Fall 2017

Phytoforensics: Applications in vapor intrusion assessment

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Recommended Citation

Wilson, Jordan Lee, "Phytoforensics: Applications in vapor intrusion assessment" (2017). *Doctoral Dissertations*. 2696.
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PHYTOFORENSICS: APPLICATIONS IN VAPOR INTRUSION ASSESSMENT

by

JORDAN LEE WILSON

A DISSERTATION

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

CIVIL ENGINEERING

2017

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PUBLICATION DISSERTATION OPTION

This dissertation consists of the following three articles which have been submitted for publication, or have been accepted for publication, as follows and have been formatted in the style used by each journal:

Paper I: Pages 12-49 have been published and reproduced with permission from Wilson, J.L., Limmer, M.A., Samaranayake, V.A., Schumacher, J.G., and Burken, J.G., Tree Sampling as a Method to Assess Vapor Intrusion Potential at a Site Characterized by VOC-Contaminated Groundwater and Soil. Environmental Science & Technology 2017, DOI: 10.1021/acs.est.7b02667. Copyright 2017 American Chemical Society.

Paper II: Pages 50-73 have been submitted for publication to Environmental Science and Technology for publication. Wilson, J.L., Samaranayake, V.A., Limmer, M.A., and Burken, J.G., Contaminant Gradients in Trees: Directional Tree Coring Reveals Boundaries of Soil and Soil-Gas Contamination with Potential Applications in Vapor Intrusion Assessment. Submitted July 08, 2017. Currently in review.

Paper III: Pages 74-110 have been submitted for publication to Public Library of Science ONE. Wilson, J.L., Limmer, M.A., Samaranayake, V.A., Burken, J.G., Phytoforensics: trees as bioindicators of potential indoor exposure via vapor intrusion. Submitted August 31, 2017. Currently in review.

ABSTRACT

Vapor intrusion (VI) occurs when contaminants in the vapor phase migrate in the shallow subsurface and enter buildings through cracks, seams, and gaps and has been recognized as a serious human-health threat as occupants are exposed to potentially harmful concentrations over long periods of time. The VI pathway has recently (2017) been identified as a primary exposure pathway and implemented into the Hazard Ranking System for inclusion on the Nation Priorities List. However, assessing VI and human exposure is not simple and current methods are time-, cost-, and labor-intensive; intrusive; and temporally and spatially variability. Trees are ideal candidates for environmental biomonitors because they are ubiquitous, active samplers of vapor and groundwater and because they are thought to sample over large spatial and temporal scales, effectively averaging variability. Sampling trees is noninvasive and does not require the construction of sampling ports in homes, increasing the likelihood of obtaining property access and VI data. Tree samples are representative of the shallow subsurface with a footprint similar to a residential building. Directional tree sampling can also be used to elucidate shallow subsurface contamination from a single tree, and tree sampling is shown to be correlated with VI samples, especially when environmental samples are averaged over months and years. However, non-uniform distributions of tree-core samples likely resulted in large interpolation error in areas where trees are sparse. Although these findings demonstrate that tree sampling can augment traditional VI assessment methods, tree sampling is best applied as a screening tool because of the many parameters, and their associate uncertainties, that control mass transfer of contaminants in the subsurface and entry into plants and the built environment.

ACKNOWLEDGMENTS

Foremost, I would like to express my sincere gratitude to my advisor, Joel Burken, for his unending support and for encouraging me throughout my academic career. I hope to emulate the leadership and mentoring qualities that he has shown.

I would like to thank Matt Limmer for providing valuable feedback all the way back in time to when I first started at Missouri S&T. Matt was the first person to take an interest in my learning on a personal level when I came to him with a chemistry question in Introduction to Environmental Engineering. Matt has not only been a great teacher and colleague but also a great friend.

I would like to especially thank John Schumacher for all the opportunities he has given me and for challenging me to be a better scientist, critical thinker, and leader. John has always pushed me to think of things differently and to stay grounded. I am proud to sit among the ranks of his mentees, and I do not only consider him a colleague but a good friend.

My sincere thanks go to Charlie Smith, Cory Pollpeter, Eric Fallon, and Tommy Goodwin for helping with tree-core collection and SPS deployment at Vienna, especially during some very hot summer days.

Financial support was provided by the Chancellor’s Fellowship and the National Science Foundation, which made working on this project much easier.

Finally, I would like to thank my beautiful wife, Casey Wilson, for giving me time to work on my research and for supporting me all the way to the end. I also want to thank Ender and Phoenix Wilson for bringing me daily joy to fuel this long journey.

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1. INTRODUCTION

1.1. ENVIRONMENTAL CONTAMINANTS

Our modern national and global landscape is dotted with current and legacy contamination from the 1,337 current Superfund sites in the US with 53 currently (2017) proposed[1] and about 340,000 currently identified and an estimated 2.5 million potential contaminated sites in 33 countries in Europe.[2] Many other sites undoubtedly do exist and will result around the planet from industrialization, particularly in developing countries.

Two predominant contaminant families at these sites are chlorinated solvents and hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes). The most commonly encountered chlorinated solvents, trichloroethylene (TCE) and perchloroethylene (PCE), are known carcinogens linked to birth defects [3-7] and have low MCLs of 5 µg/L in water and EPA risk-based action limits of 0.48 µg/L and 11 µg/L in air.[8, 9] Since its inception in 1983, only 392 Superfund sites have been deleted from the National Priorities List (NPL) after attaining cleanup goals. The more than 1,300 remaining NPL and unknown contaminated sites still pose an unquantified threat to human health. Of the over 1,700 proposed, current, and deleted NPL sites, more than 1,400 (more than 80%) are listed for volatile organic compound (VOC) contamination with 884, 393, and 278 sites currently (2017) listed for benzene, TCE, and PCE, respectively.[10] VOC pollutants also pose additional health threats because contamination can exist in the vapor form, be sorbed onto soil, or dissolved in water.

1.2. VAPOR INTRUSION

Vapor intrusion (VI) occurs when contaminants in the vapor phase migrate in the shallow subsurface and then enter residential or commercial buildings through cracks, seams, and gaps. Initially a concern because of radon exposure in residential homes in the 1980s, VI has been recognized as a serious human-health threat as occupants are exposed to potentially harmful concentrations over long periods of time.[11, 12] Although VI can occur in commercial, industrial, or residential settings, residential areas pose special problems as occupants spend a majority of their time in these spaces and are unknowingly exposed to concentrations of contaminants in indoor air, which have a much greater impact (up to three orders of magnitude more) on human health than outdoor sources.[13] As plumes often exist for decades before any identification, and sampling of residential homes is not carried out routinely, this exposure can be extremely prolonged.

The VI pathway has recently (2017) been implemented into the Hazard Ranking System[14] for inclusion on the NPL, allowing a site to be added to the NPL solely based on the existence of VI; therefore, screening for VI will be required at an increasing rate; however, measurement of VI is not simple and is time-, cost-, and labor-intensive. VI risk is often determined through multiple lines of evidence including a combination of indoor-air samples within structures, sub-slab or crawlspace samples underneath structure foundations, and soil-gas samples collected outside structures but near foundations (collectively known as VI samples) and through the inclusion of nearby groundwater and soil sample data.[14] VI samples are often collected as a time-integrated sample from a single location using SUMMA passive samplers over a 24-hour period or as a discrete sample over a short period of time (less than several minutes) using a pump, capturing relatively small subsurface volumes over small periods of time. VI samples collected outside structures introduce the risk of theft or disturbance of sampling equipment and require multiple utility clearances and drill-rig access, which complicate sampling and introduce large liabilities for contractors; whereas, samples collected inside structures require assess agreements from owners for personnel to enter homes and install one or more invasive sub-slab ports.[15, 16] Collectively, these methods are expensive, time and personnel intensive and invasive to the residential property. Simpler, quicker, less-invasive and more cost-effective screening methods are needed in order to effectively meet this demand, and such methods would allow for sampling of more suspected sites to preemptively protect human health.

Other substantial challenges in VI potential assessment include addressing the temporal and spatial variability present in VI samples. Most risk models assume long-term exposure to contamination, while VI samples provide “snap shots” of contamination, which are highly variable in indoor-air[15, 17, 18] and sub-slab and soil-gas samples.[15, 19-22] Characterizing site-specific variability is time- and cost-intensive as multiple sampling events are required within a year to capture seasonal differences in contaminant concentrations. In addition to temporal variability of contaminant concentrations in VI samples, contaminant concentrations also substantially vary spatially in the subsurface;[20, 23, 24] however, VI samples have a relatively small subsurface footprint but are often used to represent relatively large areas. Consequently, these temporal and spatial variabilities introduces large amounts of uncertainty in actual exposure of contaminants to occupants.[25]

1.3. TRADITIONAL VAPOR INTRUSION ASSESSMENT METHODS

In order to characterize the potential for VI, traditional sampling methods including groundwater, soil, soil-gas, sub-slab sampling, have been used as proxies for VI risk, measured by indoor-air samples, and each has associated advantages and disadvantages.

Groundwater sampling and analysis commonly play a role in VI investigations. Groundwater is sometimes already available because of previous site characterization efforts or is collected as part of the VI investigation. Depending on the local geology, groundwater samples are collected using direct-push technology or more time- and cost-intensive drilling efforts such as air-rotary drilling methods.[14] In all efforts, focus is put on characterization of contaminants at the water table, and groundwater concentrations are compared to the groundwater VISLs.[26] Because the contaminant concentration in groundwater is not directly representative of the indoor-air concentration, an attenuation factor is assumed based on site-specific geology. Groundwater concentrations are assumed to represent a potential upper-bound indoor-air concentration.[14] Groundwater concentrations tend to have smaller variability than other samples, but wells are invasive and expensive to drill, which limits installation and the spatial density of data, particularly at the early screening stages of an investigation.

Soil sampling may be used to characterize the general location of subsurface vapor sources, and is commonly conducted using direct-push drill rigs. Because of the potential for volatilization during soil sampling, preservation, and chemical analysis, the EPA does not recommend the use of soil sampling for estimating VI potential and does not publish VISLs for soil samples. Because of the existence of utilities near buildings, drilling can be difficult or impossible for logistical or safety reasons.

Soil-gas sampling is an inexpensive sampling method that is often used to identify and locate subsurface vapor sources and to assess potential preferential pathways for vapor transport. Soil-gas sampling generally consists of driving a probe into the subsurface and establishing a negative pressure, thereby evacuating the vapor in the interstitial pore space. Soil-gas samples are typically collected less than a few feet below ground surface as grab samples, rather than time-integrated samples, but equilibration times between 2 to 48 hours are recommended to allow subsurface conditions to equilibrate after the probe has been installed.[27] Samples are collected as close as possible to the building of interest. Modeling results indicate that soil-gas samples collected outside the footprint of the building tend to be smaller than directly under the building. Given these modeling results and some supporting field evidence, soil-gas concentrations from the exterior of buildings are generally not expected to accurately estimate sub-slab or indoor-air concentrations. Several rounds of soil-gas sample are recommended to develop an understanding of the temporal variability of soil-gas concentrations. The consequent repeat rounds of sampling each incur personnel and equipment mobilization costs, and costs negatively impact the frequency and amount of data collected. As with soil sampling, the existence of utilities near buildings can complicate the drilling process, making it logistically difficult to collect sample and compromising safety.

Sub-slab sampling is one of the most common VI sampling methods used to assess VI potential where soil-gas is sampled from the air space immediately below the foundation of the building. To collect sub-slab samples, sampling ports are installed on the lowest floor of the house by drilling approximately 1-inch holes through the foundation, and leak tests are conducted to ensure that an air-tight port has been established. Sub-slab samples are the most accurate sample that assesses VI potential. Currently, it is recommended to collected sub-slab samples alongside indoor-air samples to establish multiple lines of evidence for VI. When combined with other methods (e.g., groundwater or soil-gas), sub-slab samples can be used to assess whether the VI pathway is complete (i.e., contaminant vapor are capable of being transported from the source into the building). Using an attenuation factor, contaminant concentrations in sub-slab samples can be used to estimate indoor-air concentrations and the potential for VI. Although sub-slab samples are the most representative sample for VI potential, substantial variability in concentration both spatially and temporally is frequently encountered; [15, 19-22] therefore, EPA recommends multiple samples in space and time to accurately characterize VI potential.[14] Also, this method is highly invasive to the property owner, making it difficult to acquire permission from building owners to install sub-slab ports, and takes between one to three days per house to install the port. The entry and sampling can certainly cause elevated concern and anxiety by the homeowner. The cost, invasive nature, and unsettling nature of sub-slab sampling often result in delayed use of sub-slab sampling as a screening tool, and thereby prolonging potential exposure. As with soil and soil-gas sampling, because of the existence of utilities under buildings, drilling can be difficult or impossible for logistical or safety reasons.

Indoor-air sampling is the only VI sampling method that truly measures VI exposure; however, several issues commonly confound the exclusive use of indoor-air samples to complete the VI pathway. Indoor-air samples are commonly collected in evacuated canisters (i.e., SUMMA canisters) over a period of time, commonly 24 hours.[14] One potential issue in indoor-air sampling is the existence of contaminants in the indoor environment that are unrelated to subsurface contamination (e.g., indoor sources such as consumer products, combustion processes, building materials and outdoor sources such as airborne releases from nearby, regional, and global sources);[14] without the collection of other samples (e.g., sub-slab samples), the VI pathway cannot be completed.[14] The spatial and temporal variability of indoor-air samples is also high because of soil-gas entry rates, exchange rates, intra-building mixing, as well as other factors. [14, 15, 17, 18] Although less invasive than sub-slab samples because no ports are installed, indoor-air sampling is intrusive to occupants who often refuse entry because of the imposition of the process.[15]

1.4. UPTAKE OF CONTAMINANTS BY TREES

Tree-root systems occupy large subsurface volumes similar to the same subsurface horizon as basements of structures and have tremendous surface areas that are in direct contact with multiple environmental media, are sessile, and uptake vapors and groundwater from the subsurface as well as moderately hydrophobic compounds in corresponding vapor[28-32] and aqueous phases.[31, 33-36] Translocation of groundwater is active[31], not passive, and is driven by wind, solar radiation, and water vapor pressure deficits in the atmosphere. Many of the common contaminants (e.g., TCE, PCE, and benzene) are readily taken up, translocate up via xylem tissue, and are slowly released into the atmosphere where they degrade rapidly (Figure 1.1).[37] Uptake of contaminants occurs and is limited across the root-membrane boundary[38-41] within the tree's subsurface sampling zone, where contaminants are thought to be spatially averaged.[42, 43] As contaminants translocation through the xylem tissue they experience retardation, which results in a time-weighted average.[44, 45] These properties of plants provide long-term averaging of complex subsurface environments over large areas analogous to the chronic exposure characterized by VI.

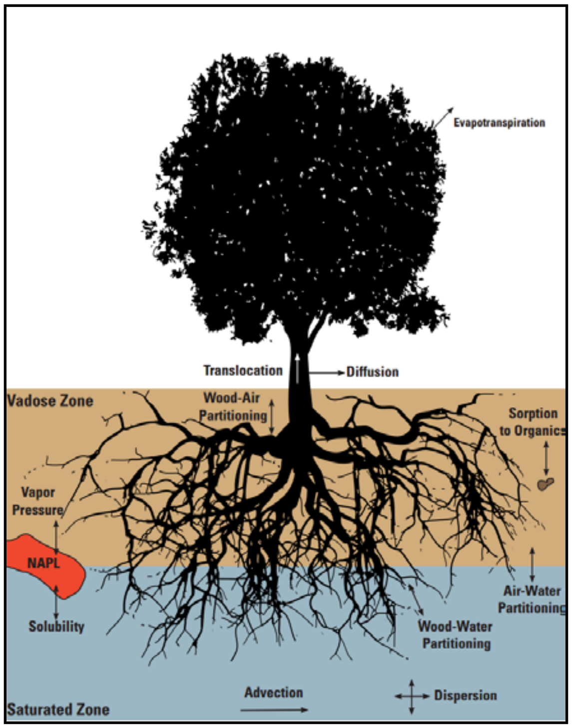

Figure 1.1. Depiction of the various fate and transport mechanisms that control the ultimate fate of environmental chemicals in the vadose, saturated, and above-ground zones.

1.5. PHYTOSCREENING

Trees have been used as biomonitors, a practiced called phytoscreening.[33, 34, 36, 43, 46-49] Trees are ideal candidates for biomonitors because they are ubiquitous active samplers and because they are thought to sample over large spatial and temporal scales. Sampling trees is noninvasive and, unlike direct VI sampling, does not require entry into peoples' homes and the construction of sampling ports, greatly increasing the likelihood of obtaining property access and VI data.

Tree cores are collected using low-cost field equipment. Typically, a five-millimeter core is extracted from the outside of the tree, 100 centimeters above ground and placed into a septum-capped glass vial using forceps. The sample is allowed to equilibrate overnight and analyzed for VOCs using headspace gas chromatography (GC). Results should be only interpreted semi-quantitatively to indicate relative concentrations because of the numerous fate and transport mechanisms in the tree system (Figure 1.1). Comparisons of concentrations in tree tissue with concentrations in other media (e.g., groundwater) are tenuous; however, concentrations in tree tissue have been shown to correlate better with concentrations in soil vapor than in water (Figure 1.2).[28]

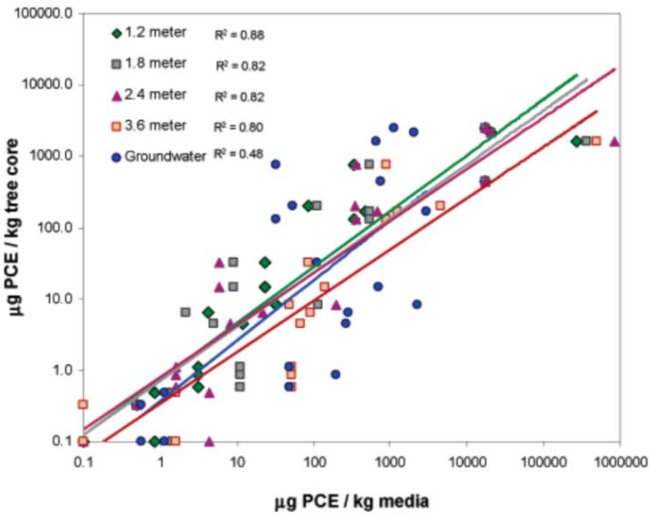

Figure 1.2. Relationship of PCE in tree cores collected at the New Haven Superfund site plotted versus the groundwater concentrations and soil concentrations measured at several soil depths. Taken from figure 6 of reference [28].

Trees are often not restricted to the same limitations and negative impacts as traditional sampling techniques. The common practice in site assessment of soil is to characterize contamination down to the refusal depth of the instrument, which is highly dependent on the site-specific residuum and underlying bedrock properties. In contrast, tree roots commonly penetrate through small cracks in physical barriers (e.g., bedrock, concrete foundations, and septic lines) in order to reach water and nutrients.

Exploiting the ability of trees to access domains unavailable to traditional methods makes it an ideal candidate for site assessment; however, tree sampling is not without its limitations (Table 1.1). Because root systems grow to a depth of adequate moisture, shallow clayey soils, which have high water-holding capacities and large mechanical impedances, restrict root growth to shallower depths.[50] Additionally, occasional false negatives in data occur and could be a result of a number of things. For example, BTEX compounds can readily degrade in the rhizosphere in the presence of oxygen, which is increased in the vicinity of trees as diurnal fluctuations of the water table increase oxygen transport in the subsurface.[51, 52] Without taking into account this rhizodegradation, results would be interpreted incorrectly. Also, due to the proximity of roots with the surface, large rainfall events deliver contaminant-free water to the root zone quickly and effectively can cause dilution of the contaminants.[53] Other disadvantages of phytoscreening include the semi-quantitate nature of tree-core results because of the number of site-specific parameters that control contaminant partitioning and transport[54] and the phytotoxicity of contaminants at high concentrations.

Even with these limitations, the combination of simplicity, speed, and cost-effectiveness make trees ideal candidates for VI potential surrogates; however, more field-scale research needs to be done to determine the subsurface volumes (representative footprint and depth) sampled by trees, understand characteristics of directional uptake in the field, and establish correlations between tree-core samples and measure VI samples.

Table 1.1. Advantages and disadvantages of tree sampling.

Advantages	**Disadvantages**
Temporal-averaging	Susceptible to rainwater infiltration
Spatial-averaging	Limited to root zone
Ubiquitous	Semi-quantitative
Cost-effective	Trees won't survive if contamination too high
Active sampler	False negatives
Noninvasive	

2. GOALS AND OBJECTIVES

The overarching goal of this research is to improve VI assessment through the use of plant sampling (i.e., phytoscreening). Specifically, the targeted goal is to improve the knowledge of how trees interact with the subsurface and to relate that knowledge to the field of VI assessment, thereby advancing phytoforensic technologies in VI assessment and protecting human health. To reach this specific goal, a set of specific objectives was developed, and completing these objectives will assess a set of scientific hypotheses that, if supported, will result in completing the stated goal.

- Objective 1: Determine the lateral extent (i.e., footprint) sampled by trees as a function of measured physical tree properties.
    - Hypothesis: The environmental footprint of a tree will be directly proportionate to its diameter, and larger trees will occupy a footprint and sample an environmental volume similar to the footprint of a typical residential home.
- Objective 2: Assess the depth sampled by trees through correlation between contaminant concentrations in trees and multiple media.
    - Hypothesis: Contaminant concentrations in trees are more representative of shallow, rather than deep, subsurface contamination in soil and groundwater.
- Objective 3: Characterize factors that affect the relationship between contaminant distributions in directional tree-core samples and the subsurface.
    - Hypothesis: Sectorial uptake of contaminants can be quantified and elucidate contaminant distribution in the subsurface via directional tree-core sampling in a field setting, and disagreement between contaminant distributions in directional tree-core samples and the subsurface can be attributed to *in-planta* concentration gradients.

- Objective 4: Assess the potential for directional tree sampling to indicate the direction of shallow soil-gas contamination.
    - Hypothesis: Directional tree-sampling can indicate the direction of shallow soil-gas contamination.
- Objective 5: Correlate field tree-sampling results with characterized soil-gas contamination and VI potential at the field scale.
    - Hypothesis: Tree-core samples will be well correlated over large urban areas with VI samples and other subsurface media sampling methods.

By completing the above objectives, conclusive support of the underlying hypotheses was attained and the overall goal to improve the knowledge base of VI assessment through the use of plant sampling (i.e., phytoscreening) was achieved. The fundamental understanding of how trees interact with the subsurface was notably enhanced in multiple ways that related to improved characterization approaches. The following publications present data and statistical analyses that map to the above objectives, and the collective knowledge gained has direct and immediate benefit to the field of VI assessment. The new knowledge and directly applicable techniques have thereby advanced phytoforensic technologies in VI assessment and offer increased and rapid protection of human health.

PAPER

I. TREE SAMPLING AS A METHOD TO ASSESS VAPOR INTRUSION POTENTIAL AT A SITE CHARACTERIZED BY VOC-CONTAMINATED GROUNDWATER AND SOIL

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ABSTRACT

Vapor intrusion (VI) by volatile organic compounds (VOCs) in the built environment presents a threat to human health. Traditional VI assessments are often labor-, time-, and cost-intensive; whereas traditional subsurface methods sample a relatively small volume in the subsurface and are difficult to collect within and near structures. Trees could provide a similar subsurface sample where roots act as the “sampler’ and are already onsite. Regression models were developed to assess the relation between PCE concentrations in over 500 tree-core samples with PCE concentrations in over 50 groundwater and 1,000 soil samples collected from a tetrachloroethylene- (PCE-) contaminated Superfund site and analyzed using gas chromatography. Results indicate that in-planta concentrations are significantly and positively related to PCE concentrations in groundwater samples collected at depths less than 20 m (adjusted R2 values greater than 0.80) and in soil samples (adjusted R2 values greater than 0.90). Results indicate that a 30-cm diameter tree characterizes soil concentrations at depths less than 6 m over an area of 700 to 1,600 m2, the volume of a typical basement. These findings indicate that tree sampling may be an appropriate method to detect contamination at shallow depths at sites with VI.

INTRODUCTION

Subsurface pollutants remain a human-health burden with over 1,700 sites on the Superfund National Priorities List (NPL) in the United States with an additional 53 proposed sites.[1] Since its inception in 1983, only 392 sites have been deleted from the NPL after attaining cleanup goals. The more than 1,300 NPL sites remaining and unknown contaminated sites still pose an unquantified threat to human health. Of the over 1,700 NPL sites, more than 1,400 are listed for volatile organic compound (VOC) contamination with 884, 393, and 278 sites listed for benzene, trichloroethene (TCE), and tetrachloroethene (PCE), respectively.[2] VOC pollutants also pose additional health threats because contamination can exist in the vapor form, be sorbed onto soil, or dissolved in water.

