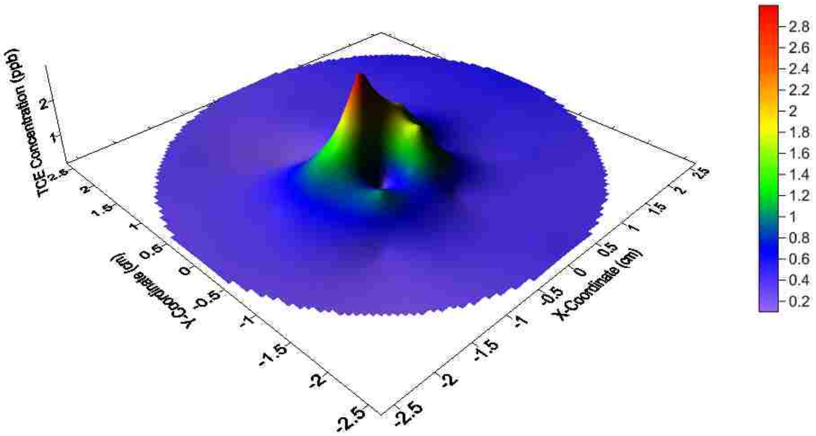
45 cm above
ground surface



30 cm above
ground surface

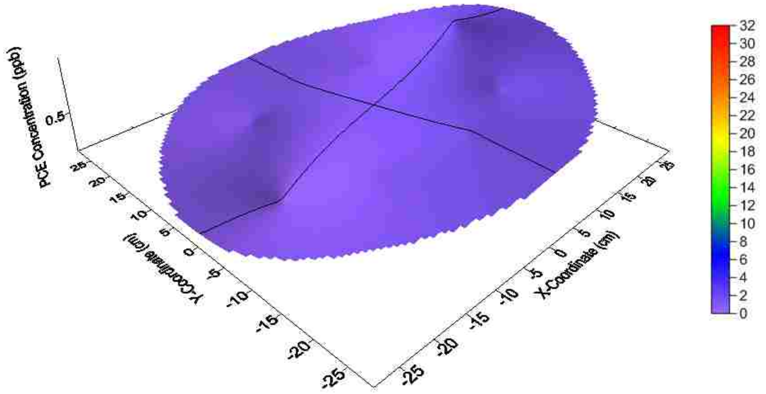


15 cm above
ground surface

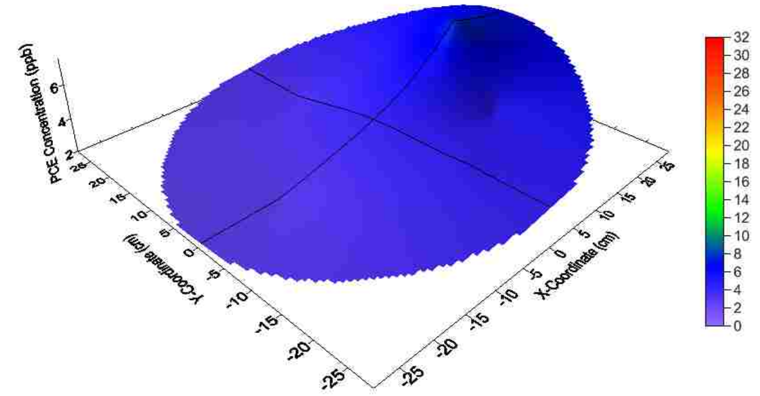


Tree B4 Soil PCE Profile

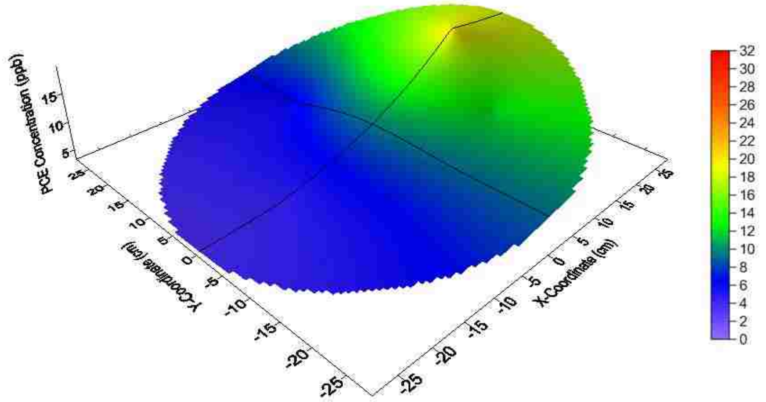
1 cm below ground surface



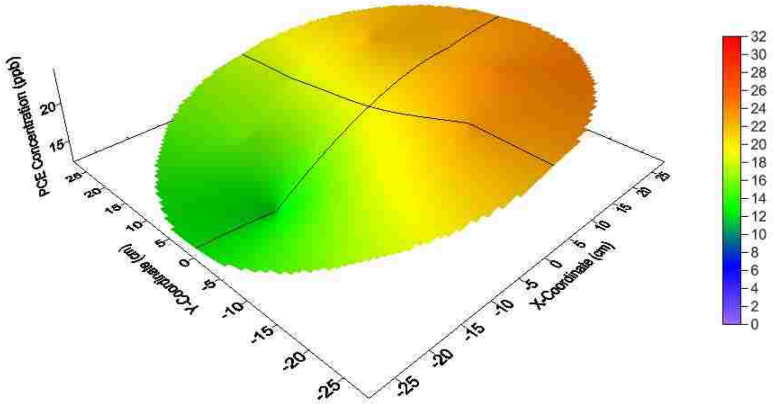
15 cm below ground surface



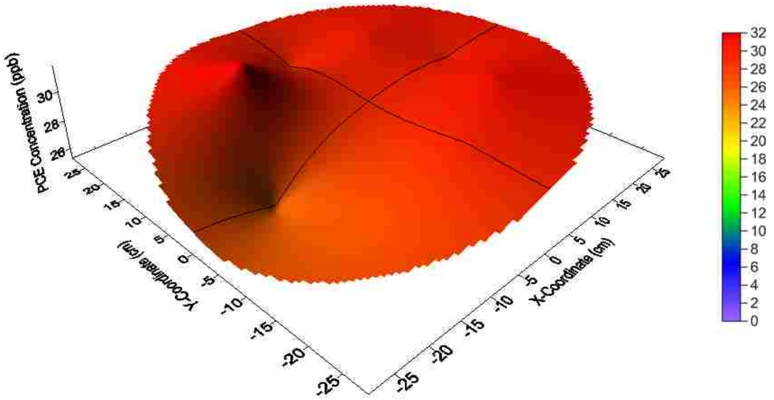
30 cm below ground surface