Of particular concern is vapor intrusion (VI) of VOCs in the built environment.[3, 4] Vapor intrusion occurs when contaminants in the vapor phase migrate in the shallow subsurface and enter residential or commercial buildings through cracks, seams, and gaps (Figure 1). Initially a concern because of radon exposure in residential homes in the 1980s, VI has been recognized as a serious human-health threat as occupants are exposed to potentially harmful concentrations over long periods of time.[5, 6] Two such common carcinogens are tetrachloroethylene (PCE) and trichloroethylene (TCE), which have maximum contaminant levels of 5 µg/L in drinking water[7] and vapor intrusion screening levels of 11 µg/m^3 for PCE and 0.48 µg/m^3 for TCE[8]. TCE is of particular concern because of the carcinogenic effects on fetuses with low-level exposure to TCE during the first trimester.[3] Because indoor-air quality is highly spatially and temporally variable, and because many of the chemicals that pose threats can be derived from sources inside buildings, such as cleaning products or building materials, the presence of contaminant concentrations in the shallow subsurface below structures (i.e., the VI potential) is measured and used to screen for VI risk, which is based on a target excess lifetime cancer risk of 1 x 10^{-9} and Hazard Quotient of 1.[8] Vapor intrusion potential is typically measured with direct methods (e.g., sub-slab sampling of soil gas) or indirect methods (e.g., groundwater, soil, or soil-gas sampling). These direct and indirect methods for measurement of VI risk and potential are invasive, time, and resource intensive (on the order of thousands to hundreds of thousands of dollar),[9, 10] or may not be done at all due to the inability to safely collect samples. Accurate characterization of subsurface contamination near and under the foundation of buildings is paramount in determining VI risk and potential; however, the subsurface volume sampled by traditional soil-gas samples is relatively small and limited by soil porosity, tortuosity, and the pumped soil-gas volume.[11]

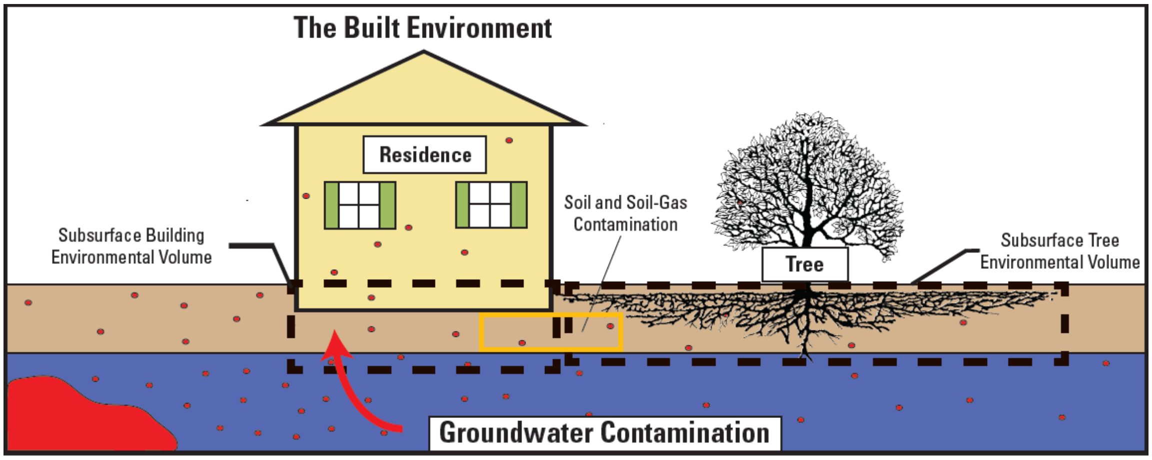


Figure 1. Schematic of the relationship between vapor intrusion from a hypothetical groundwater source, the built environment, and tree assessment of soil, soil-gas, and groundwater contamination distribution.

Tree-root systems occupy large subsurface volumes and surface areas that are in direct contact with multiple environmental media, are sessile, and uptake vapors and groundwater from the subsurface. Trees can take up moderately hydrophobic contaminants dissolved in water after entry across the root-membrane boundary,[12-14] a process that is viewed as primarily being controlled by the octanol-water partitioning coefficient (log K_{OW}).[15] Plants are also active in vapor-phase gas exchange via root-tissue respiration. For deciduous trees in particular (as well as some evergreens), the rooting volume (lateral[16] and vertical[17] penetration) can be substantial; therefore, trees interact directly with contaminants in groundwater, soil, and soil gas over large subsurface volumes and over long periods of time. Roots can also occupy the same subsurface horizon as basements of structures (Figure 1). Pollutant molecules collected from the subsurface by tree roots can move to aboveground tissues via the translocation pathway, allowing for easily accessible, above-ground tissue sampling to be used as a method to analyze for pollutants that reside in the subsurface above the saturated zone. Translocation is driven by wind, solar radiation, and water vapor pressure deficits in the atmosphere and is active, not passive, because trees are essentially hydraulic pumps. Tree-coring is the most common method of tissue collection and is cost- and time-efficient, with sample collection taking only minutes per tree. Analysis of the collected sample has been shown to be rapid, sensitive, and cost effective depending on site conditions and the analytical methods used.[18-21] Tree-coring as a screening tool for site characterization has gained national and international regulatory acceptance by the United States (U.S.) Environmental Protection Agency (EPA) in 2008[22] and the European Union in 2012.[23]

Although recent research has addressed the use of trees to measure contaminant concentrations in water[24] and soil gas in the natural environment,[11] the authors are aware of only limited studies[22, 25] that have compared the use of tree-core sample collection and analysis of VOCs to traditional methods of VOC sampling to assess VI risks to the built environment. Additionally, the impact of tree characteristics (such as tree species, size, and rooting characteristics) on relationships between groundwater, soil, and vapor concentrations and *in-planta* concentrations is fairly well known,[22, 26, 27] but little is known about how these tree characteristics affect the spatial representation of plant sampling.

Study Site

To investigate the subsurface volume that is effectively sampled by trees and if trees can be used to assess VI risk, the Vienna Wells site, a Superfund site in Vienna, Missouri, was selected, and tree-core, groundwater, and soil samples were collected. The site is characterized primarily by PCE and trichlorotrifluoroethane (CFC-113) contamination from historical use of chlorinated solvents as degreasers during hat-manufacturing processes. In 2006, the PCE concentration in one pubic-supply well about 150 meters (m) north of the hat factory building exceeded the EPA's maximum contaminant level of 5.0 micrograms per liter (µg/L), and after a site investigation, the EPA concluded that the former hat factory was the likely source of PCE contamination in the public-supply well.[28]

The 32,000-m^2 site is composed of the former hat factory building and about 16,000 m^2 of heavily wooded area. Overburden near the hat factory is composed primarily of clay and chert to the west, and a sandstone layer outcrops to the east. Thickness of the clay overburden ranges from less than about 1 m overlying sandstone bedrock to the east to between 2 and 4 m in the remainder of the site to the west (Figure 2).

The total depths of monitoring wells ranged from 0 to 53 m below ground surface (Table S1) and had 3-m screened intervals at the bottom of each well (Figure 2). Wells with total depths ranging from less than 20 m below ground surface were designated "shallow wells" (9 wells), and wells with total depths below 20 m were designated "deep wells" (8 wells). Depths to groundwater vary from 9 m on the west part of the hat factory property to about 11 m on the east part of the site.[29]

METHODS

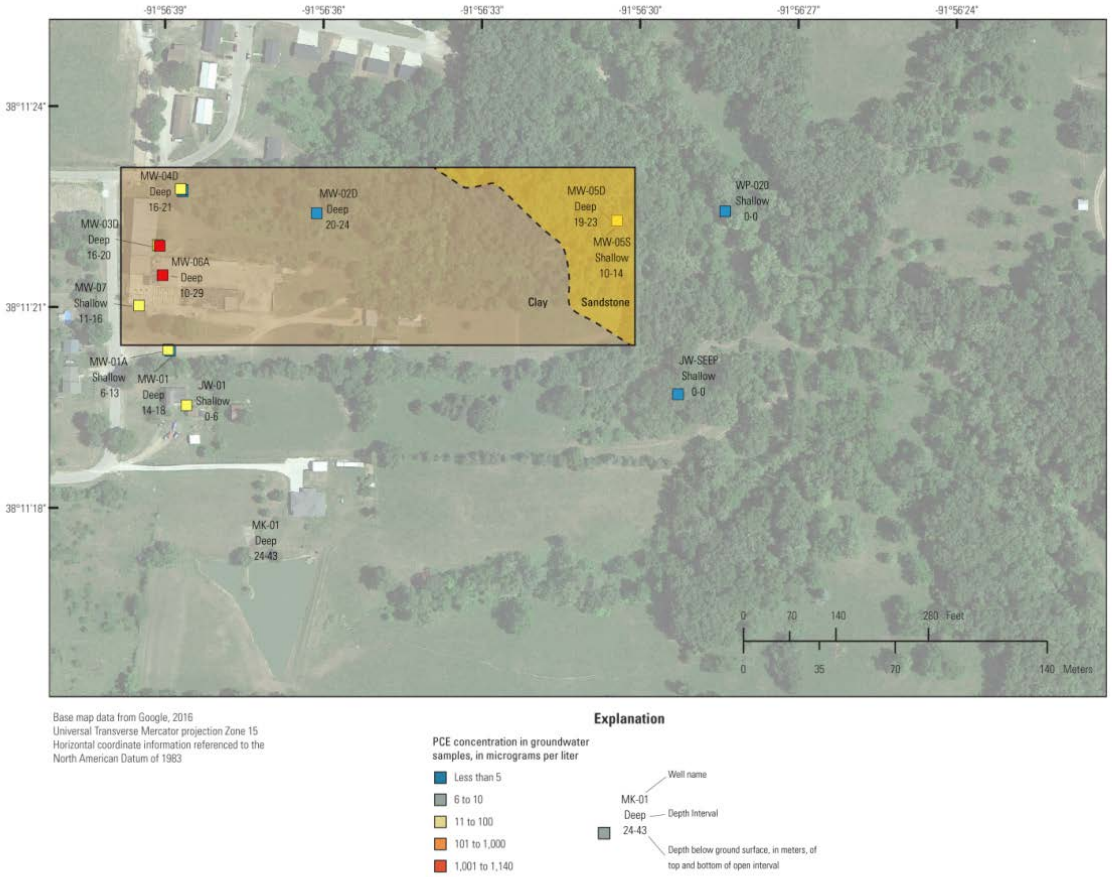
Tree-core, groundwater, and soil samples were collected at the Vienna Wells site from May 2013 to April 2016. Global positioning system (GPS) locations were collected for each tree using either a Trimble GeoExplorer XH® (Trimble Navigation Limited, Sunnyvale, California) with a sub-meter accuracy or using smart phones (iPhone 5 [Apple, Cupertino, California] and Samsung S5 [Samsung, Seoul, South Korea]), which have been shown to have an average accuracy of about 5–8 m.[24, 30] All tree-core, averaged groundwater (2013-2016 sample concentrations), and soil data used in this paper are available at U.S. Geological Survey (USGS) ScienceBase, https://doi.org/10.5066/F71835D8. Raw (non-averaged) groundwater data are available in the USGS National Water Information System (NWIS), http://dx.doi.org/10.5066/F7P55KJN (see table S1 for NWIS station IDs).

Tree-Core Sampling and Analysis

Tree-core sampling was conducted over seven days during six major phases occurring during September 2011, May 2013, August 2013, July 2014, May 2015, and October 2015. A total of 525 tree-core samples were collected and analyzed using established methods.[22, 31] Briefly, samples were collected at about 1 m above land surface using an increment borer and cores were transferred using a pair of stainless steel forceps into a 20-milliliter (mL) glass vial fitted with a Teflon-lined septum cap. Predominant tree types sampled included cedar (*Cedrus sp.*), oak (*Quercus sp.*), elm (*Ulmaceae sp.*), sycamore (*Plantanus sp.*), ash (*Fraxinus sp.*), and walnut (*Juglandaceae sp.*). The diameter of each tree sampled was measured to the nearest centimeter using diameter tape at the sample-collection height. After overnight equilibration with room temperature at the Center for Research in Energy and Environment (CREE) at the Missouri University of Science and Technology (Missouri S&T), the headspace in tree-core samples was analyzed by gas chromatograph (GC) using an Agilent 7890 gas chromatograph (Agilent Technologies, Inc., Santa Clara, California) equipped with a micro-electron-capture detector (μECD) fitted with a CombiPAL solid-phase microextraction (SPME) fiber auto sampler with a 100-μm polydimethylsiloxane (PDMS) SPME fiber. All concentrations in tree-core samples were reported as mass of constituent per volume of water in the tree core using a mass balance approach to account for partitioning of constituents into tree tissue.[32] The method detection levels (MDLs) for PCE and TCE were previously determined to be 0.47 and 7.7 nanograms per liter (ng/L), respectively.[33]

Groundwater Sampling and Analysis

A total of 56 groundwater samples were collected from monitoring wells on five separate occasions between July 2013 and April 2016 (Figure 2). Conventional sampling methods were used to collect groundwater samples.[34] Briefly, groundwater was pumped from each monitoring well using a submersible pump until at least 1.5 well volumes had been removed and once physical properties (e.g. temperature, pH) and chemical characteristics (e.g., dissolved oxygen) had stabilized.[35] All samples were analyzed using EPA method 8260B by one of two laboratories (RTI Laboratories, Inc., Livonia, Michigan and National Water Quality Laboratory, Denver, Colorado) using gas chromatography-mass spectrometry (GC-MS) with detection limits of 0.022, 0.022, and 1 µg/L for PCE, TCE, and CFC-113, respectively.



Base map data from Google, 2016
Universal Transverse Mercator projection Zone 15
Horizontal coordinate information referenced to the
North American Datum of 1983

Figure 2. Maximum concentration of tetrachloroethylene (PCE) and construction information in groundwater wells and surficial lithology (primarily clay and sandstone).

Soil Sampling and Analysis

Over 1,000 soil samples were collected by the USGS and the EPA across the site from 366 boreholes using a truck-mounted Geoprobe™ (Geoprobe Systems, Salina, Kansas) drill rig. Continuous soil cores were collected over 54 cumulative days using a 50-millimeter by 1.2-m long core barrel fitted with disposable acetate sleeve. Depth-to-refusal, as defined as the maximum possible drilling depth, across the site ranged from 0.6 m to about 5.5 m, with shallower refusal depths on the east part of the site (0.69–2.4 m). For samples collected by the USGS, a disposable plastic syringe was used to collect 5-mL samples at 0.5- or 1-m intervals. Soil samples were quickly transferred into a standard 40-mL VOC vial pre-filled with 20 mL of organic free deionized water and heated for 35 minutes to 40 $^{\circ}$C in a heater block. A gas-tight syringe was used to withdraw a 100-µL headspace sample for injection into an Inficon Voyager portable GC (Inficon, Bad Ragaz, Switzerland) equipped with a photoionization detector (PID). The analysis was run using nitrogen as a carrier gas at a pressure of 55 kilopascals and an oven temperature of 63 °C with a total runtime of 6 minutes. The MDLs for PCE and TCE were determined to be 11 and 8.4 micrograms per kilogram soil (µg/kg), respectively. Because the PID was used rather than an electron capture detector (ECD), CFC-113 was not measured in soil samples by the portable GC. For samples collected by the EPA, samples were collected according to EPA method 5035 and analyzed by EPA Region 7 laboratory. Additionally, a total of 51 soil samples were collected by the USGS and analyzed by a USGS contract lab (RTI Laboratories, Livonia, Michigan) for analysis of PCE, TCE, and CFC-113 using EPA method 8260B to validate and augment the dataset analyzed by the portable GC. These quality control/quality assurance data (Figure S1) indicate good correlation (coefficient of determination [R^2] of 0.89) between soil samples analyzed by the contract laboratory GC and the portable GC.

Statistical Methods

Simple and multiple linear regression approaches were used to develop explanatory models that express the concentrations of PCE, TCE, and CFC-113 in groundwater and soil samples as a function of concentrations of PCE, TCE, and CFC-113 in tree-core samples. All model residuals were normally distributed after concentration data were log-transformed; therefore, linear regression was conducted on the log-transformed concentrations using the Python module StatsModels (Python Software Foundation, Delaware) with a significance level of 0.05. For simple linear regression (SLR), the model was:

$$Log_{10}(C_{GW\ or\ Soil}) = \beta_1 * Log_{10}(C_{Tree}) + \beta_2 + \varepsilon$$

where $Log_{10}(C_{GW\ or\ Soil})$ is the logarithm of the concentration in groundwater, in µg/L, or soil, in µg/kg; β_1 and β_2 are coefficients, $Log_{10}(C_{Tree})$ is the logarithm of the concentration in the tree-core sample in ng/L; and ε is the error term.

Tree diameter was negatively skewed (Figure S2), so tree diameters were placed into three classes (class 1: diameters ≤ 25 cm [50th percentile], class 2: diameters > 25 cm and < 41 cm [75th percentile], and class 3: diameters ≥ 41 cm). For multiple linear regression (MLR), the model was:

$$Log_{10}(C_{GW\ or\ Soil}) = \beta_1 * Log_{10}(C_{Tree}) + \beta_2 * Diameter\ Class + \beta_3 + \varepsilon$$

where $Diameter\ Class$ is the tree-diameter class categorical variable, and β_1, β_2 , and β_3 are coefficients.

Samples with PCE concentrations less than the MDL (4% of groundwater samples, 70% of soil samples, and 30% of tree-core samples) were replaced with the MDL and used in statistical analysis. Samples with TCE and CFC-113 concentrations less than the MDL were not included in the statistical analysis. The adjusted coefficient of determination (R^2), which accounts for spurious increases in model fits with an increase in the number of explanatory variables, was used to measure model fit.

Because TCE contamination was measured in air blanks during the October 2015 sampling event (likely occurring from pairs of recently purchased synthetic gloves), gloves were no longer used, and field PCE contamination was suspected in tree-core samples collected during the October 2015 event; therefore, the 56 tree-core samples collected during October 2015 were excluded from the tree-core dataset and subsequent models.

Integrated Sampling Areas and Volumes

To develop regression models between pairs of tree-core and groundwater sample results, a well-centric approach was used by developing different buffer radii, or circular sampling areas, ranging from 1 to 149 m in 2-m increments around each monitoring well sampled (Figure 3). For each well, trees sampled within each buffer were averaged into the three diameter size classes previously defined and paired with the average groundwater sample result, producing up to three data points per well, and used in regression analysis.

To develop regression models between tree-core and soil samples, a tree-centric approach was used by creating representative volumes around each tree with the assumption that the subsurface volumes that equate to tree root lateral and vertical distribution are best represented by a cylinder (Figure 3). To assess whether the lateral extent of the buffer was proportional to the tree diameter, two sets of volumes were created: a volume with a constant radius and a volume with radii linearly proportionate to tree-trunk diameter. To assess the volume sampled by each tree, a variety of buffer radii and depth interval combinations were assessed. Constant-radius volumes were created from 3 to 90 m in 3-m increments. Linearly-proportionate volumes were created using a hypothetical root-to-trunk (R/T) diameter ratio ranging from 0.1 to 6 meters per centimeter (m/cm) in increments of 0.1 m/cm. The depth intervals included all possible combinations of depths from 0 to 5.5 m, the largest refusal depth at the Vienna Wells site. All soil samples contained within each tree buffer radius and depth interval combination were averaged and used in the regression analysis.

Concentrations of contaminants in tree-cores have been shown to vary temporally on a daily, weekly, monthly, and yearly basis,[17, 33] and the typical range of concentrations in an individual tree is approximately an order of magnitude from periods of little evapotranspiration to periods of large evapotranspiration. These temporal changes in contaminant concentrations in tree-cores likely contribute to error in regression models because time is not taken into account but do not negate the approach used for method evaluation in this paper.

Python was used to pre- and post-process all sample data and conduct spatial joins between tree data, groundwater, and soil data. The Python module ArcPy (Environmental Systems Research Institute, Redlands, California) was used to construct buffers and average soil samples within each resulting volume.

RESULTS AND DISCUSSION

Areas with large PCE concentrations in soil samples (greater than 1,000 µg/kg) generally were co-located with areas with large PCE concentrations in tree-core samples (greater than 1,000 ng/L). A total of 382 of the 525 tree-core samples contained PCE concentrations greater than the detection limit (Figure 4). Tree-core samples with large PCE concentrations were clustered near and northeast of the former hat factory and to the east in the vicinity of the sandstone outcrop area (Figure 2). PCE was detected in 310 soil samples, and PCE concentrations were largest in soil samples in two of the three areas of contamination indicated by tree-core sampling: near and northeast of the former hat factory. This discrepancy between PCE concentrations in tree-core and soil samples in the sandstone outcrop area likely exists because many trees were sampled across the property line, and soil sampling across the property boundary was not plausible because of steep slopes; however, the presence of the sandstone unit resulted in shallow refusal depths during soil sampling and may act as a barrier for vapor transport in the subsurface that trees roots are able to locally penetrate.

Groundwater

SLR models based on PCE in tree-core and shallow groundwater samples gave the best relation (Figure 5), with an adjusted R^2 of 0.84. Measures of model fits (adjusted R^2 values) were low (< 0.3) for SLR models based on PCE in tree-core and combined shallow and deep groundwater samples for buffer radii between 21 and 42 m and >109 m. Model fit measures were highest when including trees less than 41 m from wells and generally decreased with increasing buffer radii distance. Model fits also may be high at distances < about 27 m for SLR models incorporating only shallow groundwater because very few wells had trees present within 27 m. Lack of data at buffer radii <27 m makes interpretation indeterminate and does not necessarily disprove correlation. Most MLR models were not significant, which indicates that tree diameter adds little information about PCE groundwater concentrations. The adjusted R^2 increase at 39 m from 0.28 in the SLR model incorporating shallow and deep groundwater to 0.75 in the SLR model incorporating only shallow groundwater indicates that these trees are better indicators of shallow groundwater than deep groundwater. Although CFC-113 and TCE were detected in many trees, CFC-113 and TCE were not detected in enough samples to build a robust, significant model or to draw specific conclusions.

Soil

Models describing PCE in soil samples using tree-core samples with a constant buffer radius had poor fits (R^2<0.1) for buffer radii between 6 and 12 m and at greater depths (> 3 m; Figure 6). At buffer radii greater than 12 m, measures of model fit decreased quickly to a R^2 of around 0 at buffer radii of 18 to 30 m. These poor model fits indicate that representing the subsurface volume sampled by trees as a constant radius is a poor approach.

SLR models between PCE in soil and tree-cores using diameter-dependent buffers (Figure 7) had notably better fits than models with constant-diameter buffers (Figure 6). Measures of model fit ranged from an adjusted R^2 of about 0.5 to just less than 1 at buffer distances between a hypothetical R/T ratio of 0.8 and 1.8 m/cm. Although models for shallow and deep soil intervals were significant, models fits were higher for shallow soils. MLR models incorporating tree diameter as an explanatory variable generally were not better, likely because the diameter-dependent buffer limited the number of soil samples to be included in the model, capturing differences in sampling volume between trees. However, the large difference between model fit measures in the constant-diameter (Figure 6) and diameter-dependent buffers (Figure 7) indicates that trees interact with a subsurface volume directly proportionate to their diameter, an important aspect to consider when collecting and interpreting tree-core data; therefore, tree-core samples from larger trees represent a proportionally larger environmental volume.

Comparison and Contrast to Previous Studies

Findings reported from this investigation compare well with other studies that explored the effects of tree sampling characteristics on relationships of groundwater, soil, and soil-gas concentrations to *in-planta* concentrations and the spatial representation of plant sampling. Several studies have found significant correlation coefficients between contaminants in tree-core and groundwater samples [18, 21, 36, 37] and between tree-core and soil samples [36]. Struckhoff et al. demonstrated higher correlations between contaminants in tree-core samples and shallow soil samples than between contaminants in tree-core

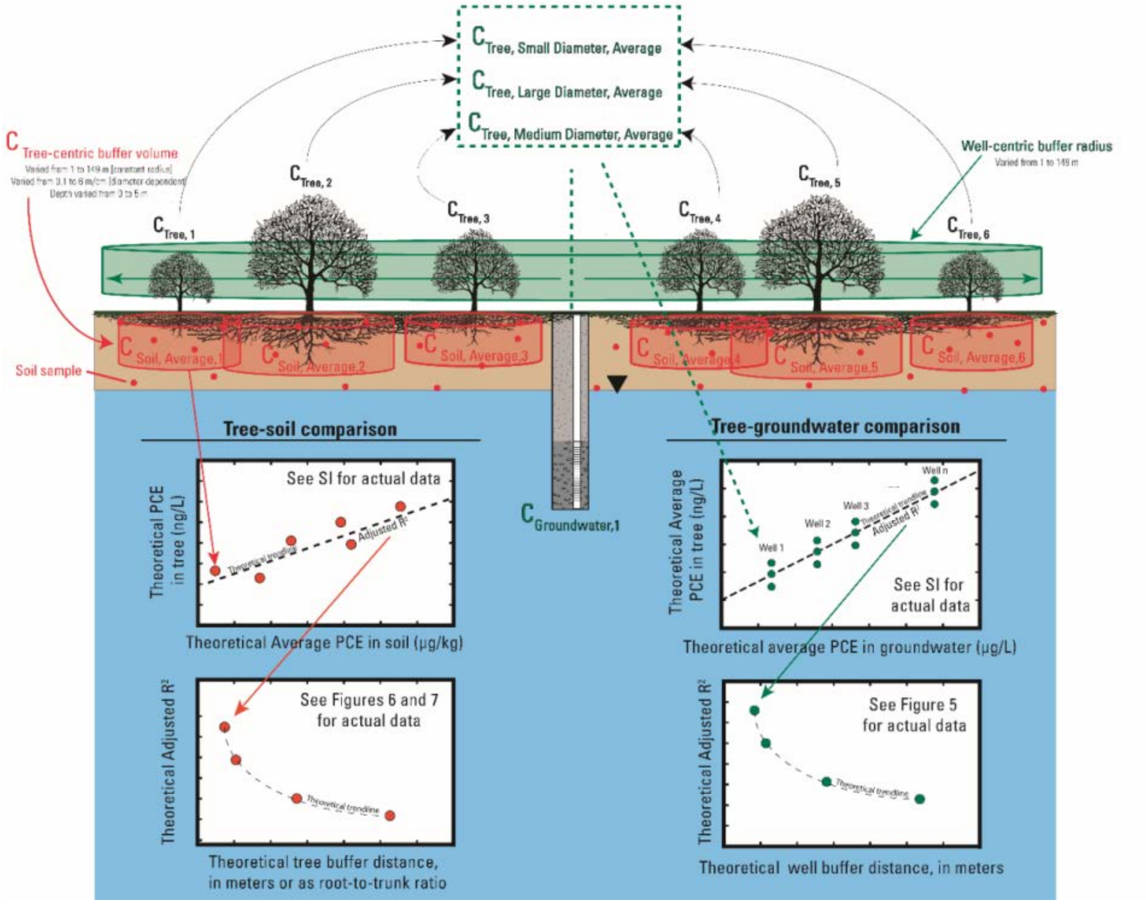
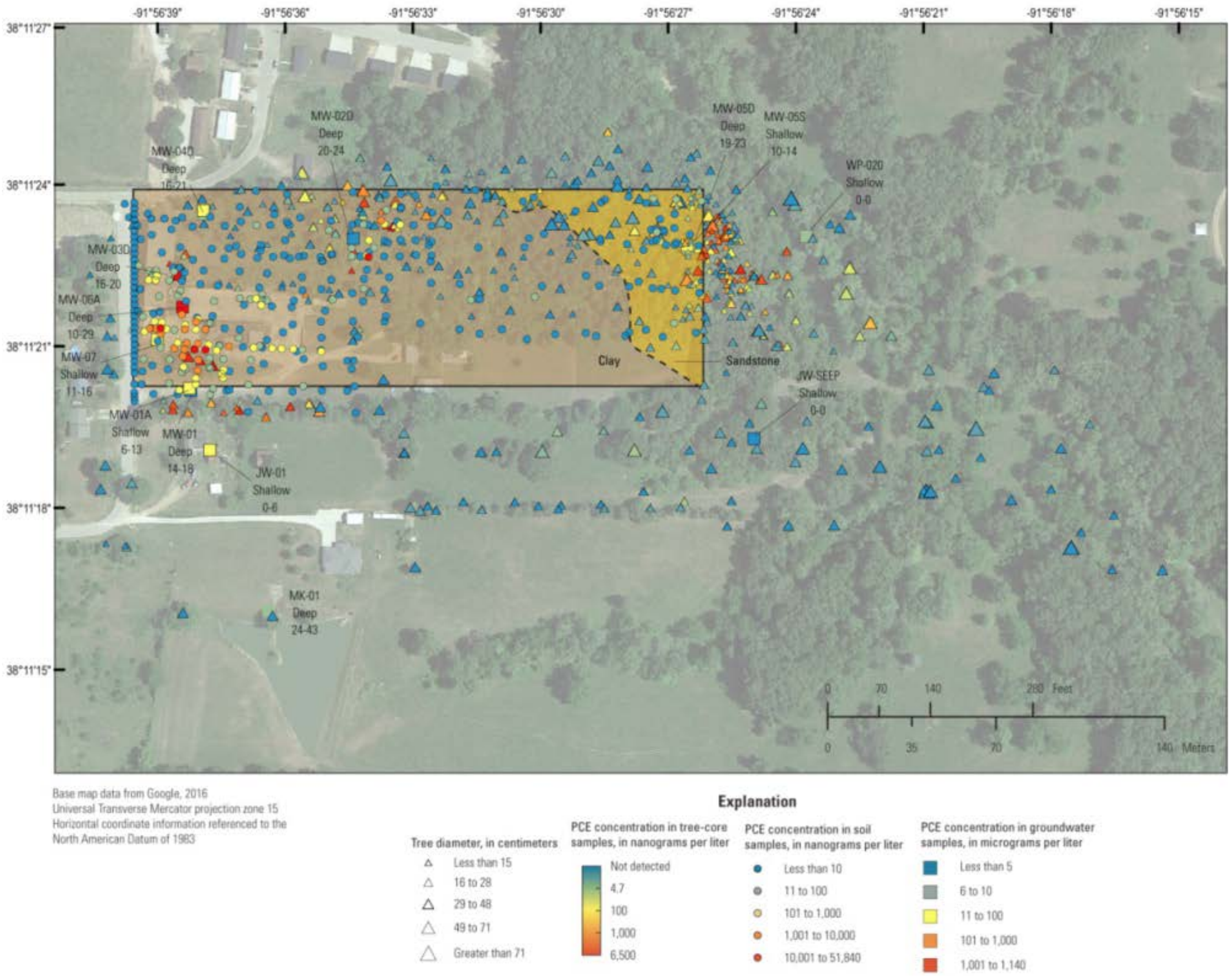


Figure 3. Schematic illustrating sampling areas for well-centric buffer radii and sample volumes for tree-centric buffer radii. For comparisons between PCE concentrations in tree-core and groundwater samples, tree-core samples are averaged within a given well-centric buffer radius and within three tree size classes and used to build regressions for that given buffer distance. For comparisons between PCE concentrations in tree-core and soil samples, soil samples within a given tree-centric buffer are averaged for a given depth interval and used to build a regression for that given buffer distance. Plots are only for illustrative purposes and do not include actual data; theoretical values increase from bottom to top and left to right.

samples and deeper soil and groundwater samples [38]. The effects of tree diameter as well as other tree characteristics in 1,913 trees from 39 field sites were also examined and revealed that trees of larger diameter had significantly higher PCE concentrations but explained only a small portion of the variance in PCE concentrations in groundwater.[39] Although tree species is another important factor in relating contaminant concentrations in tree-core samples with other media, tree size has been shown to dominate.[39] Findings



Base map data from Google, 2016
Universal Transverse Mercator projection zone 15
Horizontal coordinate information referenced to the
North American Datum of 1983

Figure 4. Maximum concentrations of PCE in soil and groundwater samples and average concentrations of PCE in tree-core samples, Vienna, Missouri, 2012-2015.

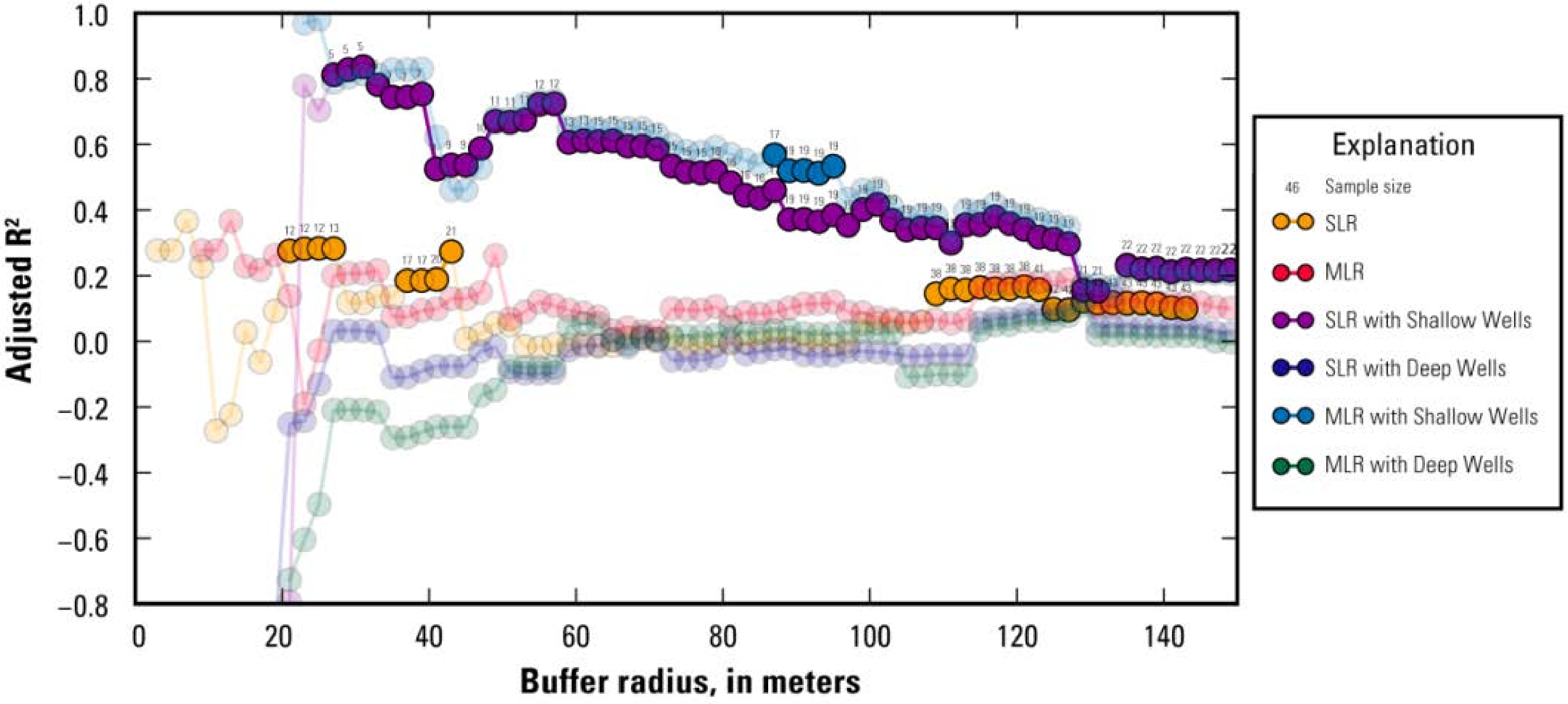


Figure 5. Measures of model fit in SLR and MLR models between PCE in groundwater and tree-core samples at different buffer distances around wells. Yellow and red dots are models that include shallow and deep groundwater samples. Transparent markers indicate insignificant models (p-value > 0.05) and opaque markers indicate significant (p-value ≤ 0.05) models. Values adjacent to symbols indicate sample size.

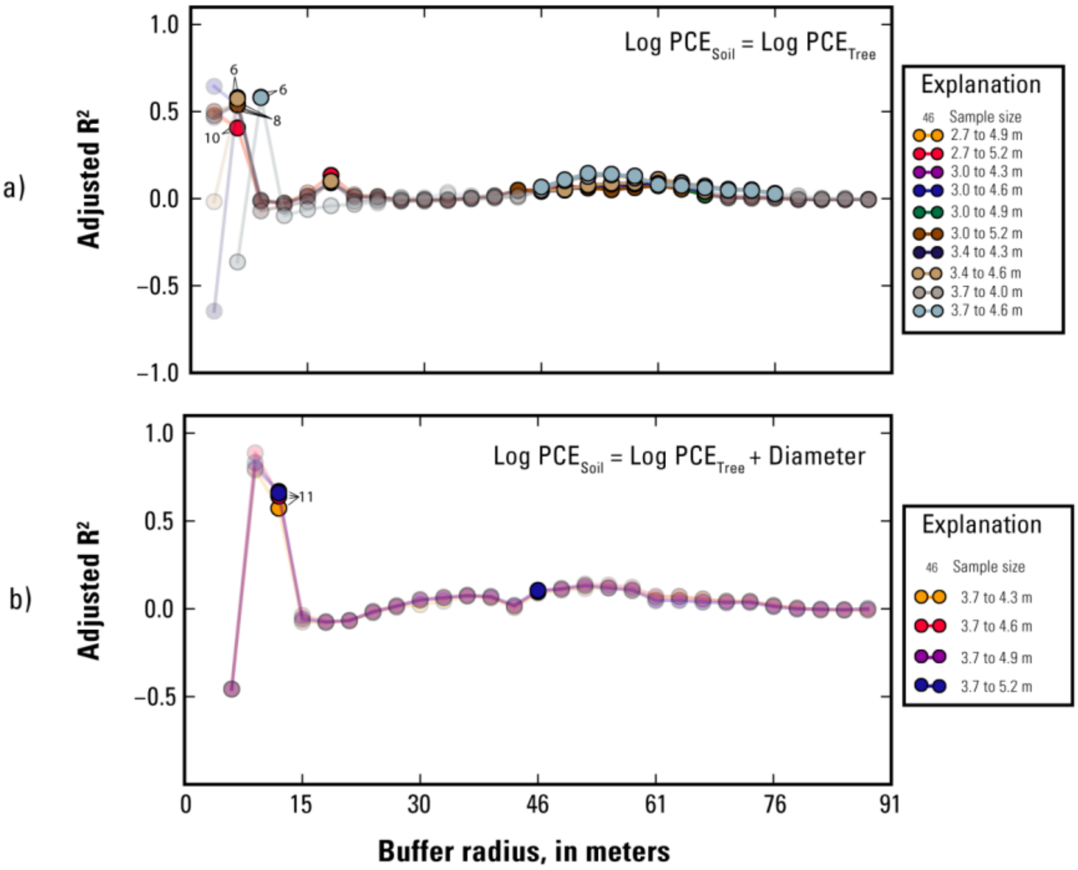


Figure 6. Measures of model fit in a) SLR and b) MLR models between PCE in soil and tree-core samples with at least one significant model with an adjusted R^2 value above 0.4. Soil samples used in each model were located within a constant buffer distance around each tree. Transparent markers indicate insignificant models (p-value > 0.05) and opaque markers indicate significant (p-value ≤ 0.05) models. Different colors denote differing soil-sample depth intervals. Values adjacent to symbols indicate sample size.

presented in this study demonstrate a direct relationship between tree-trunk diameter and the representative subsurface volume sampled by trees.

Implications

These findings indicate that the tree species sampled are indicators of shallow (< 20 m) PCE contamination in soil (2-4 m) and groundwater but are poorer indicators of deeper (>20 m) PCE contamination at this site. Although this study focused primarily on PCE because of its variable and wide-spread distribution, similar findings were observed with TCE and CFC-113 concentrations in the groundwater and soil samples collected (see SI).

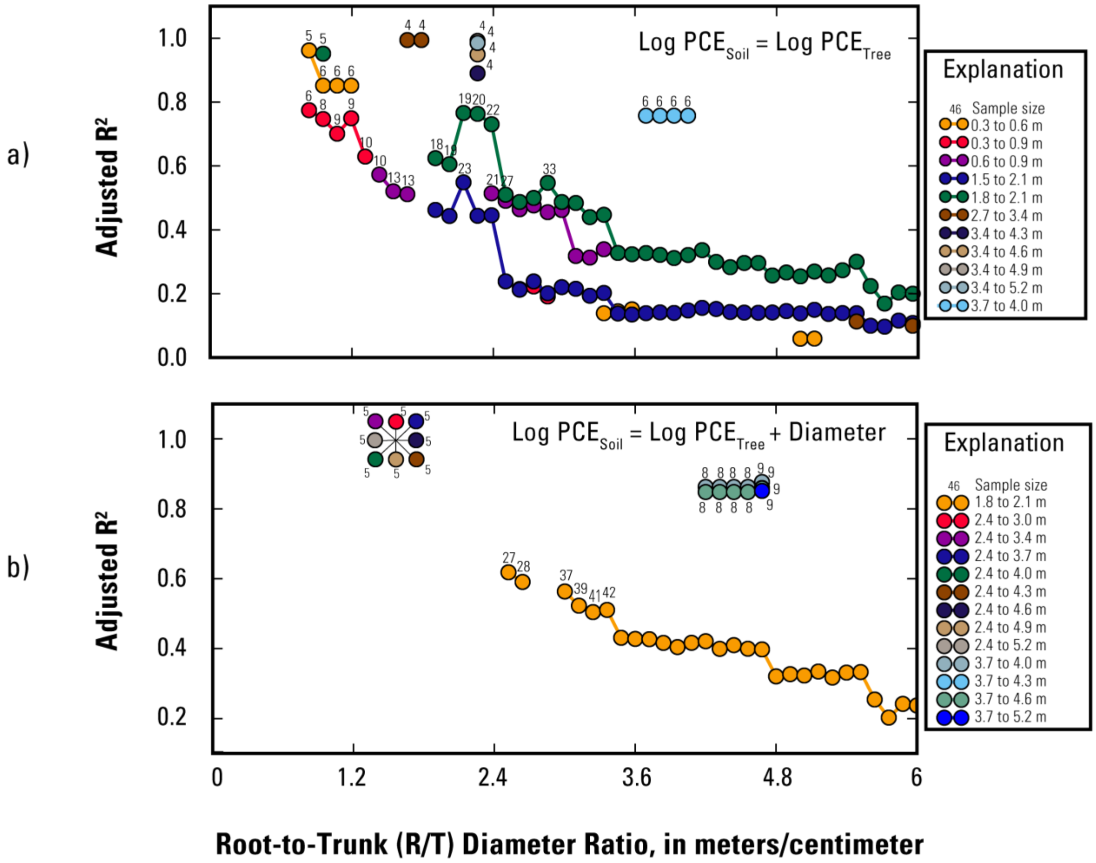


Figure 7. Measures of model fit in a) SLR and b) MLR models between PCE in soil samples at various depth intervals and tree-core samples with at least one significant model with an adjusted R^2 value above 0.4. Soil samples used in each model were located within a diameter-dependent buffer distance around each tree. Different colors denote differing soil-sample depth intervals. Values adjacent to symbols indicate sample size.

The sample density and frequency carried out at this site in tree, groundwater, and soil would not have been feasible at a populated residential site; therefore, this endeavor does not directly demonstrate a link between tree-core concentrations and site-specific, measured VI in homes. However, the close physical connection between tree roots and shallow (< 20 m) subsurface contamination demonstrated in this paper and the well-established connection between shallow groundwater, soil, and soil-gas samples with VI demonstrated repeatedly in the literature[4, 40-43] serve to affirm that tree sampling is a well-suited screening tool for potential VI risk. Tree sampling is also applicable in VI screening because trees are typically present in areas where humans are located, especially in residential areas where VI presents the most substantial health risk.[3] The highest model fits for shallow subsurface soil contamination were at hypothetical R/T ratios between 1 and 1.5 m/cm, which equates to an area between 700 and 1,600 m^2 (30- and 60-m-diameter circle) for a typical tree with a trunk diameter of 30 cm. In summary, the representative subsurface volume sampled by larger trees is similar to the volume of a typical basement.

Plant properties, particularly trunk diameter, are important factors to consider when interpreting tree-core data not only because of the diffusive loss that must be taken into account,[22, 26, 27, 31] but because these findings indicate trees may integrate contaminants in the soil zone in a volume proportional to their diameter. In practice, sampling larger trees likely will provide more information on the large-scale contaminant variability in soil, whereas smaller trees will provide information on the small-scale variability. For VI or groundwater screening purposes, larger trees are preferred because they have less diffusive loss and have higher probabilities of capturing contamination if present because of their larger subsurface sampling volumes; however, concentrations of contaminants in larger trees could be diluted if zones of contamination in the vadose zone are mixed with larger zones of clean water, but this kind of subsurface heterogeneity might be determined if directional tree-coring is used.[44]

Tree sampling is cost-effective, rapid, and likely provides subsurface information over larger volumes (greater than several hundred m^2 in a tree with a diameter of 30 cm) than traditional VI and subsurface samples. No heavy equipment is required and sampling of each tree requires less than 10 minutes time of one field technician. Because trees are essentially preinstalled “samplers,” tree sampling is less invasive than VI and traditional sampling, eliminating problems with underground utilities or concerns of theft or disruption of sampling canisters and increasing the likelihood of obtaining permissions from home or business owners. Although tree sampling offers many benefits over traditional methods, tree sampling is best applied as a pre-screening tool in conjunction with VI or traditional methods because concentrations in tree-core samples cannot be used to quantify groundwater, soil, or soil-gas concentrations, but tree-core sampling can be accurately used to indicate the presence of contamination and aid in determining areas where to focus VI and traditional efforts.

SUPPORTING INFORMATION

Additional information including a list of wells sampled for groundwater, a histogram of tree diameters sampled, figures of model results for CFC-113 and TCE concentrations, detailed model results for PCE, residual plots for select PCE models, and a plot of quality control/quality assurance data is available free of charge at pubs.acs.org.

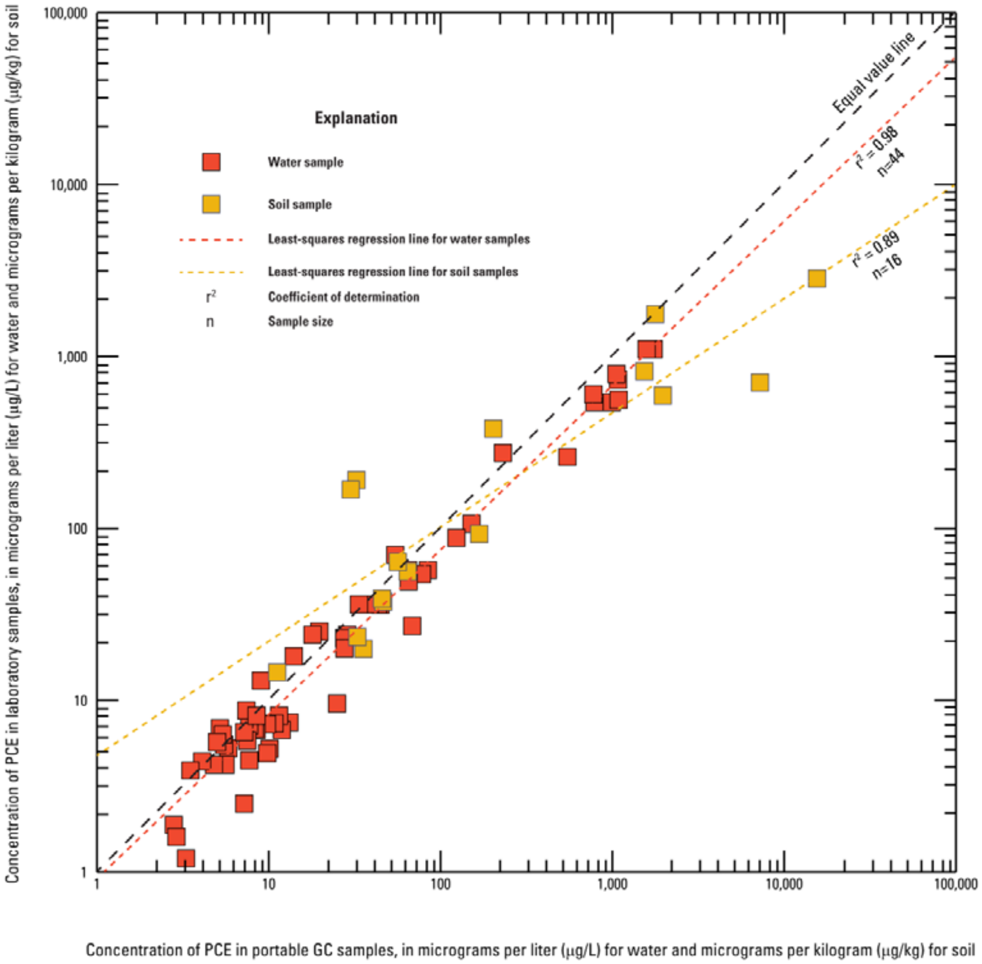


Figure S1. Relation between concentration of tetrachloroethylene (PCE) in laboratory samples and portable gas chromatograph (GC) samples from groundwater and soil samples.

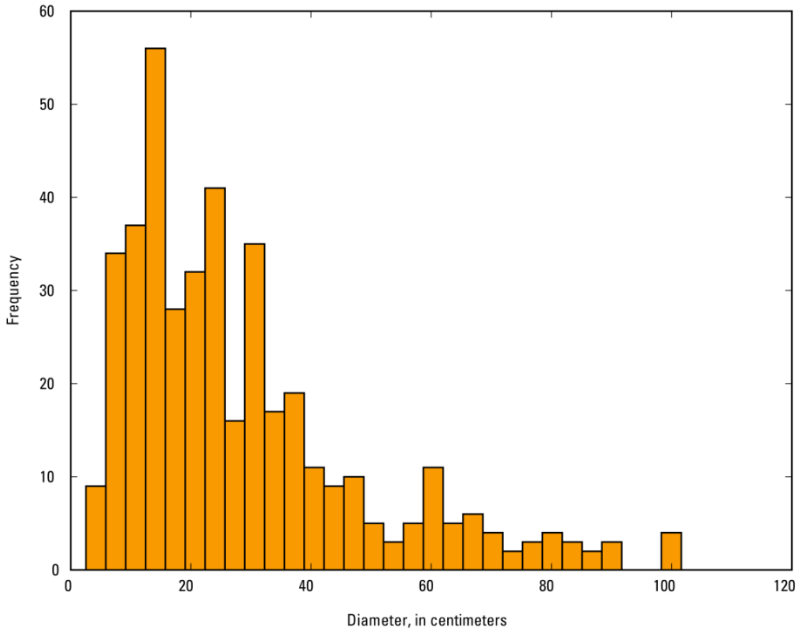


Figure S2. Histogram of tree diameters sampled at the Vienna Wells site and used in statistical analyses.

Table S1. Well names and National Water Information System station IDs for groundwater samples.