45 cm below ground surface

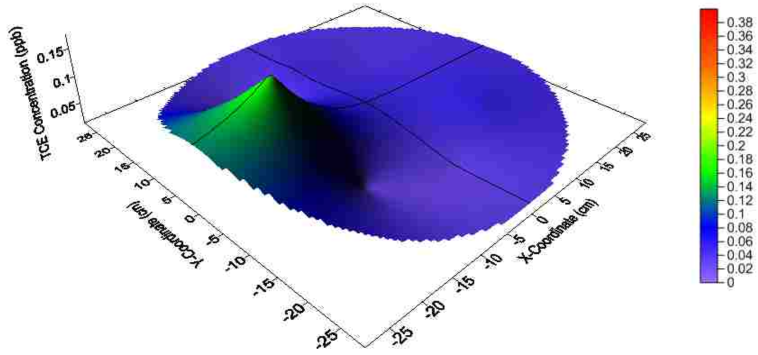


60 cm below ground surface

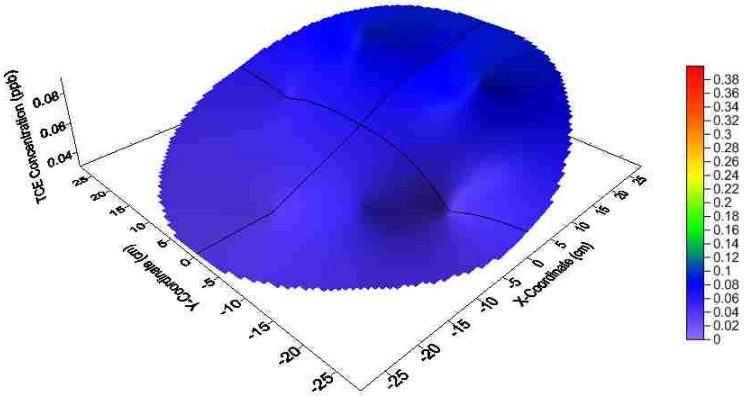


Tree B4 Soil TCE Profiles

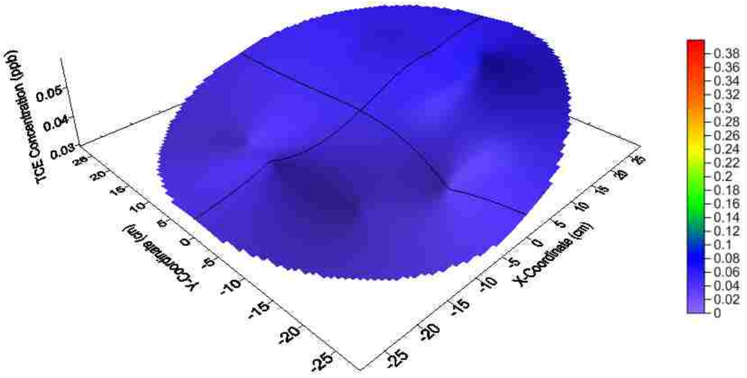
1 cm below ground surface



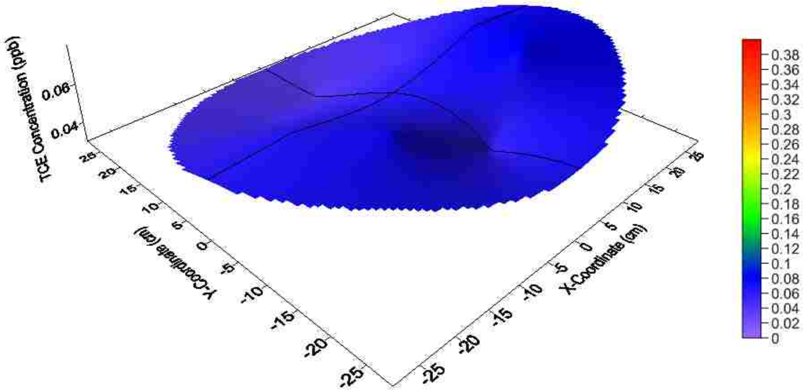
15 cm below
ground surface



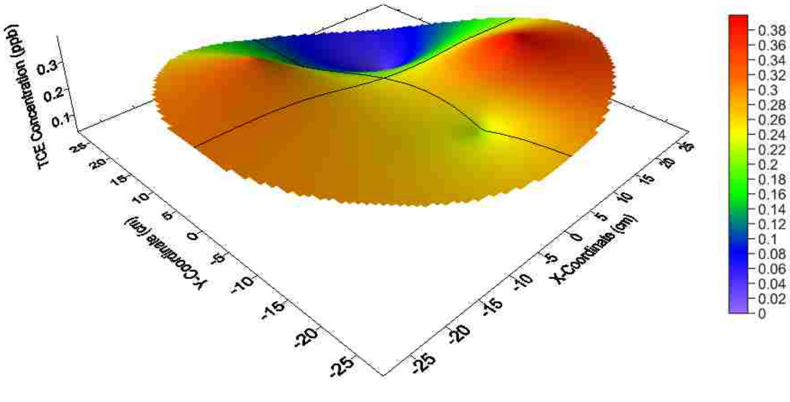
30 cm below
ground surface



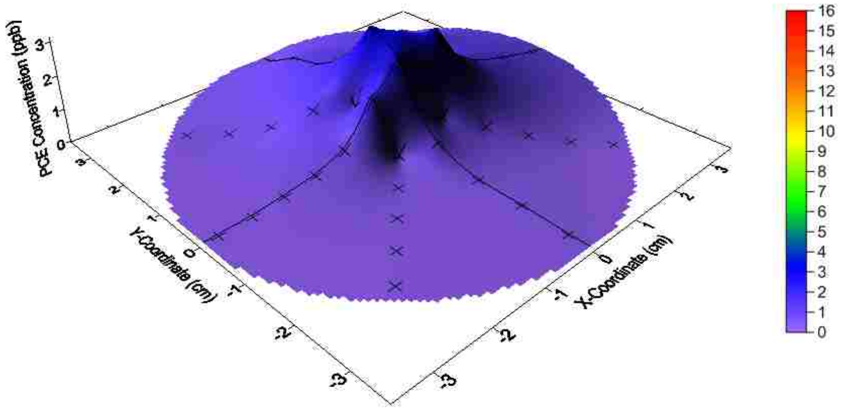
45 cm below
ground surface



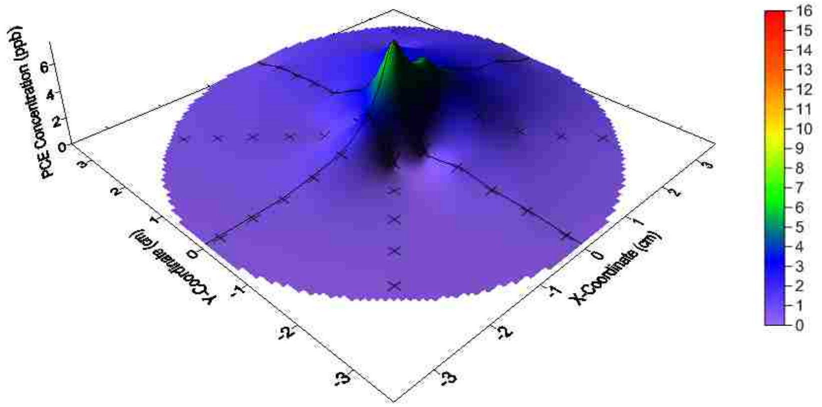