Well name	NWIS Station ID	Total Depth, in meters
JW-01	383636091123802	6
JW-SEEP	381120091563802	0
MK-01	383638091125001	43
MW-01	383638091125001	18
MW-01A	383638091125002	13
MW-02D	383639091125901	24
MW-03D	383639091125901	20
MW-03S	381122091563801	15
MW-04D	383639091125901	21
MW-04S	383640091130701	14
MW-05D	383640091130701	23
MW-05S	383640091130702	14
MW-06	383644091131601	36
MW-06A	383648091124501	29
MW-07	383648091124501	16
MW-08A	381122091563902	53
WP-020	383631091124801	0

Table S2. Measures of model fit and coefficients in simple linear regression model between tetrachloroethylene (PCE) concentrations in all tree-core and groundwater samples. Shallow (<20 m) and deep (≥20 m) groundwater samples are combined in these models.

Buffer distance, in meters	Adjusted R^2 for PCE	Sample Size	P-Values		Model Coefficients	
			Intercept	Log C_{Tree}	Intercept	Log C_{Tree}
1	-	-	-	-	-	-
3	0.277	3	0.142	0.411	2.45	-0.772
5	0.277	3	0.142	0.411	2.45	-0.772
7	0.366	4	0.029	0.240	2.45	-0.672
9	0.228	4	0.039	0.303	2.44	-0.730
11	-0.273	5	0.158	0.731	2.15	-0.245
13	-0.224	6	0.092	0.784	2.00	-0.138
15	0.028	7	0.043	0.328	1.19	0.267
17	-0.064	10	0.010	0.516	1.15	0.123
19	0.092	10	0.027	0.205	0.936	0.280
21	0.276	12	0.003	0.046	0.879	0.292
23	0.282	12	0.003	0.044	0.876	0.295
25	0.283	12	0.003	0.043	0.874	0.294
27	0.283	13	0.002	0.036	0.879	0.291
29	0.118	15	0.004	0.114	0.844	0.238
31	0.117	15	0.004	0.115	0.844	0.237
33	0.138	15	0.004	0.095	0.827	0.247
35	0.135	15	0.005	0.098	0.816	0.245
37	0.185	17	0.003	0.048	0.814	0.262
39	0.185	17	0.003	0.048	0.814	0.262
41	0.188	20	0.003	0.032	0.744	0.267
43	0.273	21	0.003	0.009	0.653	0.313
45	0.007	23	0.001	0.294	1.04	0.159
47	0.022	23	0.001	0.235	1.02	0.174
49	0.056	24	0.001	0.139	0.930	0.212
51	0.049	24	0.001	0.153	0.935	0.207
53	-0.015	26	0.000	0.437	1.01	0.098
55	-0.019	26	0.000	0.476	1.02	0.090
57	-0.010	28	0.000	0.397	1.02	0.099
59	-0.012	29	0.000	0.421	0.989	0.096
61	-0.007	29	0.000	0.378	0.975	0.107
63	-0.014	29	0.000	0.438	0.990	0.096
65	-0.013	29	0.000	0.434	0.993	0.097
67	0.010	30	0.002	0.263	0.880	0.142
69	0.008	30	0.002	0.276	0.888	0.138

Table S2. (continued) Measures of model fit and coefficients in simple linear regression model between tetrachloroethylene (PCE) concentrations in all tree-core and groundwater samples. Shallow (<20 m) and deep (≥20 m) groundwater samples are combined in these models.

Buffer distance, in meters	Adjusted R^2 for PCE	Sample Size	P-Values		Model Coefficients	
			Intercept	Log C_{Tree}	Intercept	Log C_{Tree}
71	0.007	30	0.002	0.281	0.890	0.137
73	0.009	31	0.001	0.270	0.909	0.138
75	-0.016	31	0.000	0.475	0.989	0.090
77	-0.007	31	0.001	0.385	0.955	0.111
79	-0.010	31	0.001	0.408	0.954	0.113
81	-0.006	32	0.001	0.372	0.952	0.125
83	-0.003	34	0.001	0.352	0.953	0.119
85	0.005	34	0.001	0.287	0.922	0.136
87	0.005	34	0.001	0.288	0.923	0.136
89	0.009	34	0.001	0.260	0.909	0.144
91	-0.004	34	0.001	0.359	0.957	0.121
93	-0.001	34	0.001	0.333	0.945	0.130
95	-0.010	34	0.001	0.421	0.973	0.118
97	-0.013	34	0.001	0.456	0.987	0.110
99	0.053	36	0.003	0.094	0.858	0.242
101	0.055	36	0.003	0.090	0.853	0.245
103	0.059	36	0.003	0.082	0.846	0.251
105	0.053	36	0.002	0.095	0.871	0.239
107	0.058	36	0.004	0.084	0.845	0.253
109	0.145	38	0.010	0.011	0.726	0.356
111	0.160	38	0.013	0.007	0.696	0.374
113	0.157	38	0.012	0.008	0.704	0.370
115	0.164	38	0.012	0.007	0.696	0.382
117	0.160	38	0.013	0.007	0.696	0.381
119	0.159	38	0.012	0.008	0.701	0.379
121	0.166	38	0.013	0.006	0.692	0.386
123	0.158	41	0.001	0.006	0.819	0.330
125	0.097	42	0.000	0.025	0.958	0.269
127	0.095	42	0.000	0.027	0.965	0.267
129	0.122	43	0.000	0.012	0.907	0.295
131	0.117	43	0.000	0.014	0.921	0.288
133	0.117	43	0.000	0.014	0.921	0.289
135	0.115	43	0.000	0.015	0.924	0.288
137	0.116	43	0.000	0.014	0.921	0.289
139	0.114	43	0.000	0.015	0.926	0.285
141	0.102	43	0.000	0.021	0.947	0.272
143	0.099	43	0.000	0.022	0.952	0.269

Table S3. Model fits and coefficients for multiple linear regression between tetrachloroethylene (PCE) concentrations in all tree-core and groundwater samples. Shallow (<20 m) and deep (≥20 m) groundwater samples are combined in these models.

Buffer distance, in meters	Adjusted R^2 for PCE	Sample Size	P-Values			Model Coefficients		
			Intercept	Log C_{Tree}	Tree Diameter	Intercept	Log C_{Tree}	Tree Diameter
1	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-
17	0.217	5	0.661	0.303	0.232	0.644	1.79	-0.143
19	0.263	6	0.957	0.185	0.153	0.071	2.16	-0.146
21	0.138	7	0.052	0.809	0.270	1.91	0.072	-0.018
23	-0.191	10	0.037	0.594	0.715	1.28	0.109	-0.006
25	-0.028	10	0.079	0.264	0.801	1.02	0.268	-0.004
27	0.199	12	0.035	0.077	0.831	0.944	0.283	-0.003
29	0.206	12	0.035	0.074	0.834	0.939	0.286	-0.003
31	0.207	12	0.036	0.073	0.841	0.935	0.285	-0.002
33	0.216	13	0.024	0.059	0.808	0.949	0.282	-0.003
35	0.076	15	0.023	0.175	0.534	1.05	0.214	-0.008
37	0.075	15	0.024	0.176	0.536	1.05	0.213	-0.008
39	0.094	15	0.026	0.151	0.554	1.02	0.224	-0.008
41	0.098	15	0.024	0.145	0.505	1.03	0.223	-0.008
43	0.130	17	0.020	0.059	0.826	0.866	0.259	-0.002
45	0.130	17	0.020	0.059	0.824	0.867	0.259	-0.002
47	0.149	20	0.010	0.035	0.692	0.816	0.270	-0.003
49	0.262	21	0.008	0.012	0.414	0.814	0.305	-0.006
51	0.068	23	0.001	0.279	0.140	1.39	0.159	-0.014
53	0.090	23	0.000	0.202	0.125	1.37	0.181	-0.014
55	0.120	24	0.001	0.121	0.121	1.29	0.216	-0.015
57	0.109	24	0.001	0.142	0.130	1.30	0.206	-0.014
59	0.094	26	0.000	0.227	0.060	1.39	0.149	-0.016
61	0.086	26	0.000	0.262	0.064	1.39	0.138	-0.016
63	0.075	28	0.000	0.204	0.078	1.34	0.148	-0.014
65	0.032	29	0.000	0.264	0.148	1.25	0.134	-0.011
67	0.041	29	0.000	0.224	0.138	1.24	0.150	-0.012
69	0.030	29	0.000	0.277	0.150	1.24	0.136	-0.011

Table S3. (continued) Model fits and coefficients for multiple linear regression between tetrachloroethylene (PCE) concentrations in all tree-core and groundwater samples. Shallow (<20 m) and deep (≥20 m) groundwater samples are combined in these models.

Buffer distance, in meters	Adjusted R^2 for PCE	Sample Size	P-Values			Model Coefficients		
			Intercept	Log C_{Tree}	Tree Diameter	Intercept	Log C_{Tree}	Tree Diameter
71	0.030	29	0.000	0.272	0.149	1.25	0.137	-0.011
73	0.099	30	0.000	0.112	0.063	1.18	0.201	-0.014
75	0.096	30	0.000	0.118	0.064	1.19	0.198	-0.014
77	0.094	30	0.000	0.123	0.066	1.19	0.195	-0.014
79	0.105	31	0.000	0.118	0.052	1.22	0.193	-0.014
81	0.072	31	0.000	0.231	0.063	1.28	0.150	-0.014
83	0.088	31	0.000	0.167	0.055	1.25	0.176	-0.014
85	0.083	31	0.000	0.183	0.057	1.24	0.181	-0.014
87	0.089	32	0.000	0.158	0.052	1.24	0.197	-0.014
89	0.101	34	0.000	0.130	0.037	1.25	0.193	-0.014
91	0.113	34	0.000	0.100	0.034	1.22	0.209	-0.014
93	0.114	34	0.000	0.099	0.034	1.22	0.210	-0.014
95	0.119	34	0.000	0.088	0.033	1.21	0.216	-0.015
97	0.088	34	0.000	0.174	0.048	1.26	0.177	-0.013
99	0.088	34	0.000	0.176	0.051	1.25	0.177	-0.013
101	0.072	34	0.000	0.251	0.059	1.27	0.165	-0.013
103	0.067	34	0.000	0.282	0.061	1.29	0.155	-0.013
105	0.058	36	0.002	0.058	0.285	1.02	0.287	-0.008
107	0.061	36	0.002	0.055	0.282	1.02	0.289	-0.008
109	0.066	36	0.002	0.049	0.272	1.01	0.297	-0.008
111	0.054	36	0.002	0.063	0.311	1.03	0.277	-0.007
113	0.065	36	0.002	0.050	0.271	1.01	0.301	-0.008
115	0.163	38	0.004	0.005	0.191	0.936	0.399	-0.009
117	0.179	38	0.005	0.004	0.186	0.908	0.416	-0.009
119	0.175	38	0.005	0.004	0.187	0.916	0.412	-0.009
121	0.183	38	0.005	0.003	0.189	0.908	0.422	-0.009
123	0.181	38	0.005	0.004	0.176	0.911	0.425	-0.009
125	0.180	38	0.005	0.004	0.179	0.915	0.423	-0.009
127	0.187	38	0.005	0.003	0.174	0.908	0.430	-0.009
129	0.167	41	0.001	0.004	0.237	1.04	0.343	-0.007
131	0.105	42	0.000	0.019	0.250	1.18	0.283	-0.008
133	0.104	42	0.000	0.020	0.240	1.19	0.283	-0.008
135	0.125	43	0.000	0.009	0.293	1.10	0.314	-0.007
137	0.120	43	0.000	0.010	0.287	1.12	0.308	-0.007
139	0.121	43	0.000	0.010	0.287	1.12	0.308	-0.007
141	0.119	43	0.000	0.010	0.290	1.12	0.307	-0.007
143	0.119	43	0.000	0.010	0.297	1.11	0.307	-0.007
145	0.116	43	0.000	0.011	0.296	1.12	0.304	-0.007
147	0.104	43	0.000	0.015	0.301	1.14	0.291	-0.007
149	0.101	43	0.000	0.016	0.311	1.14	0.287	-0.007

Table S4. Measures of model fit and parameter coefficients in simple linear regression models between tetrachloroethylene (PCE) concentrations in tree-core and shallow (<20 m) and deep (≥20 m) groundwater samples.

Buffer distance, in meters	Adjusted R^2 for PCE	Sample Size	P-Values		Model Coefficients		Adjusted R^2 for PCE	Sample Size	P-Values		Model Coefficients	
			Intercept	Log C_{Tree}	Intercept	Log C_{Tree}			Intercept	Log C_{Tree}	Intercept	Log C_{Tree}
	Shallow Groundwater						Deep Groundwater					
1	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-	-	-	-	-
19	-0.863	3	0.004	0.831	1.78	0.001	-	-	-	-	-	-
21	-0.795	3	0.004	0.793	1.78	0.002	-0.252	4	0.259	0.594	1.12	0.272
23	0.778	4	0.026	0.077	1.08	0.353	-0.243	6	0.109	0.888	1.10	0.041
25	0.703	4	0.067	0.104	0.928	0.420	-0.130	6	0.168	0.551	0.900	0.204
27	0.812	5	0.007	0.024	0.967	0.331	0.031	7	0.082	0.325	0.828	0.248
29	0.828	5	0.006	0.021	0.960	0.332	0.032	7	0.081	0.323	0.829	0.250
31	0.837	5	0.006	0.019	0.956	0.332	0.032	7	0.082	0.324	0.828	0.249
33	0.782	6	0.002	0.012	0.951	0.319	0.026	7	0.081	0.330	0.832	0.247
35	0.744	7	0.001	0.008	0.876	0.345	-0.110	8	0.105	0.599	0.810	0.140
37	0.744	7	0.001	0.008	0.876	0.345	-0.109	8	0.106	0.597	0.809	0.140
39	0.754	7	0.001	0.007	0.872	0.344	-0.091	8	0.113	0.543	0.783	0.160
41	0.525	7	0.008	0.040	0.873	0.307	-0.077	8	0.109	0.505	0.773	0.172
43	0.537	9	0.002	0.015	0.884	0.298	-0.076	8	0.109	0.504	0.773	0.172
45	0.537	9	0.002	0.015	0.884	0.298	-0.077	8	0.109	0.505	0.773	0.172
47	0.587	10	0.001	0.006	0.824	0.319	-0.030	10	0.094	0.417	0.694	0.179
49	0.671	11	0.004	0.001	0.631	0.407	-0.018	10	0.091	0.385	0.686	0.190
51	0.668	11	0.004	0.001	0.633	0.406	-0.093	12	0.012	0.806	1.34	-0.068
53	0.675	11	0.004	0.001	0.633	0.390	-0.098	12	0.013	0.900	1.30	-0.035
55	0.722	12	0.005	0.000	0.528	0.446	-0.098	12	0.013	0.900	1.30	-0.034
57	0.723	12	0.005	0.000	0.527	0.446	-0.096	12	0.012	0.845	1.32	-0.053
59	0.606	13	0.009	0.001	0.557	0.365	-0.027	13	0.006	0.427	1.42	-0.182
61	0.611	13	0.009	0.001	0.554	0.366	-0.014	13	0.005	0.381	1.45	-0.200
63	0.608	15	0.004	0.000	0.569	0.349	-0.014	13	0.005	0.381	1.45	-0.200
65	0.611	15	0.004	0.000	0.568	0.350	0.002	14	0.005	0.330	1.40	-0.223
67	0.595	15	0.003	0.000	0.594	0.351	-0.017	14	0.007	0.394	1.37	-0.199
69	0.595	15	0.003	0.000	0.594	0.351	0.011	14	0.006	0.307	1.45	-0.246

Table S4. (continued) Measures of model fit and parameter coefficients in simple linear regression models between tetrachloroethylene (PCE) concentrations in tree-core and shallow (<20 m) and deep (≥20 m) groundwater samples.

Buffer distance, in meters	**Adjusted R^2 for PCE**	**Sample Size**	**P-Values**		**Model Coefficients**		**Adjusted R^2 for PCE**	**Sample Size**	**P-Values**		**Model Coefficients**	
			Intercept	**Log C_{Tree}**	**Intercept**	**Log C_{Tree}**			**Intercept**	**Log C_{Tree}**	**Intercept**	**Log C_{Tree}**
	Shallow Groundwater						**Deep Groundwater**					
71	0.585	15	0.002	0.001	0.612	0.350	0.001	14	0.006	0.335	1.42	-0.228
73	0.534	15	0.005	0.001	0.606	0.348	-0.058	15	0.021	0.635	1.22	-0.114
75	0.516	15	0.004	0.002	0.621	0.344	-0.058	15	0.021	0.633	1.22	-0.115
77	0.513	15	0.004	0.002	0.624	0.343	-0.056	15	0.021	0.624	1.23	-0.118
79	0.517	16	0.003	0.001	0.634	0.349	-0.049	15	0.017	0.565	1.26	-0.139
81	0.484	16	0.005	0.002	0.634	0.345	-0.001	15	0.007	0.340	1.38	-0.223
83	0.445	16	0.004	0.003	0.670	0.339	-0.039	15	0.015	0.505	1.29	-0.160
85	0.436	16	0.006	0.003	0.642	0.357	-0.034	15	0.015	0.474	1.33	-0.184
87	0.460	17	0.008	0.002	0.613	0.383	-0.024	15	0.015	0.427	1.37	-0.214
89	0.371	19	0.005	0.003	0.657	0.324	-0.023	15	0.014	0.421	1.38	-0.215
91	0.372	19	0.005	0.003	0.656	0.324	-0.042	15	0.021	0.522	1.31	-0.173
93	0.364	19	0.005	0.004	0.663	0.322	-0.044	15	0.021	0.536	1.30	-0.166
95	0.385	19	0.006	0.003	0.647	0.326	-0.044	15	0.021	0.533	1.30	-0.170
97	0.354	19	0.004	0.004	0.678	0.329	-0.031	15	0.017	0.461	1.35	-0.201
99	0.401	19	0.005	0.002	0.647	0.354	-0.031	15	0.017	0.461	1.35	-0.201
101	0.417	19	0.013	0.002	0.581	0.421	-0.033	15	0.017	0.472	1.34	-0.197
103	0.369	19	0.012	0.003	0.614	0.404	-0.037	15	0.018	0.492	1.32	-0.187
105	0.339	19	0.008	0.005	0.653	0.386	-0.046	17	0.072	0.591	1.01	0.140
107	0.346	19	0.008	0.005	0.649	0.387	-0.045	17	0.072	0.584	1.01	0.142
109	0.346	19	0.008	0.005	0.649	0.387	-0.042	17	0.072	0.558	0.995	0.152
111	0.299	19	0.004	0.009	0.712	0.359	-0.042	17	0.072	0.558	0.995	0.152
113	0.355	19	0.008	0.004	0.643	0.400	-0.043	17	0.077	0.570	0.997	0.149
115	0.356	19	0.011	0.004	0.625	0.408	0.057	19	0.126	0.167	0.810	0.323
117	0.379	19	0.010	0.003	0.616	0.414	0.069	19	0.148	0.145	0.766	0.346
119	0.359	19	0.009	0.004	0.636	0.402	0.069	19	0.148	0.144	0.767	0.346
121	0.341	19	0.009	0.005	0.643	0.404	0.083	19	0.149	0.123	0.746	0.365
123	0.317	19	0.012	0.007	0.644	0.401	0.083	19	0.149	0.123	0.747	0.365
125	0.311	19	0.011	0.008	0.653	0.397	0.084	19	0.146	0.122	0.749	0.365
127	0.297	19	0.010	0.009	0.668	0.388	0.096	19	0.155	0.106	0.724	0.380
129	0.155	21	0.000	0.044	0.922	0.255	0.130	20	0.093	0.066	0.736	0.378
131	0.153	21	0.000	0.045	0.920	0.257	0.046	21	0.020	0.178	1.02	0.266
133	0.140	21	0.000	0.053	0.935	0.251	0.046	21	0.020	0.178	1.02	0.266
135	0.232	22	0.000	0.014	0.816	0.317	0.046	21	0.019	0.177	1.02	0.267
137	0.221	22	0.000	0.016	0.832	0.311	0.042	21	0.017	0.187	1.03	0.259
139	0.223	22	0.000	0.015	0.830	0.311	0.042	21	0.017	0.186	1.03	0.259
141	0.212	22	0.000	0.018	0.837	0.309	0.042	21	0.017	0.186	1.03	0.259
143	0.220	22	0.000	0.016	0.827	0.313	0.042	21	0.017	0.187	1.04	0.259
145	0.216	22	0.000	0.017	0.831	0.310	0.040	21	0.016	0.192	1.04	0.255
147	0.216	22	0.000	0.017	0.832	0.309	0.026	21	0.013	0.229	1.08	0.235
149	0.217	22	0.000	0.017	0.829	0.307	0.024	21	0.011	0.236	1.09	0.231

Table S5. Measures of model fit and parameter coefficients in multiple linear regression models between tetrachloroethylene (PCE) concentrations in tree-core and shallow (<20 m) and deep (≥ 20 m) groundwater samples.

Buffer distance, in meters	Adjusted R^2 for PCE	Sample Size	P-Values			Model Coefficients			Adjusted R^2 for PCE	Sample Size	P-Values			Model Coefficients		
			Intercept	Log C_{Tree}	Tree Diameter	Intercept	Log C_{Tree}	Tree Diameter			Intercept	Log C_{Tree}	Tree Diameter	Intercept	Log C_{Tree}	Tree Diameter
	Shallow Groundwater								Deep Groundwater							
1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-	-	-0.727	4	0.439	0.947	0.624	2.21	-0.059	-0.024
23	0.969	4	0.043	0.068	0.169	1.29	0.478	-0.026	-0.605	6	0.252	0.999	0.774	1.33	0.000	-0.008
25	0.981	4	0.041	0.054	0.115	1.09	0.631	-0.033	-0.497	6	0.364	0.674	0.896	1.00	0.182	-0.003
27	0.788	5	0.047	0.056	0.501	1.13	0.333	-0.010	-0.210	7	0.301	0.440	0.961	0.859	0.242	-0.001
29	0.805	5	0.045	0.052	0.505	1.12	0.333	-0.009	-0.209	7	0.298	0.438	0.958	0.862	0.243	-0.001
31	0.814	5	0.044	0.049	0.509	1.11	0.333	-0.009	-0.210	7	0.300	0.439	0.960	0.860	0.242	-0.001
33	0.812	6	0.011	0.017	0.291	1.16	0.328	-0.012	-0.216	7	0.297	0.446	0.955	0.867	0.240	-0.001
35	0.827	7	0.004	0.006	0.139	1.18	0.348	-0.015	-0.294	8	0.232	0.757	0.717	1.05	0.096	-0.008
37	0.827	7	0.004	0.006	0.139	1.18	0.348	-0.015	-0.293	8	0.234	0.756	0.718	1.05	0.097	-0.008
39	0.830	7	0.004	0.006	0.147	1.17	0.346	-0.015	-0.278	8	0.252	0.698	0.741	1.00	0.120	-0.007
41	0.622	7	0.015	0.031	0.206	1.23	0.324	-0.019	-0.261	8	0.241	0.645	0.739	0.980	0.137	-0.007
43	0.461	9	0.010	0.026	0.896	0.902	0.300	-0.001	-0.261	8	0.242	0.645	0.741	0.979	0.137	-0.007
45	0.461	9	0.010	0.026	0.896	0.902	0.300	-0.001	-0.261	8	0.241	0.645	0.740	0.980	0.137	-0.007
47	0.528	10	0.006	0.012	0.995	0.824	0.319	0.000	-0.165	10	0.189	0.459	0.787	0.805	0.175	-0.004
49	0.681	11	0.007	0.002	0.289	0.810	0.395	-0.006	-0.148	10	0.180	0.423	0.773	0.801	0.187	-0.004
51	0.678	11	0.007	0.002	0.288	0.813	0.394	-0.006	-0.077	12	0.015	0.890	0.312	1.75	-0.038	-0.018
53	0.722	11	0.003	0.001	0.150	0.851	0.385	-0.008	-0.080	12	0.015	0.981	0.307	1.72	-0.006	-0.018
55	0.731	12	0.009	0.000	0.274	0.714	0.436	-0.007	-0.080	12	0.015	0.987	0.307	1.71	0.004	-0.018
57	0.733	12	0.009	0.000	0.275	0.712	0.436	-0.007	-0.079	12	0.015	0.926	0.310	1.73	-0.025	-0.018
59	0.650	13	0.005	0.001	0.154	0.778	0.378	-0.008	0.045	13	0.005	0.712	0.205	1.83	-0.085	-0.020
61	0.653	13	0.005	0.001	0.156	0.774	0.378	-0.008	0.054	13	0.004	0.635	0.210	1.85	-0.109	-0.020
63	0.645	15	0.002	0.000	0.150	0.749	0.367	-0.007	0.054	13	0.004	0.636	0.210	1.85	-0.108	-0.020
65	0.647	15	0.002	0.000	0.151	0.746	0.367	-0.007	0.006	14	0.006	0.491	0.330	1.70	-0.162	-0.015
67	0.648	15	0.001	0.000	0.110	0.790	0.376	-0.008	-0.008	14	0.008	0.564	0.315	1.68	-0.138	-0.015
69	0.648	15	0.001	0.000	0.110	0.790	0.376	-0.008	0.017	14	0.006	0.440	0.322	1.76	-0.189	-0.015

Table S5. (continued) Measures of model fit and parameter coefficients in multiple linear regression models between tetrachloroethylene (PCE) concentrations in tree-core and shallow (<20 m) and deep (≥ 20 m) groundwater samples.

Buffer distance, in meters	Adjusted R^2 for PCE	Sample Size	P-Values			Model Coefficients			Adjusted R^2 for PCE	Sample Size	P-Values			Model Coefficients		
			Intercept	Log C_{Tree}	Tree Diameter	Intercept	Log C_{Tree}	Tree Diameter			Intercept	Log C_{Tree}	Tree Diameter	Intercept	Log C_{Tree}	Tree Diameter
	Shallow Groundwater								Deep Groundwater							
71	0.629	15	0.001	0.000	0.137	0.801	0.372	-0.008	0.006	14	0.007	0.490	0.325	1.72	-0.167	-0.015
73	0.598	15	0.002	0.000	0.105	0.810	0.382	-0.009	0.016	15	0.010	0.911	0.186	1.59	-0.027	-0.018
75	0.579	15	0.002	0.001	0.112	0.826	0.378	-0.009	0.015	15	0.010	0.913	0.186	1.59	-0.026	-0.018
77	0.576	15	0.002	0.001	0.112	0.829	0.377	-0.009	0.016	15	0.010	0.888	0.187	1.60	-0.034	-0.018
79	0.591	16	0.001	0.000	0.083	0.845	0.377	-0.009	0.018	15	0.009	0.830	0.194	1.62	-0.052	-0.018
81	0.570	16	0.001	0.001	0.073	0.850	0.380	-0.010	0.043	15	0.005	0.561	0.229	1.71	-0.138	-0.016
83	0.552	16	0.001	0.001	0.058	0.896	0.387	-0.011	0.024	15	0.008	0.744	0.200	1.65	-0.078	-0.017
85	0.537	16	0.001	0.001	0.065	0.862	0.406	-0.011	0.026	15	0.008	0.707	0.204	1.68	-0.096	-0.017
87	0.568	17	0.001	0.000	0.046	0.835	0.437	-0.011	0.032	15	0.008	0.647	0.210	1.71	-0.123	-0.017
89	0.519	19	0.000	0.000	0.024	0.905	0.385	-0.012	0.034	15	0.008	0.635	0.210	1.72	-0.127	-0.017
91	0.520	19	0.000	0.000	0.024	0.905	0.385	-0.012	0.024	15	0.010	0.742	0.196	1.67	-0.088	-0.017
93	0.511	19	0.000	0.000	0.025	0.911	0.384	-0.012	0.022	15	0.010	0.765	0.195	1.66	-0.080	-0.018
95	0.533	19	0.000	0.000	0.022	0.896	0.387	-0.012	0.023	15	0.010	0.755	0.195	1.67	-0.084	-0.017
97	0.432	19	0.001	0.002	0.086	0.905	0.360	-0.009	0.029	15	0.009	0.684	0.205	1.69	-0.111	-0.017
99	0.461	19	0.002	0.001	0.108	0.865	0.374	-0.008	0.029	15	0.009	0.684	0.205	1.69	-0.111	-0.017
101	0.464	19	0.005	0.001	0.135	0.789	0.437	-0.008	0.027	15	0.009	0.696	0.203	1.69	-0.106	-0.017
103	0.410	19	0.005	0.002	0.160	0.819	0.418	-0.008	0.026	15	0.009	0.715	0.200	1.68	-0.099	-0.017
105	0.378	19	0.004	0.004	0.170	0.857	0.402	-0.008	-0.107	17	0.082	0.523	0.693	1.11	0.190	-0.006
107	0.384	19	0.004	0.003	0.170	0.853	0.402	-0.008	-0.106	17	0.081	0.515	0.688	1.11	0.193	-0.006
109	0.384	19	0.004	0.003	0.170	0.853	0.402	-0.008	-0.101	17	0.080	0.486	0.670	1.10	0.208	-0.006
111	0.311	19	0.004	0.009	0.270	0.898	0.362	-0.006	-0.101	17	0.080	0.486	0.670	1.10	0.208	-0.006
113	0.399	19	0.004	0.003	0.154	0.850	0.418	-0.008	-0.104	17	0.084	0.501	0.681	1.10	0.203	-0.006
115	0.394	19	0.005	0.003	0.169	0.828	0.423	-0.008	0.035	19	0.095	0.127	0.443	1.02	0.387	-0.011
117	0.415	19	0.005	0.002	0.172	0.817	0.426	-0.007	0.050	19	0.107	0.108	0.426	0.985	0.414	-0.011
119	0.394	19	0.005	0.003	0.179	0.837	0.415	-0.007	0.051	19	0.106	0.108	0.424	0.986	0.414	-0.011
121	0.385	19	0.004	0.003	0.156	0.850	0.422	-0.008	0.062	19	0.111	0.096	0.444	0.967	0.422	-0.010
123	0.372	19	0.004	0.004	0.134	0.855	0.428	-0.008	0.062	19	0.111	0.096	0.444	0.968	0.422	-0.010
125	0.362	19	0.004	0.004	0.144	0.862	0.422	-0.008	0.063	19	0.109	0.095	0.441	0.971	0.423	-0.010
127	0.347	19	0.004	0.005	0.148	0.877	0.414	-0.008	0.077	19	0.112	0.082	0.429	0.952	0.438	-0.011
129	0.174	21	0.000	0.044	0.248	1.14	0.253	-0.007	0.109	20	0.082	0.058	0.460	0.984	0.403	-0.009
131	0.172	21	0.000	0.045	0.247	1.13	0.255	-0.007	0.020	21	0.029	0.155	0.486	1.26	0.291	-0.009
133	0.166	21	0.000	0.048	0.225	1.15	0.253	-0.007	0.020	21	0.029	0.156	0.487	1.26	0.290	-0.009
135	0.225	22	0.001	0.012	0.373	0.963	0.328	-0.005	0.021	21	0.028	0.154	0.485	1.27	0.291	-0.009
137	0.214	22	0.001	0.014	0.370	0.981	0.322	-0.005	0.017	21	0.026	0.161	0.480	1.28	0.285	-0.009
139	0.217	22	0.001	0.013	0.364	0.981	0.324	-0.005	0.017	21	0.026	0.161	0.483	1.28	0.285	-0.009
141	0.206	22	0.001	0.016	0.373	0.986	0.321	-0.005	0.017	21	0.026	0.161	0.483	1.28	0.285	-0.009
143	0.210	22	0.001	0.015	0.393	0.971	0.323	-0.005	0.017	21	0.026	0.161	0.481	1.28	0.285	-0.009
145	0.207	22	0.001	0.015	0.390	0.976	0.320	-0.005	0.015	21	0.025	0.165	0.481	1.29	0.282	-0.009
147	0.207	22	0.001	0.015	0.389	0.977	0.319	-0.005	0.000	21	0.022	0.197	0.488	1.32	0.262	-0.009
149	0.206	22	0.001	0.016	0.409	0.969	0.315	-0.005	-0.002	21	0.021	0.203	0.490	1.34	0.259	-0.009

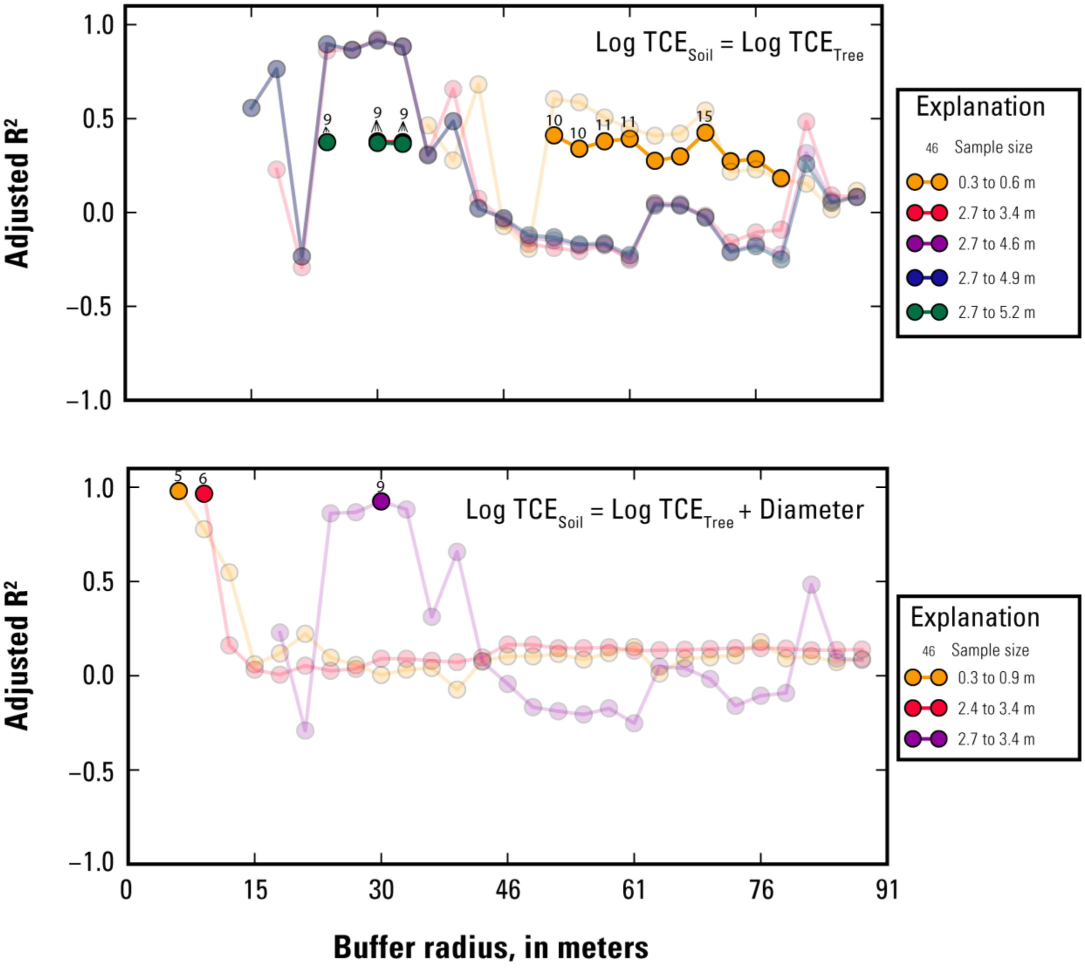


Figure S3. Measures of model fit in a) simple linear regression (SLR) and b) multiple linear regression (MLR) models between TCE in soil and tree-core samples with at least one significant model with an adjusted R^2 value above 0.3. Soil samples used in each model were located within a constant buffer radius around each tree. Transparent markers indicate insignificant models (p-value > 0.05) and opaque markers indicate significant (p-value ≤ 0.05) models. Values adjacent to symbols indicate sample size

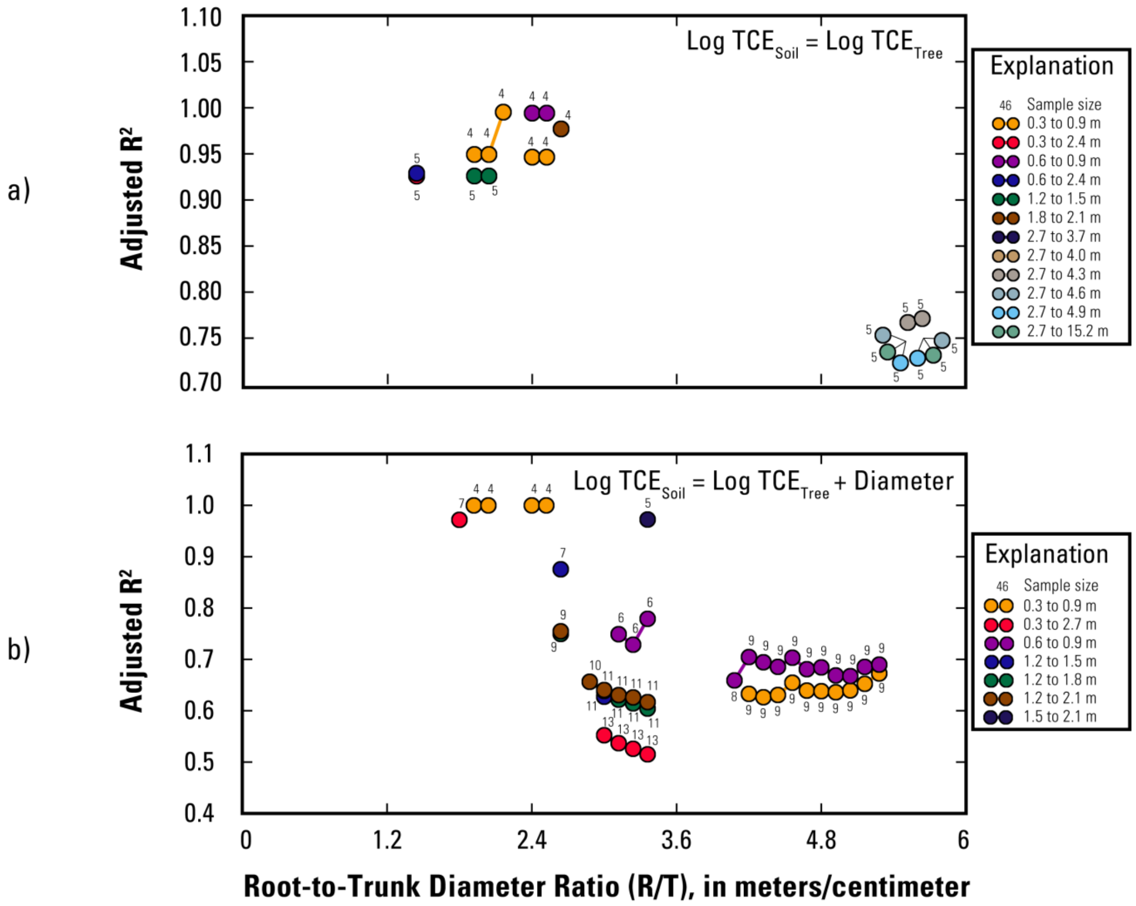
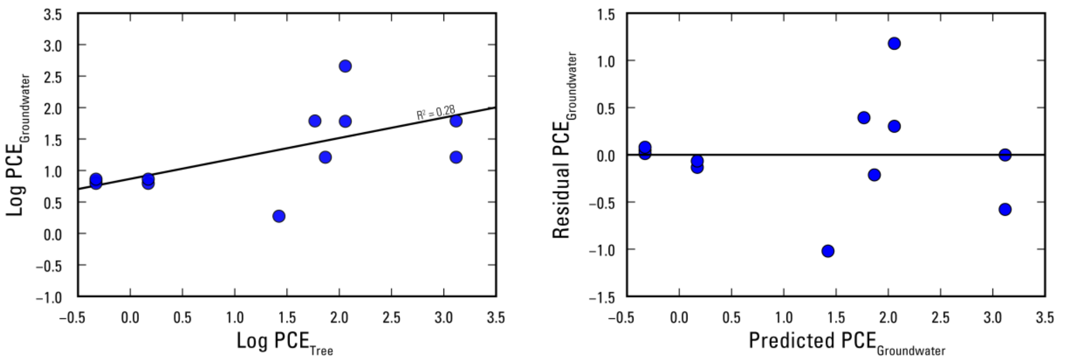
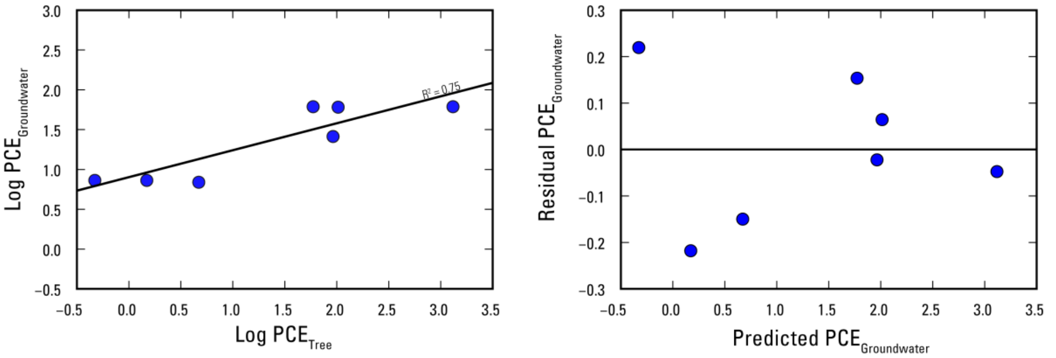


Figure S4. Measures of model fit in a) simple linear regression (SLR) and b) multiple linear regression (MLR) models between trichloroethylene (TCE) in soil and tree-core samples with at least one significant model with an adjusted R^2 value above 0.4Soil samples used in each model were located within a hypothetical diameter-dependent buffer distance radius around each tree. Values adjacent to symbols indicate sample size



Simple linear regression with shallow and deep groundwater



Simple linear regression with shallow groundwater

Figure S5. Simple linear regression models and model residuals between tetrachloroethylene (PCE) in shallow (< 20 meters below ground surface) and deep (> 20 meters below ground surface) groundwater and trees within 39 meters of wells.

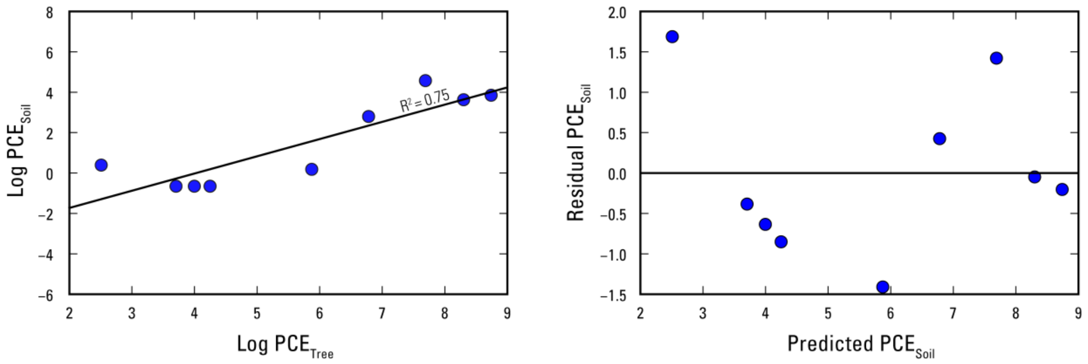


Figure S6. Simple linear regression model and model residuals between tetrachloroethylene (PCE) in soil and tree-core samples. All soil samples were located within 0.3 to 0.9 meters below ground surface and within a trunk-to-root ratio of 1.2 meter/centimeter around each tree.

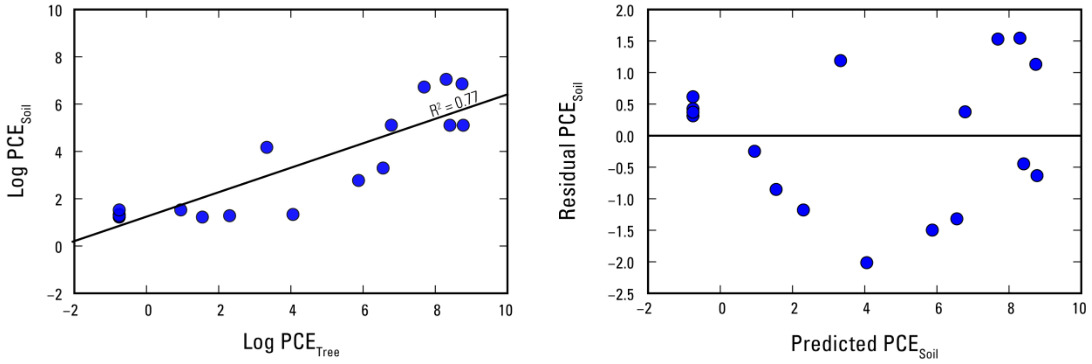


Figure S7. Simple linear regression model and model residuals between tetrachloroethylene (PCE) in soil and tree-core samples. All soil samples were located within 1.8 to 2.1 meters below ground surface and within a trunk-to-root ratio of 2.2 meters/centimeter around each tree.

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under grant no. #1336877. Support was given by the United States Environmental Protection Agency Region 7, with special assistance from Hoai Tran. Special thanks to D. Charlie Smith, Cory Pollpeter, and Paul Brenden of the USGS and Dr. Honglan Shi, Eric Fallon, Rahul Sukharia, and Tommy Goodwin with the Environmental Engineering

Program and the Center for Research in Energy and Environment at Missouri S&T. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

REFERENCES

1. USEPA Superfund: National Priorities List (NPL). https://www.epa.gov/superfund/superfund-national-priorities-list-npl (July, 2017).

2. USEPA Superfund Enterprise Management System (SEMS). http://cumulis.epa.gov/supercpad/cursites/srchsites.cfm (July 2017).

3. Forand, S. P.; Lewis-Michl, E. L.; Gomez, M. I., Adverse birth outcomes and maternal exposure to trichloroethylene and tetrachloroethylene through soil vapor intrusion in New York State. *Environ Health Perspect* **2012,** *120*, (4), 616-21. DOI: 10.1289/ehp.1103884.

4. USEPA, Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air. In Office of Solid Waste and Emergency Response, Ed. 2015; p 267.

5. Little, J. C.; Daisey, J. M.; Nazaroff, W. W., Transport of subsurface contaminants into buildings. *Environmental Science & Technology* **1992,** *26*, (11), 2058-2066. DOI: 10.1021/es00035a001.

6. Moseley, C. L.; Meyer, M. R., Petroleum contamination of an elementary school: a case history involving air, soil-gas, and groundwater monitoring. *Environmental Science & Technology* **1992,** *26*, (1), 185-192. DOI: 10.1021/es00025a023.

7. USEPA National Primary Drinking Water Regulations. https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations (April 2017).

8. USEPA Vapor Intrusion Screening Level (VISL) Calculator https://www.epa.gov/vaporintrusion/vapor-intrusion-screening-levels-visls (April 2017).

9. Fitzgerald, J., One regulatory perspective on the vapor intrusion pathway. *Groundwater Monitoring & Remediation* **2009,** *29*, (1), 51-52. DOI: 10.1111/j.1745-6592.2008.01213.x.

10. McAlary, T.; Ettinger, R.; Johnson, P.; Eklund, B.; Hayes, H.; Chadwick, D.; Rivera-Duarte, I. *Review of Best Practices, Knowledge and Data Gaps, and Research Opportunities for the US Department of Navy Vapor Intrusion Focus Areas*; DTIC Document: 2009.

11. MDHSS, Public health assessment: Vienna Wells, Maries County, Missouri. In 2015; p 84.

12. Briggs, G. G.; Bromilow, R. H.; Evans, A. A., Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pesticide Science* **1982,** *13,* (5), 495-504. DOI: 10.1002/ps.2780130506.

13. Burken, J. G.; Schnoor, J. L., Predictive Relationships for Uptake of Organic Contaminants by Hybrid Poplar Trees. *Environmental Science & Technology* **1998,** *32,* (21), 3379-3385. DOI: 10.1021/es9706817.

14. Cressie, N., Spatial prediction and ordinary kriging. *Mathematical Geology* **1988,** *20,* (4), 405-421. DOI: 10.1007/bf00892986.

15. Dettenmaier, E. M.; Doucette, W. J.; Bugbee, B., Chemical Hydrophobicity and Uptake by Plant Roots. *Environmental Science & Technology* **2009,** *43,* (2), 324-329. DOI: 10.1021/es801751x.

16. Dobson, M. C.; Moffat, A. J., A Re-Evaluation of Objections to Tree Planting On Containment Landfills. *Waste Management & Research* **1995,** *13,* (6), 579-600. DOI: 10.1177/0734242X9501300607.

17. Sorek, A.; Atzmon, N.; Dahan, O.; Gerstl, Z.; Kushisin, L.; Laor, Y.; Mingelgrin, U.; Nasser, A.; Ronen, D.; Tsechansky, L.; Weisbrod, N.; Graber, E. R., “Phytoscreening”: The Use of Trees for Discovering Subsurface Contamination by VOCs. *Environmental Science & Technology* **2007,** *42,* (2), 536-542. DOI: 10.1021/es072014b.

18. Larsen, M.; Burken, J.; Machackova, J.; Karlson, U. G.; Trapp, S., Using Tree Core Samples to Monitor Natural Attenuation and Plume Distribution After a PCE Spill. *Environmental Science & Technology* **2008,** *42,* (5), 1711-1717. DOI: 10.1021/es0717055.

19. Limmer, M. A.; Balouet, J.-C.; Karg, F.; Vroblesky, D. A.; Burken, J. G., Phytoscreening for Chlorinated Solvents Using Rapid in Vitro SPME Sampling: Application to Urban Plume in Verl, Germany. *Environmental Science & Technology* **2011,** *45,* (19), 8276-8282. DOI: 10.1021/es201704v.

20. Schumacher, J. G.; Struckhoff, G. C.; Burken, J. G., *Assessment of Subsurface Chlorinated Solvent Contamination Using Tree Cores at the Front Street Site and a Former Dry Cleaning Facility at the River-front Superfund Site, New Haven, Missouri, 1999-2003*. US Department of the Interior, US Geological Survey: 2004; p 41.

21. Wahyudi, A.; Bogaert, P.; Trapp, S.; Macháčková, J., Pollutant plume delineation from tree core sampling using standardized ranks. *Environmental Pollution* **2012,** *162*, 120-128. DOI: http://dx.doi.org/10.1016/j.envpol.2011.11.010.