60 cm below
ground surface



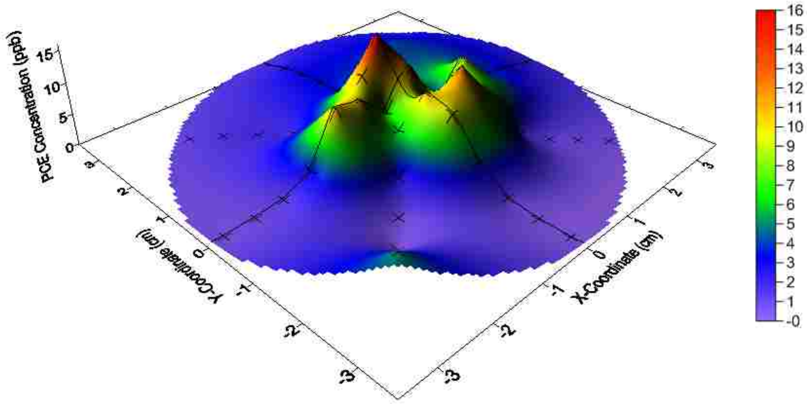
Tree B4 PCE Profiles



45 cm above
ground surface



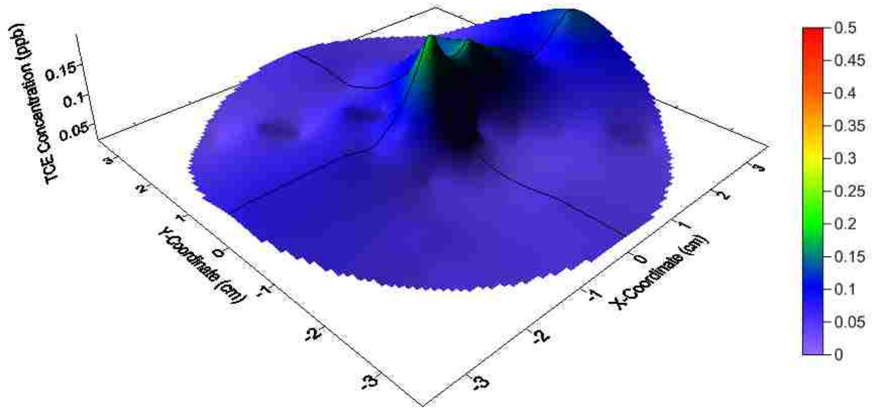
30 cm above
ground surface



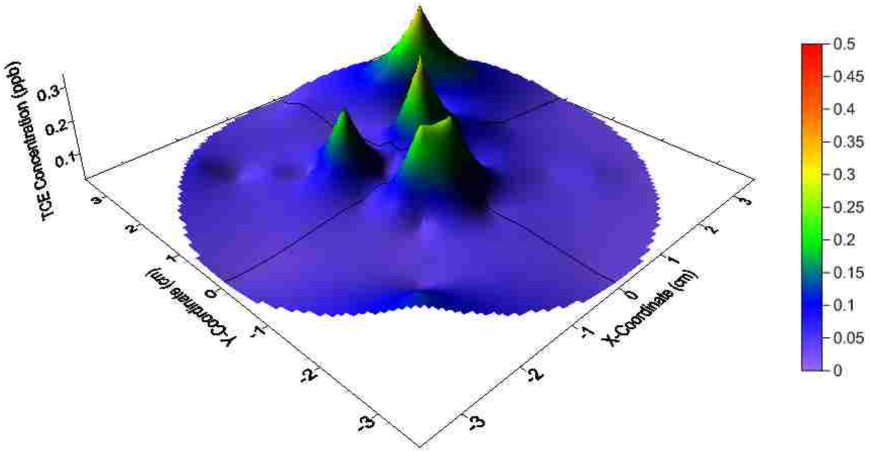
15 cm above
ground surface

Tree B4 TCE Profiles

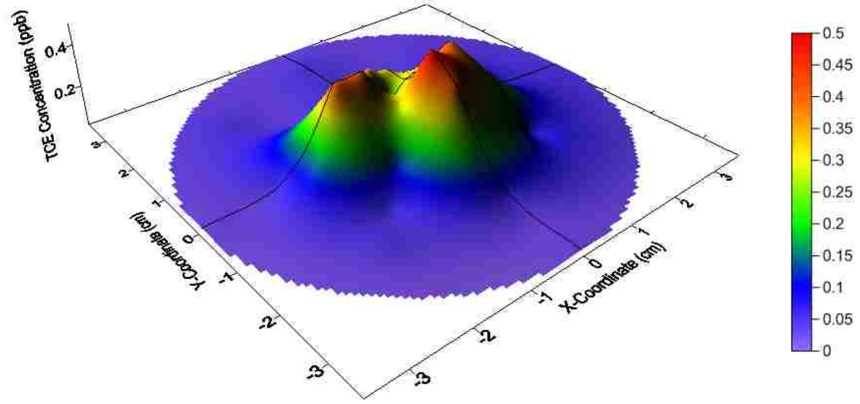
45 cm above
ground surface



30 cm above
ground surface

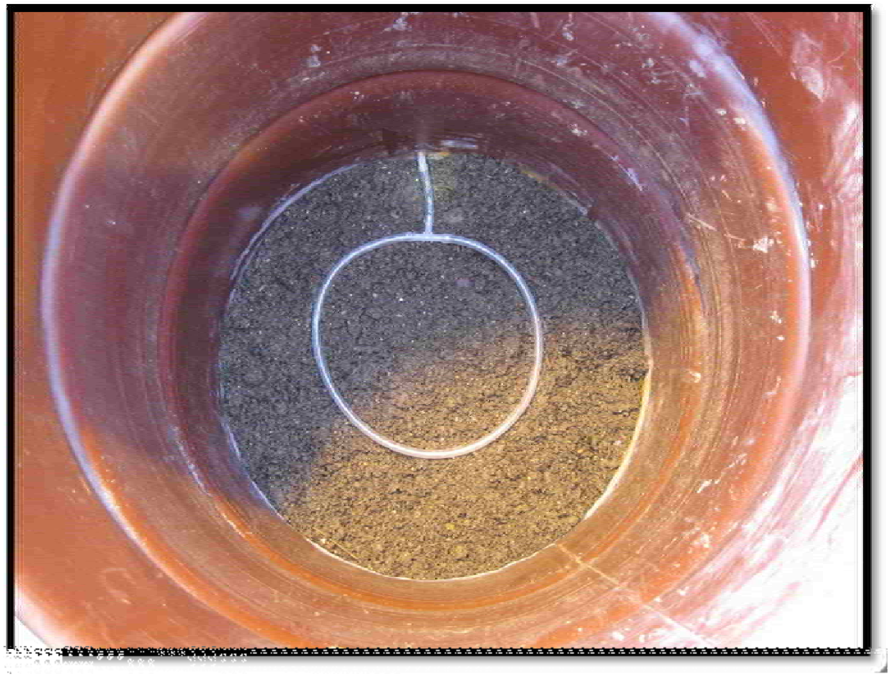


15 cm above
ground surface



APPENDIX E

EXPERIMENTAL PHOTOS



200-L reactor showing water distribution ring

200-L reactor showing 40-SPSs placed in subsurface

Willow trees growing in 200-L reactors

200-L reactor showing 20-L water reservoir

VITA

Matthew Alan Limmer was born and raised in Oregon, Ohio. He graduated from Clay High in 2004. During high school, he worked at the Woodville Road Nursery and the Stone Yard. He graduated from The Ohio State University in June 2009 with a Bachelor of Science in Mechanical Engineering and a minor in Horticulture. During undergrad, he was a four-year undergraduate teaching assistant for the First Year Engineering Honors program. He also worked internships at the Scotts Miracle-Gro Company, H.J. Heinz and Owens Corning. He received a Master of Science degree in Environmental Engineering in May 2011 from the Missouri University of Science and Technology, where he will also pursue a Ph.D.