22. Vroblesky, D. A., *User's Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds*. 2008; p 59.

23. Trapp, S.; Larsen, M.; Legind, C. N.; Burken, J.; Macháčková, J.; Karlson, U. G. *A guide to vegetation sampling for screening of subsurface pollution*; BIOTOOL Project GOCE003998; European Union Publication: 2012; pp 1-5.

24. Rein, A.; Holm, O.; Trapp, S.; Popp-Hofmann, S.; Bittens, M.; Leven, C.; Dietrich, P., Comparison of Phytoscreening and Direct-Push-Based Site Investigation at a Rural Megasite Contaminated with Chlorinated Ethenes. *Groundwater Monitoring & Remediation* **2015,** *35*, (4), 45-56. DOI: 10.1111/gwmr.12122.

25. Vroblesky, D. A.; Willey, R. E.; Clifford, S.; Murphy, J. J. *Real-Time and Delayed Analysis of Tree and Shrub Cores as Indicators of Subsurface Volatile Organic Compound Contamination, Durham Meadows Superfund Site, Durham, Connecticut, August 29, 2006*; 2007-5212; 2008.

26. Vroblesky, D. A.; Clinton, B. D.; Vose, J. M.; Casey, C. C.; Harvey, G. J.; Bradley, P. M., Ground Water Chlorinated Ethenes in Tree Trunks: Case Studies, Influence of Recharge, and Potential Degradation Mechanism. *Ground Water Monitoring & Remediation* **2004,** *24*, (3), 124-138. DOI: 10.1111/j.1745-6592.2004.tb01299.x.

27. Kuehster, T.; Folkes, D.; Wannamaker, E. In *Seasonal Variation of Observed Indoor Air Concentrations due to Vapor Intrusion*, Midwestern States Risk Assessment Symposium, Indianapolis.(www. envirogroup. com), 2004; 2004.

28. McAlary, T.; Dollar, P.; de Haven, P.; Moss, R.; Wilkinson, G.; Llewellyn, J.; Crump, D. In *Assessment of Subsurface Vapour Transport Through Triassic Sandstone and Quarry Fill into Indoor Air in Weston Village, Runcorn,* Indoor Air, 2002; 2002.

29. Wilson, J. L., Remedial Investigation of the Vienna Wells Site: Maries County, Missouri, 2011-2016. In U.S. Geological Survey, Ed. 2017; p 101.

30. Zandbergen, P. A., Accuracy of iPhone Locations: A Comparison of Assisted GPS, WiFi and Cellular Positioning. *Transactions in GIS* **2009,** *13,* 5-25. DOI: 10.1111/j.1467-9671.2009.01152.x.

31. Ma, X.; Burken, J., Modeling of TCE Diffusion to the Atmosphere and Distribution in Plant Stems. *Environmental Science & Technology* **2004,** *38,* (17), 4580-4586. DOI: 10.1021/es035435b.

32. Baduru, K. K.; Trapp, S.; Burken, J. G., Direct Measurement of VOC Diffusivities in Tree Tissues: Impacts on Tree-Based Phytoremediation and Plant Contamination. *Environmental Science & Technology* **2008,** *42,* (4), 1268-1275. DOI: 10.1021/es071552l.

33. Limmer, M. A.; Holmes, A. J.; Burken, J. G., Phytomonitoring of Chlorinated Ethenes in Trees: A Four-Year Study of Seasonal Chemodynamics in Planta. *Environmental Science & Technology* **2014,** *48,* (18), 10634-10640. DOI: 10.1021/es502680p.

34. Wilde, F.; Radtke, D.; Gibs, J.; Iwatsubo, R., Collection of Water Samples: US Geological Survey Techniques of Water-Resources Investigations. In Book: 1999.

35. Wilde, F. Guidelines for field-measured water-quality properties. v. 2.0. https://water.usgs.gov/owq/FieldManual/Chapter6/Chapter6.0v2.pdf

36. Algreen, M.; Kalisz, M.; Stalder, M.; Martac, E.; Krupanek, J.; Trapp, S.; Bartke, S., Using pre-screening methods for an effective and reliable site characterization at megasites. *Environ Sci Pollut Res* **2015,** *22,* (19), 14673-14686. DOI: 10.1007/s11356-015-4649-6.

37. Wittlingerova, Z.; Machackova, J.; Petruzelkova, A.; Trapp, S.; Vlk, K.; Zima, J., One-year measurements of chloroethenes in tree cores and groundwater at the SAP Mimoň Site, Northern Bohemia. *Environ Sci Pollut Res* **2013,** *20,* (2), 834-847. DOI: 10.1007/s11356-012-1238-9.

38. Struckhoff, G. C.; Burken, J. G.; Schumacher, J. G., Vapor-Phase Exchange of Perchloroethene between Soil and Plants. *Environmental Science & Technology* **2005,** *39,* (6), 1563-1568. DOI: 10.1021/es049411w.

39. Limmer, M. A.; Burken, J. G., Phytoscreening with SPME: Analysis of Variability. *International Journal of Phytoremediation* **2015,** *17*, (11), 1115-1122. DOI: 10.1080/15226514.2015.1045127.

40. USEPA, Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). In Office of Solid Waste and Emergency Response, Ed. 2002.

41. Department of Defense, DoD Vapor Intrusion Handbook. Rev. 4.0, Draft Final. January 2009. In 2009.

42. McAlary, T.; Ettinger, R.; Johnson, P.; Eklund, B.; Hayes, H.; Chadwick, D. B.; Rivera-Duarte, I., Review of best practices, knowledge and data gaps, and research opportunities for the US Department of Navy Vapor Intrusion Focus Areas. In 2009.

43. Interstate Technology Regulatory Council, Vapor Intrusion Pathway: A Practical Guideline. In Washington, DC, 2007.

44. Limmer, M. A.; Shetty, M. K.; Markus, S.; Kroeker, R.; Parker, B. L.; Martinez, C.; Burken, J. G., Directional Phytoscreening: Contaminant Gradients in Trees for Plume Delineation. *Environmental science & technology* **2013,** *47*, (16), 9069-9076. DOI: 10.1021/es400437q.

II. DIRECTIONAL TREE SAMPLING TO LOCATE SOIL AND SOIL-GAS PLUMES WITH APPLICATIONS IN VAPOR INTRUSION

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ABSTRACT

Contaminated sites pose ecological and human-health risks through exposure to contaminated soil and groundwater. Whereas we can readily locate, monitor, and track contaminants in groundwater, it is often harder to perform these tasks in the vadose zone. In this study, tree-core samples were collected at a Superfund site to determine if the sample-collection location around a particular tree could reveal the subsurface location, or direction, of soil and soil-gas contaminant plumes. Contaminant-centroid vectors were calculated from tree-core data to reveal contaminant distributions in directional tree samples at a higher resolution, and vector directions were correlated with soil-gas characterization collected using conventional methods. Results clearly demonstrated that directional tree coring around tree trunks can indicate gradients in soil and soil-gas contaminant plumes, and the strength of the correlations were directly proportionate to the magnitude of tree-core concentration gradients. Given the existing link between soil-gas and vapor intrusion, this study also indicates that directional tree coring might be applicable in vapor intrusion assessment.

INTRODUCTION

Legacy contamination in the United States comprises 1,337 current (2017) Superfund sites with 53 proposed,[1] and in 33 countries in Europe[2] such contamination comprises about 340,000 currently identified sites with an estimated 2.5 million potential contaminated sites. Sites with contaminants can present a human health risk because of exposure to contaminated soil, soil-gas, or groundwater, especially in residential or commercial areas. Whereas we can readily locate, monitor, and track contaminants in groundwater, it is often harder to perform these tasks in the vadose zone.

Because of the large number of contaminated sites, the uncertain behavior of processes that affect contaminant concentrations in the vapor phase is a major hurdle in our understanding of contaminant movement in the subsurface. When faced with the challenge of characterizing subsurface contamination, the conventional approach is to collect soil or soil-gas samples (on the order of thousands of dollars per sample) to provide information on the distribution of contaminants in soil and install temporary piezometers or monitoring wells, which both require drilling equipment (on the order of hundreds to thousands of dollars per location or more), to characterize groundwater contamination extent and direction. These conventional methods are time and cost intensive, require multiple site visits per location, provide information from a relatively small subsurface volume, and large subsurface heterogeneity often confounds delineation of contamination.[3-6] The conventional approach may be appropriate at small scales (on the order of hundreds of m^2) but quickly becomes cost prohibitive to capture the same amount of variation at larger scales, and many chlorinated VOC plumes can be kilometers long. Variations on the conventional methods (such as incremental soil sampling) capture more of the subsurface variation but are time and resource intensive.[7, 8]

Many common contaminants (e.g., PCE, TCE, and benzene) are taken up in the aqueous [9-12] and vapor phase[13] by trees, translocated via xylem, and released into the atmosphere. Samples of tree-cores can be collected in minutes. Unlike conventional sample collection methods used to assess VI, which extrapolate one-dimensional data to two and three dimensions, core samples from trees are thought to provide three-dimensional data through averaging of subsurface contaminant concentrations over large subsurface volumes[14, 15] and long time-scales.[16, 17] With a few exceptions[18-21], xylem on one side of a tree typically derives from similar tissues from roots on the same side,[22-25] and flow is primarily sectorial up the trunk;[26] therefore, tree-core samples collected around the trunk of a particular tree should provide information on plume directionality. It has also been shown in the controlled laboratory setting that tree-core samples provide directional information on concentrations of contaminants in mesocosms relative to the tree when tree-core samples are collected around the trunk radially, a practice termed directional tree coring.[27] Several studies have observed variation in contaminant concentrations in directional tree samples,[10, 15, 20, 28] but directional tree coring was never the focus of the studies and none were able to conclude substantial correlation with groundwater, soil, or soil-gas. One study focused on using directional tree coring to located groundwater contamination but found poor agreement between contaminant gradient directions in groundwater and directional tree cores;[29] however, many of the samples were located in areas with small concentration gradients in groundwater, and directional tree coring may not point to the source of contamination, but rather point across subsurface contaminant gradients. No studies have adequately assessed tree directionality with respect to soil and soil-gas contamination at the field scale, but, if proven to be accurate, tree directionality could have focused applications in soil-gas characterization.

Study Site

To assess the applicability of the directionality of trees with soil and soil-gas contamination in a field setting, the Vienna Wells site, a Superfund site in Vienna, Missouri, was characterized using tree-core, soil, and soil-gas sampling. The site is contaminated primarily by PCE from historical use of chlorinated solvents. The 32,000-m^2 site is composed of a former hat factory building and approximately 16,000 m^2 of heavily wooded area. Overburden near the hat factory is composed primarily of approximately 1 to 5 m thick cherty clay to the west, and less than 1 meter (m) of sandy clay where sandstone outcrops (approximately 160 m) to the east. In 2006, the PCE concentration in one pubic-supply well about 150 m north of the hat factory building exceeded the EPA’s maximum contaminant level of 5.0 µg/L, and a Missouri Department of Natural Resources site investigation concluded that the former hat factory was the likely source of PCE contamination in the public-supply well.[30] Topographic relief across the site is large with about a 30-m decrease in altitude from the western to the eastern property boundary. Depth to groundwater varies from about 11 m near the western boundary to about 9 m near the eastern boundary (Figure 1).

METHODS

Directional sampling for soil gas was assessed at both the site-wide and individual-tree scale at the Vienna Wells site. At the site-wide scale, PCE in soil samples was characterized using traditional direct-push soil-sampling techniques, and directional tree sampling was conducted in several trees across a majority of the site. On the individual-tree scale, soil-gas concentrations were characterized over a small (approximately 1,100 m^2) area to the east of the hat factory property (Figure 1) using equilibrium passive samplers, and directional tree sampling was conducted at a higher resolution. This was done to better capture *in-planta* variation.

Tree-Core Sampling and Analysis

Tree-core samples were collected and analyzed using established methods[31, 32] at the Vienna Wells site on July 29, 2014 (Figure 1) as part of the site-wide assessment and May 21, 2015, as part of an individual-tree assessment. Tree genus (and number of trees sampled, n) sampled during the site-wide study included elm (*Ulmaceae sp.*; n=5), oak (*Quercus sp.*; n=5), sycamore (*Plantanus sp.*; n=1), ash (*Fraxinus sp.*; n=1), and maple (*Acer sp.*; n=1). Tree-core samples were collected at azimuths of 0°, 90°, 180°, and 270° corresponding to the cardinal directions (north, east, south, and west), determined using a compass to an accuracy of +/- 5 degrees. Diameter tape was used to measure the diameter of each tree at breast height to an accuracy of 0.6 cm. Samples were collected with an increment borer and cores were transferred using stainless-steel forceps into a 20-milliliter (mL) glass vial fitted with a Teflon-lined septum cap. After overnight equilibration at room temperature, the headspace in tree-core samples was analyzed for PCE using an Agilent 7890 gas chromatograph (Agilent Technologies, Inc., Santa Clara, California) equipped with a micro-electron-capture detector (µECD) fitted with a CombiPAL solid-phase microextraction (SPME) fiber auto sampler. Equilibrium partitioning coefficients were used to report concentrations in nanograms per liter (ng/L) of sap in tree-core samples.[12] Because the trunk of tree 12 had branched near the ground surface, making it difficult to core the east side, a tree-core at 90°, was not collected. To assess the finer-scale directionality *in-planta*, a 24.3-in oak tree (tree 29, Figure 1) was sampled on May 21, 2015, east of the hat factory property boundary. The tree was sample at azimuths of 0°, 45°, 90°, 135°, 180°, 225°, 270°, and 315° at 0.6, 1.2, and 1.8 m above ground surface.

Soil Sampling and Analysis

A total of 1,016 soil samples were collected across the site from January 2012 to April 2015 from 190 boreholes using a truck-mounted Geoprobe™ (Geoprobe Systems, Salina, Kansas) drill rig (Figure S1). Continuous soil cores were collected using a 50-millimeter by 1.2-m long core barrel fitted with disposal acetate sleeve. A disposable plastic syringe (end removed) was used to collect about 5-cm^3 subsamples at 0.3- or 0.7-m intervals. Soil samples were quickly transferred into a standard 40-mL VOC vial pre-filled with 20-mL of organic free deionized water and heated for 35 minutes to 40 $^{\circ}$C in a heater block. A gas-tight syringe was used to withdraw a 100-µL headspace sample for injection into an Inficon Voyager portable GC (Inficon, Bad Ragaz, Switzerland) equipped with a photo ionization detector (PID). The analysis was run using nitrogen as a carrier gas at a pressure of 55 kilopascals and an oven temperature of 63 °C with a total runtime of 6 minutes. The MDL for PCE was determined to be 11 micrograms per kilogram soil (µg/kg). A total of 51 soil samples were analyzed by a U.S. Geological Survey (USGS) contract lab for analysis of PCE to validate and augment the dataset analyzed by the portable GC. Regression of all 16 samples above the detection limit in both the portable GC and laboratory sample resulted in a significant model with a Pearson's correlation coefficient of 0.89.

Soil-Gas Sampling and Analysis

To characterize subsurface concentrations of PCE around tree 29, equilibrium passive samplers, called solid polymer samplers (SPSs)[33], were deployed from July 2015 to May 2016. The SPSs were made from polydimethylsiloxane (PDMS) tubing with an inner diameter of 2.4 mm, an outer diameter of 5.6 mm, total length of 26 mm, and a total mass of 0.90 ± 0.01 g. To clean the SPSs, all SPSs were washed in methanol for two days, rinsed with distilled water, and dried in an oven at 100ºC for two days. To hang the

SPSs inside of a borehole, the SPS was slid over a #4-40 x 2” stainless steel machine screw with stainless steel nuts placed at each end. Stainless steel wire with a diameter of 0.6 mm was wrapped around each screw to allow it to hang inside the borehole at a particular depth before filling and to allow retrieval of the SPS after equilibration.

A total of 42 SPS clusters (group of SPSs) were surveyed using a Trimble GeoExplorer XH® (Trimble Navigation Limited, Sunnyvale, California) with sub-meter accuracy (Figure 1). Clusters were placed at 4.6-m intervals on a 45-m by 14-m grid. At each cluster location, SPSs were installed at depths ranging from 0.2 to 1.2 m below ground surface (bgs), with targets depths of 0.3, 0.6, 0.9, and 1.2 m bgs. The total depth of each borehole was measured using a pre-marked 25.4-mm diameter tile probe used to make the boreholes. The tile probe was driven into the soil to the desired depth or refusal using a hammer drill and removed using a manual slide hammer. The SPS was then lowered to the bottom of the borehole and covered with 1 SPS-length of #30 sieved sand and 0.5 SPS-length of bentonite, and the remainder of the borehole was filled with coarse sand. All SPS samples were placed July 16–20, 2015 and retrieved May 27, 2016 to ensure that equilibrium was reached between contamination in the SPS and the subsurface. Upon retrieval, each SPS was placed into a 20-mL glass vial fitted with a Teflon-lined septum cap and analyzed using the same methods as the tree-core samples but using established SPS-air partitioning coefficients. For SPS samples, equilibrium partitioning coefficients[33] were used to report concentrations in micrograms per cubic meter (µg/m^3)

Passive samplers are contaminant sinks and have the potential to deplete the surrounding environment of contaminant before reaching equilibrium, a phenomenon termed the “starvation effect.” The starvation effect for a SPS sample in the SPS plot was estimated based on conservative values and using theoretical mass transfer equations at steady state for passive samplers. [34] Diffusion into the borehole from the surrounding soil likely limits mass transfer and diffusion through the sand pack surround the SPS is assumed instantaneous compared to diffusion into the borehole. The rate of mass transfer of PCE vapor into the borehole from the surrounding soil via vapor diffusion is given by:

$$R_{MT}1 = \frac{2\pi h D_{eff}\left(c_s - c_g\right)}{\ln\frac{r_3}{r_2}}$$

Where h is the length of the SPS (2.6 cm), c_s is the PCE concentration some distance from the SPS (assumed to be 1.00 x 10^{-6} µg/cm^3), c_g is the PCE concentration in the gas phase within the sand-filled borehole (assumed to be 0.90 x 10^{-6} µg/cm^3), r_2 is the radius of the borehole, r_3 is the radius of influence (assumed to be 150 cm), and D_{eff} is the effective diffusion coefficient into the borehole from the surrounding soil given by:

$$D_{eff} = D_{air} \frac{{\theta_a}^{10/3}}{\theta_T^2} + \frac{D_w}{H} \frac{\theta_w^{10/3}}{\theta_T^2}$$

Where D_{air} is the diffusion coefficient of PCE in air (7.20 x 10^{-2})[35], D_w is the diffusion coefficient of PCE in water (8.20 x 10^{-6})[35], θ_T is the total porosity (assumed to be a conservative 0.20 for sandy clay), θ_a is the air-filled porosity of the surrounding soil (assumed to be 0.20), θ_w is the water-filled porosity (0.00), and H is the dimensionless Henry's Law constant for PCE (0.245 at 5ºC to be conservative). The rate of mass uptake by the SPS is given by:

$$R_{MT}2 = c_g UR = c_g \frac{A}{L} D_{SPS}$$

Where A is the surface area of the SPS (4.54 cm^2), L is the diffusive path length or SPS wall thickness (0.16 cm), and D_{SPS} is the diffusion coefficient for PCE through the SPS (2.00 x 10^{-8})[33].

Centroid Determination

In order to evaluate trees ability to provide directional information of subsurface contamination, contaminant centroids were calculated for trees and soil.[27] In general, centroids were calculating as follows:

$$(x_c, y_c) = \vec{u} = \left(\frac{\sum_i C_i x_i}{\sum_i C_i}, \frac{\sum_i C_i y_i}{\sum_i C_i} \right)$$

Where (x_c, y_c) are the contaminant centroid coordinates, $\vec{u}$ is the centroid vector, C_i is the contaminant concentrations at location i, and x_i and y_i are coordinates of location i.
The angle between the azimuth vectors formed by a particular pair of tree and soil contaminant centroids was calculated by:

$$\emptyset = \arccos \left[\frac{\vec{u}_{tree} \cdot \vec{u}_{soil}}{\|\vec{u}_{tree}\| \cdot \|\vec{u}_{soil}\|} \right]$$

Where $\vec{u}_{tree}$ and $\vec{u}_{soil}$ are contaminant-centroid vectors in a tree and soil pair, and $\|\vec{u}_{tree}\|$ and $\|\vec{u}_{soil}\|$ are the magnitudes of the contaminant-centroid vectors for tree and soil samples. For the purposes of comparing contaminant centroids between tree and soil samples, contaminants centroids in tree and soil samples were normalized by tree diameter.

Based on previous work at the Vienna Well site on estimating the environmental sampling volume of trees, a tree root-to-trunk diameter ratio of 1 m/cm was used to estimate the circular area to evaluate the contaminant centroid in soil for each tree (Figure 1). Within each circle, the contaminant centroid was calculated for soil and the corresponding tree and compared. Because tree 29 was located outside of the soil-data domain, it was excluded from the directionality analysis.

Soil, Soil-Gas, Tree-Core Interpolation

Because soil samples were unevenly spaced, interpolated surfaces for PCE concentrations in soil were developed using the inverse-distance-weighting (IDW) method in ArcMap and the Python (Python Software Foundation, Delaware) module ArcPy (Environmental Systems Research Institute, Redlands, California). Because tree-core data was often at the boundary of the soil-data domain, a rectangular boundary of non-detect soil data at 1-m intervals was seeded into the IDW model to extrapolate outside of the soil-data domain (Figure 1). The IDW model was based on the mean PCE concentration at each borehole location using a power of 2 and a minimum and maximum neighbor search of 10 and 15, respectively. All PCE concentrations less than the reporting limit were replaced with the reporting limit for inclusion in interpolation. The interpolated surface was then extracted to a 1-m grid for inclusion in the centroid calculation.

In order to visualize the PCE distribution in the subsurface and *in-planta*, soil-gas and individual tree-core samples were interpolated separately using the anisotropic IDW method in RockWorks (RockWare, Inc., Golden, Colorado). Soil-gas and tree-core data were interpolated over a three-dimensional domain and visualized using voxel (three-dimensional pixel) models. Soil-gas data were interpolated at a 0.5-m interval in the x- and y-dimensions and a 0.03-m in the z-dimension, and tree-core data were interpolated at a 0.01-m interval.

RESULTS AND DISCUSSION

Interpolation of soil data resulted in two distinct areas of PCE soil contamination defined in the west area of the study area (Figure 1). To the east, PCE concentrations were generally below detection. Concentrations of PCE in tree-core samples were largest in the west area of the site in the vicinity of the largest PCE concentrations in soil samples related to the source of contamination from the hat factory. Although PCE concentrations in soil samples on the eastern part of the hat factory property were below detection, PCE concentrations in two trees (23 and 28) were large and indicated subsurface contamination (Table 1). The disparity between the soil and tree-core data in this area to the east is likely because of the drop in altitude from west to east across the site, resulting in a shallower depth to the water table (about 9 m below the surface) in the vicinity of trees 23 and 28 and tree uptake of PCE directly from the water table or through upward diffusion of vapors from the water table.

Directional Tree Coring and Soil Contamination

Concentration-centroid vectors in soil (as µg/kg) and tree-core samples (as ng/L) at the Vienna Wells site generally had an azimuthal difference (∅) less than 90˚ (Figure 2). Soil- and tree-vector pairs with the largest differences in concentration-centroid direction were generally located in areas with relatively small concentration gradients in soil or tree-core samples (Figure 2). In contrast, soil- and tree-vector pairs with the smallest differences in concentration-centroid direction were located in areas with relatively large concentration gradients in soil and tree-core samples. It should be noted that trees 1, 2, and 3 are located adjacent to the hat factory, and the effective subsurface sampling area of those trees is likely small than the extent shown because it is unlikely that tree roots would extent underneath the foundation. As a result, the soil gradient may be overestimated for these three trees. This trend in azimuthal difference between soil- and tree-vector pairs with an increase in media concentration gradient is clearly seen in Figure 2.

Table 1. Summary of tree-core sample results from the site-wide directionality assessment.

[PCE, tetrachloroethylene; ng/L, nanograms per liter; cm, centimeter; E, east; N, north; S, south; W, west]

Tree Identifier	Tree type	Diameter, in cm	Side	PCE, in ng/L	Mean relative standard deviation, in percent
1	Elm	40	E	2888	68.8
1	Elm	40	N	1600	
1	Elm	40	S	27	
1	Elm	40	W	1381	
2	Ash	54	E	1627	46.5
2	Ash	54	N	5404	
2	Ash	54	S	5073	
2	Ash	54	W	8329	
3	Ash	53	E	2892	42.9
3	Ash	53	N	1448	
3	Ash	53	S	1033	
3	Ash	53	W	1330	
7	Elm	38	E	1055	72.6
7	Elm	38	N	433	
7	Elm	38	S	70	
7	Elm	38	W	402	
8	Elm	44	E	10	64.1
8	Elm	44	N	50	
8	Elm	44	S	123	
8	Elm	44	W	72	
11	Elm	34	E	1231	76.6
11	Elm	34	N	3111	
11	Elm	34	S	44	
11	Elm	34	W	1332	
12	Maple	28	E	0.47	106.1
12	Maple	28	N	0.47	
12	Maple	28	S	4.7	
16	Sycamore	34	E	2324	36.6
16	Sycamore	34	N	4271	
16	Sycamore	34	S	1496	
16	Sycamore	34	W	3058	
19	Oak	98	E	54	78.4
19	Oak	98	N	20	
19	Oak	98	S	77	
19	Oak	98	W	0.47	
21	Elm	25	E	45	73.5
21	Elm	25	N	219	
21	Elm	25	S	819	
21	Elm	25	W	526	
23	Oak	75	E	221	56.8
23	Oak	75	N	154	
23	Oak	75	S	65	
23	Oak	75	W	49	
28	Oak	67	E	410	46.1
28	Oak	67	N	459	
28	Oak	67	S	385	
28	Oak	67	W	1020	
29	Oak	62	E	237	27.0
29	Oak	62	N	209	
29	Oak	62	S	239	
29	Oak	62	W	108	
31	Oak	72	E	4.7	59.0
31	Oak	72	N	14	
31	Oak	72	S	4.7	
31	Oak	72	W	4.7	

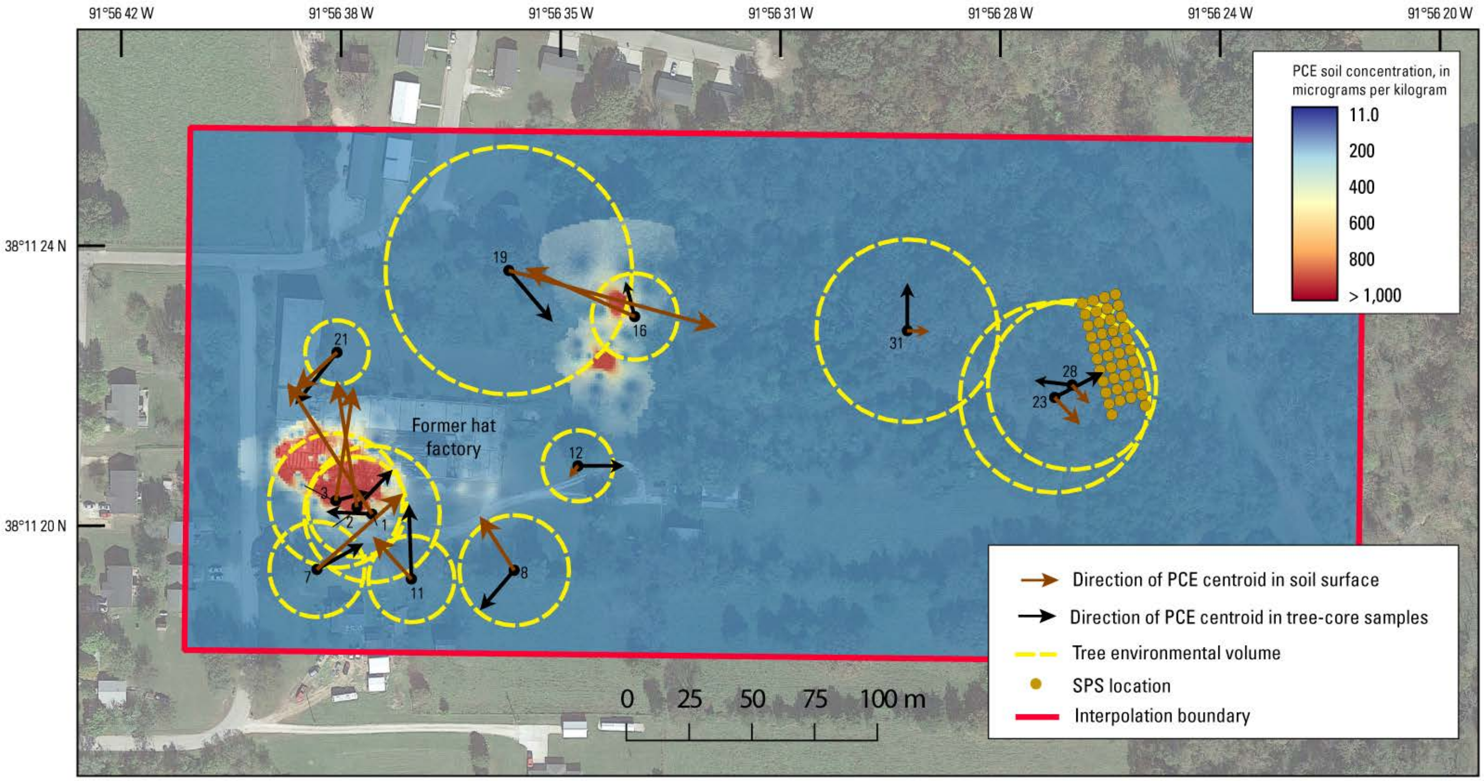

Figure 1. Concentration-centroid vectors in tree and soil samples overlaid on inverse-distance-weighting interpolation of soil data, locations of solid polymer samplers (SPSs), Vienna, Missouri, 2012-2015. The environmental volumes over which each soil concentration-centroid vector was calculated are shown in yellow-dashed circles and are proportionate to tree diameter.

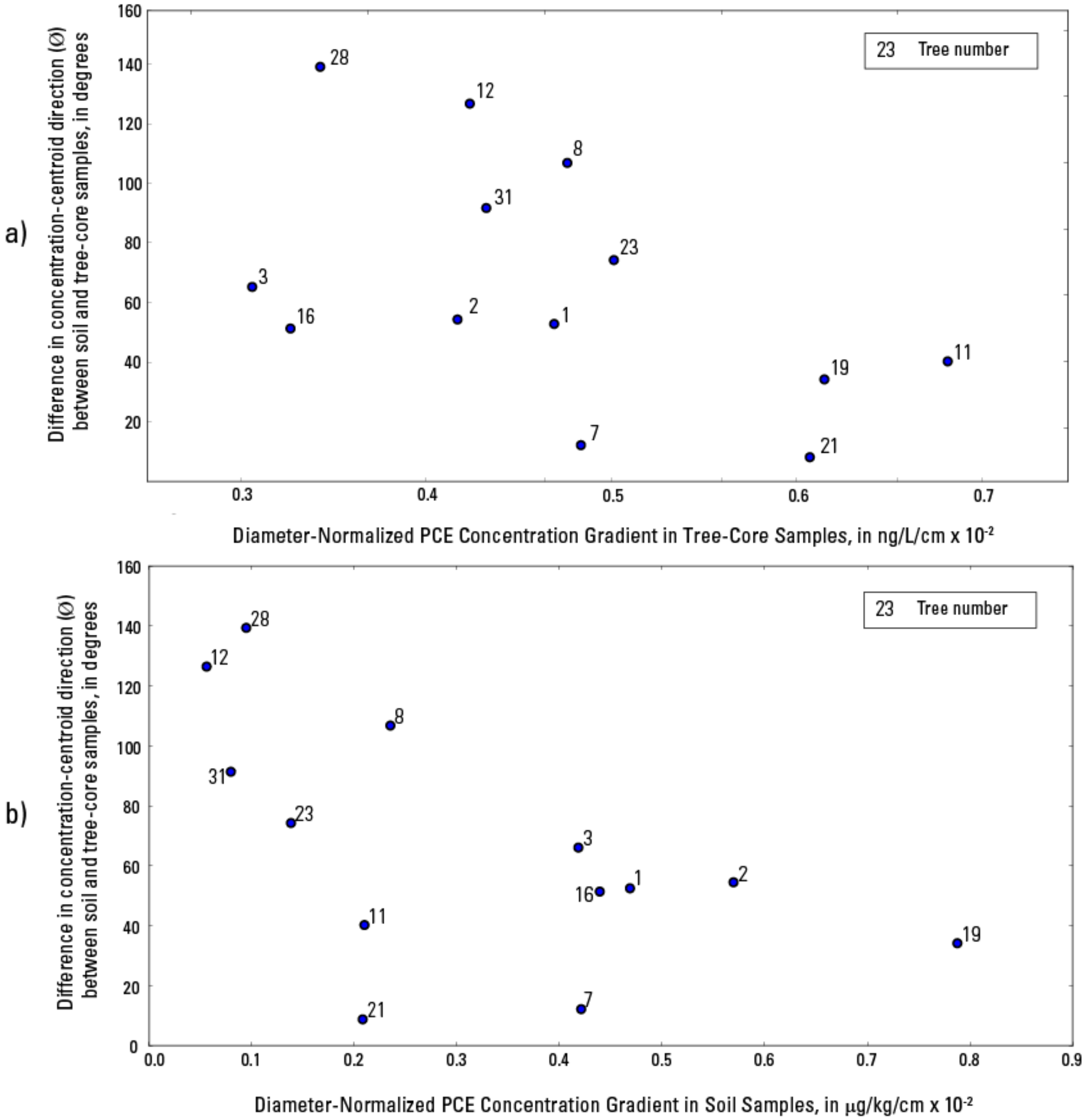

Figure 2. Azimuthal difference (Ø) between concentration-centroid vectors in tree and soil samples versus the magnitude of the concentration gradient in a) tree and b) soil samples normalized by tree diameter. Small azimuthal differences indicate agreement between the concentration-centroid vectors in soil and tree-core samples from one location. Tree numbers are shown on Figure 1.

Directional Tree Coring and Soil-Gas

The mass transfer rate of PCE to the SPS (9.8 x 10^{-9} µg/s) was found to be more than four orders of magnitude greater than the mass transfer rate of PCE into the SPS (5.15 x 10^{-13} µg/s); therefore, the starvation effect is not likely occurring (i.e., the SPSs are not depleting concentrations form the surrounding area) and can be used to accurately measure the relative soil-gas distribution.

Concentrations of PCE in soil-gas samples were largest near the middle of the SPS plot (Figures 3a and 3b) in the vicinity of the sampled tree, varied from about 486 to 3.5 µg/m^3 (reporting limit), and concentrations of PCE generally increased with depth (see Table S1 in SI). Because the depth to groundwater was about 9 m below ground surface and because of the large PCE concentrations in the northeast and southwest corners of the SPS plot, the source of this contamination is likely vapor transport from groundwater through preferential pathways in the subsurface but may also be the result of local dumping that was not detected in nearby soil samples (Figure S1).

In-planta PCE concentrations were largest on the south and southwest side of the tree in the direction of the subsurface plume (Figures 3c and 3d). Concentrations of PCE varied within the tree by over two orders of magnitude from a sample at 2,052 ng/L on the south side of the tree directly facing the subsurface plume to a sample below the reporting limit (4.7 ng/L) on the north side of the tree facing away from the subsurface plume (Table 2). This *in-plant* directionality was observed at all heights and indicates that individual trees exhibit directional information on subsurface plume location. Spreading of PCE concentration from 0.6 m to 1.2 and 1.8 m is likely the result of nonaxial flow as shown by others[18-21] and/or contaminant diffusion across vascular tissue but also may be a result of axial rotation of vascular tissue that has been hypothesized in another field study.[10]

Site Implications

The best agreement between the direction of concentration gradients in directional tree cores and soil samples occurred in areas with large subsurface concentration gradients (i.e., along the periphery of the contaminant plume) and the least agreement occurred in areas with small subsurface concentration gradients (i.e., far from or directly above the contaminant plume). These results indicate that higher confidence can be associated with directional tree-core data when tree-core concentration gradients are relatively large, and conversely, less confidence can be associated with directional tree-core data when concentration gradients are relatively small. Confidence in directional tree sampling also should be greater in areas with larger subsurface concentration gradients. The link between confidence in tree directionality and large gradients is essentially an issue of signal-to-noise because directionality essentially relies on differences in concentration (signal) above average *in-planta* concentrations (noise) to infer direction.

Table 2. Summary of directional tree-core sample results from tree 29 within the solid polymer sampler (SPS) plot.

[PCE, tetrachloroethylene; ng/L, nanograms per liter; m, meters; N, north; S, south; E, east; W, west; NE, northeast; SE, southeast; NW, northwest; SW, southwest]

PCE, in ng/L	Direction	Height, in m	Mean relative standard deviation, in percent
96	N	1.8	89.6
1,711	S		
284	E		
987	W		
193	NE		
365	SE		
232	NW		
1541	SW		
136	N	1.2	80.3
2,052	S		
407	E		
1,532	W		
564	NE		
496	SE		
250	NW		
807	SW		
4.7	N	0.6	73.3
932	S		
110	E		
166	W		
842	NE		
631	SE		
308	NW		
876	SW		

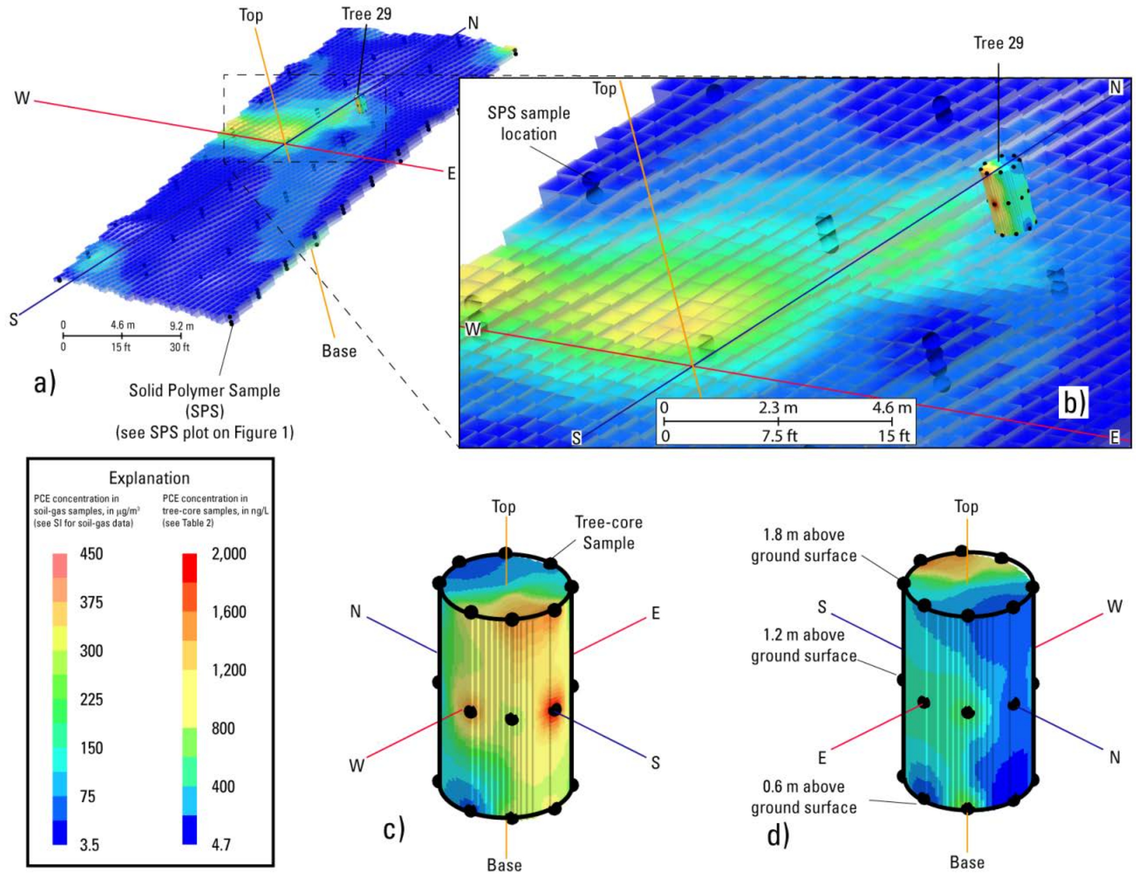

Figure 3. Spatial distribution of tetrachloroethylene (PCE) in a) solid polymer samplers (SPSs) less than 1.6 m below ground surface in the subsurface, b) agreement between in-planta and soil-gas concentration distribution, and spatial distribution of in-planta PCE concentrations in tree 29 facing c) northeast and d) southwest within the SPS plot east of the hat factory property boundary. Subparts a) and b) are viewed from oblique aerial views of 30º from the horizon and at an azimuth of 135º.

Because of the importance of concentration gradients in the subsurface, directional tree coring should be carried out across the entire site to increase the likelihood of sampling a tree that intercepts groundwater or soil gas along the periphery of the plume where subsurface concentration gradients are largest. Although sampling trees located directly in the plume are useful in indicating the plume presence at that location, only limited directional information can be obtained. Although this study concentrated on the accuracy of individual trees to indicate the direction of subsurface contaminant plumes, directional tree-core samples from more trees with less confidence (i.e., lower concentration gradients) also may be useful if the aggregation of that data indicates an overlapping area of contamination.

Ideally, directional tree coring would be conducted as a screening tool to inform future sampling activities. Because of the time- and cost-effective nature of tree coring, which takes one person only a few minutes per tree and has low analytical costs, tree-core sampling would be the initial step in the pre-screening stage of a site assessment. In areas where trees exist and concentration gradients are large in directional tree-core samples, concentration-centroid vectors can be drawn and used to triangulate areas of further investigation. Moreover, directional tree sampling has been shown here to indicate the location of shallow subsurface contamination; therefore, directional tree coring likely has application in vapor-intrusion assessment. Weights potentially could be attributed to vapor intrusion potential depending on the direction of the *in-planta* contaminant-centroid vector (facing a particular living space or not).

SUPPORTING INFORMATION

Additional information, including a figure showing the distribution of soil-samples and SPS samples results, is available free of charge at pubs.acs.org.

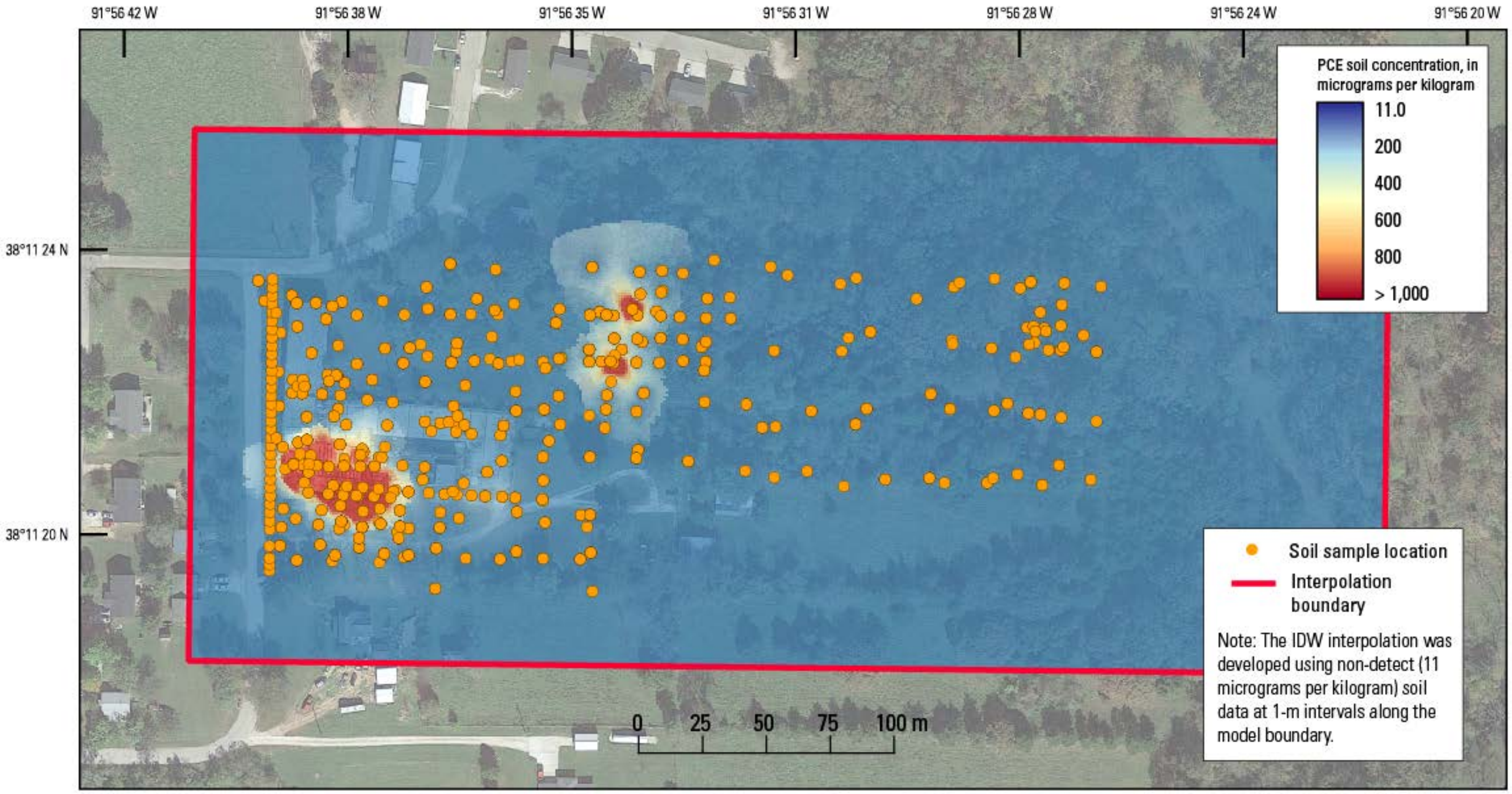

Figure S1. Soil sample locations overlaid on inverse-distance-weighting (IDW) interpolation of soil data.

Table S1. Solid polymer sampler (SPS) sample results.

[m, meters; PCE, tetrachloroethylene; µg/m3, micrograms per cubic meter]

Location	Depth, in m	PCE, in µg/m^3
1	0.2	7.6
1	0.3	55.0
1	0.3	56.6
2	0.3	52.8
2	0.6	392.1
3	0.3	6.5
3	0.3	4.4
4	0.9	40.6
5	0.3	13.4
5	0.6	18.4
5	0.9	30.3
6	0.6	54.7
6	0.9	77.1
7	0.6	408.3
7	0.9	460.0
7	1.0	444.2
7	1.2	476.0
8	0.5	28.0
8	0.8	59.7
9	0.3	17.7
9	0.6	27.7
9	1.0	98.5
10	0.3	35.8
10	0.5	27.2
10	0.6	39.1
11	0.2	28.7
11	0.4	47.7
11	0.9	103.4
13	0.3	16.8
13	1.1	93.4
14	0.3	9.0
14	0.6	17.8
15	0.3	9.9
15	0.6	12.6
15	0.9	13.4
16	0.3	9.1
16	0.6	18.3
16	0.9	19.6
17	0.3	40.5
17	0.6	77.7
17	0.9	335.7
17	1.2	388.7

Table S1. (continued) Solid polymer sampler (SPS) sample results.

[m, meters; PCE, tetrachloroethylene; µg/m3, micrograms per cubic meter]

Location	Depth, in m	PCE, in µg/m^3
18	0.4	423.4
18	0.6	486.4
19	0.3	108.6
19	0.5	452.2
19	0.6	463.9
19	0.8	475.0
20	0.3	17.9
20	0.5	33.5
21	0.5	25.6
21	0.6	33.6
22	0.3	23.2
22	0.4	20.6
22	0.6	27.8
24	0.3	19.2
25	0.3	26.0
25	0.6	47.3
25	0.7	53.7
26	0.3	34.6
26	0.6	63.6
26	0.9	107.1
27	0.3	77.2
27	0.6	105.7
27	0.9	132.9
28	0.3	38.2
28	0.6	87.3
29	0.4	29.1
29	0.6	61.7
29	0.9	91.4
29	1.2	439.7
30	0.3	74.9
30	0.6	424.7
31	0.3	15.1
31	0.3	15.6
32	0.3	18.4
32	0.7	61.0
32	0.8	51.6
33	0.3	9.3
33	0.6	17.2
33	0.9	22.1
34	0.3	12.2
34	0.7	24.4
34	0.9	38.8

Table S1. (continued) Solid polymer sampler (SPS) sample results.

[m, meters; PCE, tetrachloroethylene; µg/m3, micrograms per cubic meter]

Location	**Depth, in m**	**PCE, in µg/m³**
35	0.3	22.4
35	0.6	61.5
35	0.9	93.7
36	0.3	37.3
36	0.6	77.0
36	0.9	413.9
37	0.3	31.6
37	0.6	69.4
37	1.2	430.8
38	0.3	14.2
38	0.6	19.5
38	0.9	30.8
39	0.3	12.2
39	0.6	20.8
39	0.9	27.3
40	0.3	8.3
40	0.6	6.6
40	1.2	20.3
41	0.3	3.5
41	0.6	7.7
41	0.9	10.2
42	0.6	10.3
42	0.9	11.4
42	1.2	13.8
43	0.3	19.2
43	0.6	31.1
43	0.9	45.9
44	0.3	453.3
44	0.6	81.0

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under grant no. #1336877. Support was given by the United States Environmental Protection Agency Region 7, with special assistance from Hoai Tran. The authors also thank Madison Gibler, Eric Fallon, and Cory Pollpeter of Missouri S&T for help collecting tree-core samples. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

REFERENCES

1. USEPA, Superfund: National Priorities List (NPL). https://www.epa.gov/superfund/superfund-national-priorities-list-npl (4/1/2017).

2. Panagos, P.; Van Liedekerke, M.; Yigini, Y.; Montanarella, L., Contaminated Sites in Europe: Review of the Current Situation Based on Data Collected through a European Network. *Journal of Environmental and Public Health* **2013,** *2013*, 11. DOI: 10.1155/2013/158764.

3. Doctor, P.; Gilbert, R. *Two studies in variability for soil concentrations: with aliquot size and with distance*; 1978.

4. Schumacher, B. A.; Minnich, M. M., Extreme Short-Range Variability in VOC-Contaminated Soils. *Environmental Science & Technology* **2000,** *34*, (17), 3611-3616. DOI: 10.1021/es0008719.

5. Jenkins, T. F.; Hewitt, A. D.; Walsh, M. E.; Ranney, T. A.; Ramsey, C. A.; Grant, C. L.; Bjella, K. L., Representative Sampling for Energetic Compounds at Military Training Ranges. *Environmental Forensics* **2005,** *6*, (1), 45-55. DOI: 10.1080/15275920590913912.

6. Walsh, M. E.; Collins, C. M.; Bailey, R. N.; Grant, C. L. *Composite sampling of sediments contaminated with white phosphorus*; DTIC Document: 1997.

7. Hadley, P. W.; Bruce, M. L., On Representativeness. *Environmental Forensics* 2014, pp 1-3.

8. Hadley, P. W.; Petrisor, I. G., Incremental Sampling: Challenges and Opportunities for Environmental Forensics. *Environmental Forensics* **2013,** *14*, (2), 109-120. DOI: 10.1080/15275922.2013.790859.

9. Larsen, M.; Burken, J.; Machackova, J.; Karlson, U. G.; Trapp, S., Using Tree Core Samples to Monitor Natural Attenuation and Plume Distribution After a PCE Spill. *Environmental Science & Technology* **2008,** *42*, (5), 1711-1717. DOI: 10.1021/es0717055.

10. Schumacher, J. G.; Struckhoff, G. C.; Burken, J. G., *Assessment of Subsurface Chlorinated Solvent Contamination Using Tree Cores at the Front Street Site and a Former Dry Cleaning Facility at the River-front Superfund Site, New Haven, Missouri, 1999-2003*. US Department of the Interior, US Geological Survey: 2004.

11. Wahyudi, A.; Bogaert, P.; Trapp, S.; Macháčková, J., Pollutant plume delineation from tree core sampling using standardized ranks. *Environmental Pollution* **2012,** *162*, (0), 120-128. DOI: http://dx.doi.org/10.1016/j.envpol.2011.11.010.

12. Limmer, M. A.; Balouet, J.-C.; Karg, F.; Vroblesky, D. A.; Burken, J. G., Phytoscreening for Chlorinated Solvents Using Rapid in Vitro SPME Sampling: Application to Urban Plume in Verl, Germany. *Environmental Science & Technology* **2011,** *45*, (19), 8276-8282. DOI: 10.1021/es201704v.

13. Struckhoff, G. C.; Burken, J. G.; Schumacher, J. G., Vapor-Phase Exchange of Perchloroethene between Soil and Plants. *Environmental Science & Technology* **2005,** *39*, (6), 1563-1568. DOI: 10.1021/es049411w.

14. Dobson, M. C.; Moffat, A. J., A Re-Evaluation of Objections to Tree Planting On Containment Landfills. *Waste Management & Research* **1995,** *13*, (6), 579-600. DOI: http://dx.doi.org/10.1006/wmre.1995.0054.

15. Sorek, A.; Atzmon, N.; Dahan, O.; Gerstl, Z.; Kushisin, L.; Laor, Y.; Mingelgrin, U.; Nasser, A.; Ronen, D.; Tsechansky, L.; Weisbrod, N.; Graber, E. R., "Phytoscreening": The Use of Trees for Discovering Subsurface Contamination by VOCs. *Environmental Science & Technology* **2008,** *42*, (2), 536-542. DOI: 10.1021/es072014b.

16. MacKay, A. A.; Gschwend, P. M., Sorption of Monoaromatic Hydrocarbons to Wood. *Environmental Science & Technology* **2000,** *34*, (5), 839-845. DOI: 10.1021/es9900858.

17. Trapp, S.; Miglioranza, K. S. B., Sorption of Lipophilic Organic Compounds to Wood and Implications for Their Environmental Fate. *Environmental Science & Technology* **2001,** *35*, (8), 1561-1566. DOI: 10.1021/es000204f.

18. Waisel, Y.; Liphschitz, N.; Kuller, Z., Patterns of Water Movement in Trees and Shrubs. *Ecology* **1972,** *53*, (3), 520-523. DOI: 10.2307/1934244.

19. Shinozaki, K.; Yoda, K.; Hozumi, K.; Kira, T., A quantitative analysis of plant form-the pipe model theory: I. Basic analyses. *Japanese Journal of ecology* **1964,** *14*, (3), 97-105. DOI:

20. Vroblesky, D. A.; Nietch, C. T.; Morris, J. T., Chlorinated Ethenes from Groundwater in Tree Trunks. *Environmental Science & Technology* **1999,** *33*, (3), 510-515. DOI: 10.1021/es980848b.

21. Schumacher, J. G.; Struckhoff, G. C.; Burken, J. G. *Assessment of subsurface chlorinated solvent contamination using tree cores at the front street site and a former dry cleaning facility at the Riverfront Superfund site, New Haven, Missouri, 1999-2003*; 2004-5049; 2004.

22. Schulte, P. J.; Brooks, J. R., Branch junctions and the flow of water through xylem in Douglas-fir and ponderosa pine stems. *Journal of Experimental Botany* **2003,** *54*, (387), 1597-1605. DOI: 10.1093/jxb/erg169.

23. Orians, C. M.; Ardón, M.; Mohammad, B. A., Vascular architecture and patchy nutrient availability generate within-plant heterogeneity in plant traits important to herbivores. *American Journal of Botany* **2002,** *89*, (2), 270-278. DOI:

24. Thorn, A. M.; Orians, C. M., Modeling the influence of differential sectoriality on the photosynthetic responses of understory saplings to patchy light and water availability. *Trees* **2011,** *25*, (5), 833. DOI: 10.1007/s00468-011-0559-5.

25. Zwieniecki, M. A.; Orians, C. M.; Melcher, P. J.; Holbrook, N. M., Ionic control of the lateral exchange of water between vascular bundles in tomato. *Journal of Experimental Botany* **2003,** *54*, (386), 1399-1405. DOI: 10.1093/jxb/erg144.

26. Burgess, S. S. O.; Bleby, T. M., Redistribution of soil water by lateral roots mediated by stem tissues. *Journal of Experimental Botany* **2006,** *57*, (12), 3283-3291. DOI: 10.1093/jxb/erl085.

27. Limmer, M. A.; Shetty, M. K.; Markus, S.; Kroeker, R.; Parker, B. L.; Martinez, C.; Burken, J. G., Directional Phytoscreening: Contaminant Gradients in Trees for Plume Delineation. *Environmental science & technology* **2013,** *47*, (16), 9069-9076. DOI:

28. Vroblesky, D. A.; Clinton, B. D.; Vose, J. M.; Casey, C. C.; Harvey, G. J.; Bradley, P. M., Ground Water Chlorinated Ethenes in Tree Trunks: Case Studies, Influence of Recharge, and Potential Degradation Mechanism. *Ground Water Monitoring & Remediation* **2004,** *24*, (3), 124-138. DOI: 10.1111/j.1745-6592.2004.tb01299.x.

29. Holm, O.; Rotard, W., Effect of Radial Directional Dependences and Rainwater Influence on CVOC Concentrations in Tree Core and Birch Sap Samples Taken for Phytoscreening Using HS-SPME-GC/MS. *Environmental Science & Technology* **2011,** *45*, (22), 9604-9610. DOI: 10.1021/es202014h.

30. MDHSS, Public health assessment: Vienna Wells, Maries County, Missouri. In 2015; p 84.

31. Ma, X.; Burken, J., Modeling of TCE Diffusion to the Atmosphere and Distribution in Plant Stems. *Environmental Science & Technology* **2004,** *38,* (17), 4580-4586. DOI: 10.1021/es035435b.

32. Vroblesky, D. A., *User's Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds*. 2008; p 59.

33. Shetty, M. K.; Limmer, M. A.; Waltermire, K.; Morrison, G. C.; Burken, J. G., In planta passive sampling devices for assessing subsurface chlorinated solvents. *Chemosphere* **2014,** *104*, 149-154. DOI: http://dx.doi.org/10.1016/j.chemosphere.2013.10.084.

34. McAlary, T.; Wang, X.; Unger, A.; Groenevelt, H.; Gorecki, T., Quantitative passive soil vapor sampling for VOCs- part 1: theory. *Environmental Science: Processes & Impacts* **2014,** *16,* (3), 482-490. DOI: 10.1039/c3em00652b.

35. USEPA, EPA On-line Tools for Site Assessment Calculation. https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion-ext.html (4/1/2017).

III. TREES AS INDICATORS OF VAPOR INTRUSION

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Abstract

Human exposure to volatile organic compounds (VOCs) via vapor intrusion (VI) is an emerging public health concern with notable detrimental impact on public health. Phytoforensics, plant sampling to semi-quantitatively delineate subsurface contamination, provides a potential non-invasive screening approach to detect VI potential, and plant sampling is effective and also time- and cost-efficient. Existing VI assessment methods are time- and resource-intensive, invasive, and require access into residential and commercial buildings to drill holes through basement slabs to install sampling ports or require substantial equipment to install groundwater or soil vapor sampling outside the home. Tree-core samples collected in two days at the PCE Southeast Contamination Site in York, Nebraska were analyzed for tetrachloroethene (PCE) and results demonstrated a positive correlation with groundwater, soil, soil-gas, sub-slab, and indoor-air samples collected over a 2 year period. Results indicate moderate to high correlation with average indoor-air and sub-slab PCE concentrations over long periods of time (months to years) to an interpolated tree-core PCE concentration surface, with Spearman's correlation coefficients (ρ) ranging from 0.31 to 0.53 that are comparable to the pairwise correlation between sub-slab and indoor-air PCE concentrations (ρ=0.55, n=89). Good correlation between soil-gas, sub-slab, and indoor-air PCE concentrations and an interpolated tree-core PCE concentration surface indicate that trees are valid indicators of potential VI and human exposure to subsurface environment pollutants. The rapid and non-invasive nature of tree sampling are notable advantages: even with less than 60 trees in the vicinity of the source area, roughly 12 hours of tree-core sampling with minimal equipment at the PCE Southeast Contamination Site was sufficient to delineate vapor intrusion potential in the study area and offered comparable delineation to traditional sub-slab sampling performed at 140 properties over a period of approximately 2 years.

Introduction

Vapor intrusion (VI) of volatile organic compounds (VOCs) in the built environment is a threat to human health through migration of carcinogenic contaminants into cracks, seams, and gaps in structures (Fig 1). Although VI can occur in commercial, industrial, or residential settings, residential areas pose unique problems as occupants are unknowingly exposed to concentrations of contaminants in indoor air for long periods, which have a notably greater impact (up to three orders of magnitude more) on human health than outdoor sources [1]. Within the Superfund program, the VI pathway has recently (2017) been implemented into the Hazard Ranking System [2], allowing a site to be listed on the National Priorities List (NPL) solely because of VI. Because of this increased emphasis on VI, screening for VI will be required at an increasing rate; however, measurement of VI is not simple and is time-, cost-, and labor-intensive, requiring access agreements to enter homes to conduct testing. Simpler, quicker, and more cost-effective screening methods are needed to effectively assess VI and protect human health.

Because VI is a multimedia concern for compounds that exist in vapor, aqueous, and sorbed phases, several different methods exist to assess VI risk; however, many are either time- and resource-intensive or require assumptions that often may be violated. Vapor intrusion risk is typically measured with direct methods (e.g., indoor-air sampling or sub-slab sampling of soil gas) or indirect methods (e.g., groundwater, soil, or soil-gas sampling). These direct and indirect methods for measurement of VI risk are invasive, time and resource intensive [3, 4], or may not be done at all because of the inability to safely collect samples. The current best practice for assessing potential VI risk from environmental samples is through the application of the two-decade-old Johnson-Ettinger model [5], which estimates an attenuation factor (i.e., concentration of the contaminant in the environmental samples over the concentration of the contaminant in indoor air). The model makes numerous assumptions and attempts to capture a four-dimensional problem using a one-dimensional model. The model is also based on approximately 20 site-specific variables that are difficult to assess [2].

Trees have the potential to measure VI potential *in situ.* Through photosynthesis, trees use solar energy and water potential gradients between the atmosphere and the subsurface to translocate groundwater and in doing so draw moderately hydrophobic contaminants dissolved in groundwater and in the vapor phase across the root-membrane boundary [6, 7]. Once contaminants are in root xylem tissues, the compounds can move with the transpiration stream to aboveground xylem tissues where they can be readily measured.

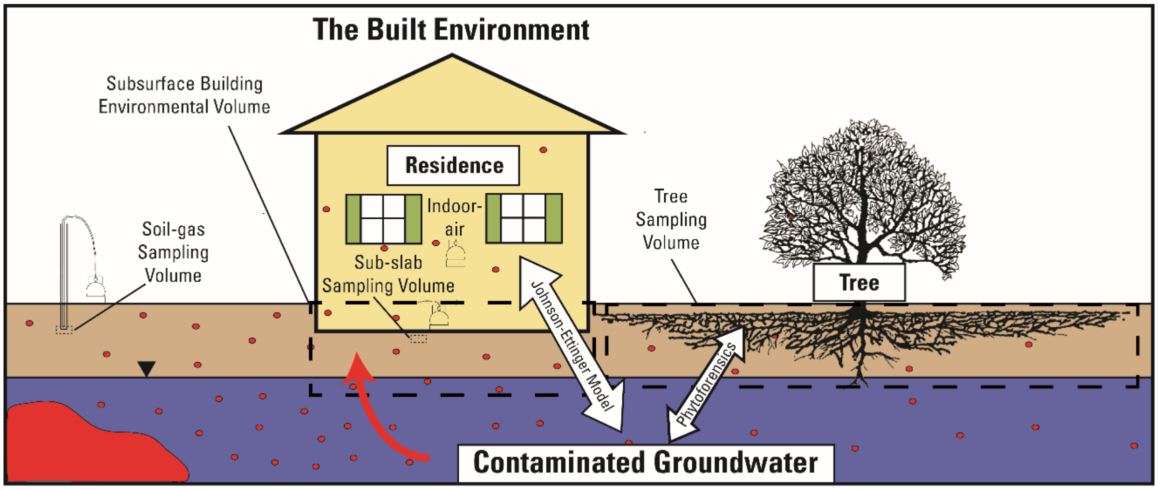


Fig 1. Schematic of the interplay between vapor intrusion, the built environment, and phytoforensic processes.

Phytoforensics has been shown to be a cost- and time-effective tool for semi-quantitatively delineating VOC contamination in groundwater [8-11] and soil vapor [12]. To correlate concentrations in aboveground tree tissue with subsurface contaminant concentrations, phytoforensic methods intercept contaminants as they transport up the xylem and diffuse radially out of the trunk [13]. Phytoforensics uses established trees in the vicinity of contaminant plumes and avoids the time and cost associated with drilling or sample-port installation for sub-slab sampling. Collection of tree-core samples can be conducted in less than five minutes per sample by a single person. Aside from the simplicity, speed, and cost-effective nature of phytoforensics, trees are thought to average subsurface contaminant concentrations by sampling over large subsurface volumes [14, 15] and long time-scales [16, 17].

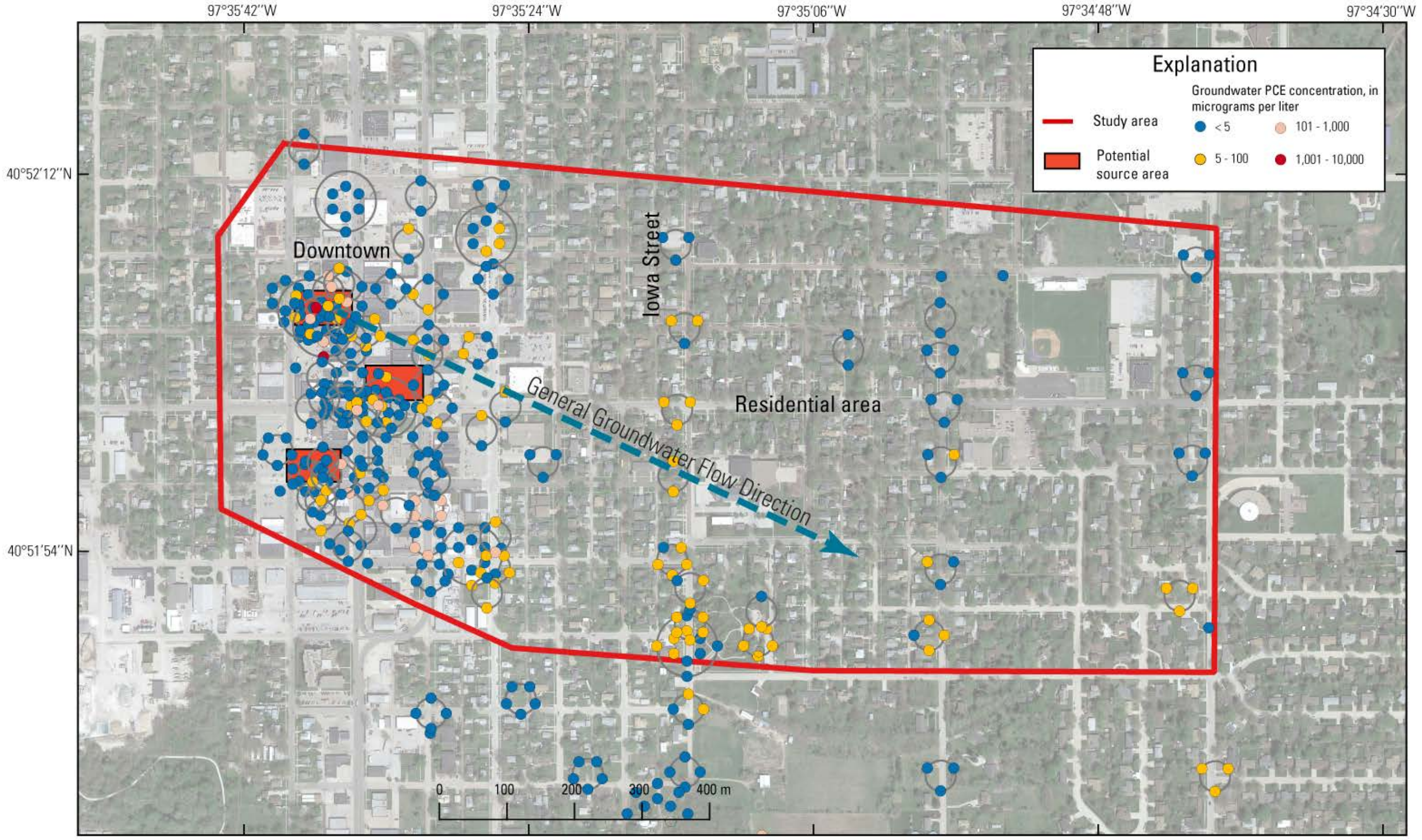
Methods

To elucidate the potential of trees to be indicators of VI potential in this study, tree-core samples were collected at the Tetrachloroethene (PCE) Southeast Contamination Site in York, Nebraska (EPA ID NEN000706200), a Superfund site contaminated primarily with PCE. The PCE Southeast Contamination Site was originally listed on the National Priorities List in May 2014 after PCE and other VOCs were detected in private drinking water wells above the EPA maximum contaminant level (MCL). Although the PCE Southeast Contamination Site covers approximately 15 km^2, the study area for this work covered approximately 2.2 km^2 encompassing downtown York and the residential area to the east and south (Fig 2). The likely sources of PCE contamination are from several former dry cleaning businesses in the downtown York area (Fig 2). During the site assessment, the EPA collected groundwater (Fig 2), soil (S4 Fig), indoor-air (Fig 4), and sub-slab (S1 Fig) samples from the commercial and residential properties in the area of the suspected plume. Residential areas surround the downtown area and extend primarily to the north and east. The underlying geology of the site primarily consists of alluvial deposits. In order of most recent to oldest deposits, the site geology consists of approximately 6 m of clay, 23 m of sand and gravel, 12 m of clay and silt, 15 m of sand, 15 m of clay and silt, and 12 m of sand underlain by Cretaceous age Carlile Shale Bedrock. Typical groundwater depths in the area range from 9 m below ground surface (bgs) in the downtown area to about 18 m bgs near the eastern boundary of the study area (Fig 2). The groundwater PCE plume originates in the downtown area and extends to the southeast, the predominant direction of groundwater flow, within the 23 m thick sand and gravel layer.

In this study, EPA groundwater, soil, soil-gas, and VI (sub-slab and indoor-air) data collected within two years of tree sampling was correlated with tree-core samples collected by the USGS to elucidate the potential for trees to be indicators of VI potential. Groundwater, soil, soil-gas, and VI samples were collected by the EPA Region 7 from January 2010 to September 2016. Within the study area, EPA collected samples over 10 separate sampling events from November 2014 to September 2016. Tree-core samples were collected at the PCE Southeast Contamination Site in York, Nebraska during November 2-3, 2016 (Fig 3). Because trees are thought to provide information about subsurface VOC concentrations over a period of time, tree-core PCE concentrations collected in November 2016 were used to develop correlations with EPA data from each of the 10 sampling events as well as with aggregations of EPA data ranging from the aggregation of all sampling events from November 2014 to September 2016 period to the aggregation of the last two sampling events (July 2016 and September 2016; Fig 6). Correlations were then compared between individual sampling events as well as over periods of time to determine over what period of time tree-core PCE data is informative of subsurface contamination and, more specifically, vapor intrusion. All data used in this paper are available at U.S. Geological Survey (USGS) ScienceBase, https://doi.org/10.5066/F7CF9P06.

Tree-core sampling

Tree-core samples were collected at the site by a two-person team over 12 hours during November 2-3, 2016, using published tree-coring methods [18]. A total of 121 samples, which included 109 environmental samples, 10 replicate samples, 1 trip-blank sample, and 1 field-blank sample, were collected. A total of 53 trees were sampled in the primarily residential area east of Iowa Street and the remaining 56 trees were sampled in



Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Fig 2. Groundwater tetrachloroethene (PCE) concentrations in the study area in York, Nebraska, from August 2011 to September 2016. Each set of points in concentric rings represents multiple samples in one area.

the vicinity of the downtown York area (Fig 3). Tree-core samples were collected using a 0.25-inch diameter by 12-inch long steel increment borer and a standard 0.2-inch diameter core sample (3 inches long) was extracted from each tree at a 1-m height. Tree-core samples were analyzed at the Environmental Research Center at the Missouri University of Science and Technology in Rolla, Missouri using published methods [11]. Tree-core samples were allowed to reach equilibrium overnight and run on an Agilent 7890 gas chromatograph (Agilent Technologies, Inc., Santa Clara, California) with a micro-electron-capture detector fitted with a CombiPAL solid-phase microextraction (SPME) fiber autosampler. Samples were mass-corrected and PCE concentrations were reported in nanograms of contaminant per liter of sap (ng/L). Global positioning system (GPS) locations were collected for each tree using a Trimble GeoExplorer XH® (Trimble Navigation Limited, Sunnyvale, California) with a sub-meter accuracy.

Although most trees were sampled in the downtown area, tree density in this area was low. In contrast, tree density in the residential area was high, but samples were only collected along a few streets in the residential area. Both sources of data sparsity left large spatial gaps in the tree-core dataset. Because the source area and many of the EPA samples were located in the downtown area where tree-core data were relatively sparse, the spatial distribution of the tree-core PCE concentration surface may not be fully defined in that area, which likely introduces more error into correlations between EPA data and the tree-core PCE concentration surface.

Groundwater, soil, and soil-gas sampling

A total of 1,198 groundwater samples were collected and analyzed by the EPA from January 2010 to September, 2016 from the site. Of the 629 samples collected between November 2014 and September 2016 (S8 Fig), 371 samples were contained within the region from where tree-core samples were collected (the “study area”). All 371 samples were collected between August 2011 and September 2016 (Fig 2) using temporary direct-push wells using a Geoprobe Screen Point 16 (Geoprobe, Salina, Kansas) apparatus containing a reusable stainless steel screen. Samples were collected between 9 and 40 m (average of approximately 15 m) in 40-mL vials. Samples were collected from multiple depths within each well with at least one sample near the top of the water table. Correlations were developed with all groundwater data as well as only the shallowest groundwater samples within each well and < 12 m deep bgs (S6 Fig) because VOC concentrations in trees have been shown to be better correlated with VOC concentrations in the shallow subsurface [12].

A total of 209 soil samples were collected and analyzed by the EPA from November 2011 to July 2016 from the study area, and 188 samples were collected in the downtown area. Of the 209 samples, 57 samples were collected between November 2014 and September 2016 (S4 Fig) from depths ranging from 0 to 27 m bgs using direct-push technology using a Macro-Core sampler fitted with a disposable polyvinyl chloride liner according to EPA standard operating procedure.[19] At a given interval selected for sampling, a tipless syringe was used to collect five grams of soil, which was transferred into a 40-mL vial for analysis by the EPA Region 7 laboratory.

EPA collected 18 soil-gas samples in April 2016 in the downtown area and collected 20 soil-gas samples in September 2016 in the residential area to the east and southeast (S2 Fig). All samples were collected using established soil-gas methods with a Geoprobe® Post Run Tubing (PRT) soil-gas sampling system. Samples were collected as a discrete concentration (30- to 60-second time-weighted average [TWA]) using Tedlar® bags and a small pump. All samples were analyzed onsite by the EPA Region 7 mobile laboratory with gas chromatography-mass spectrometry (GC-MS).

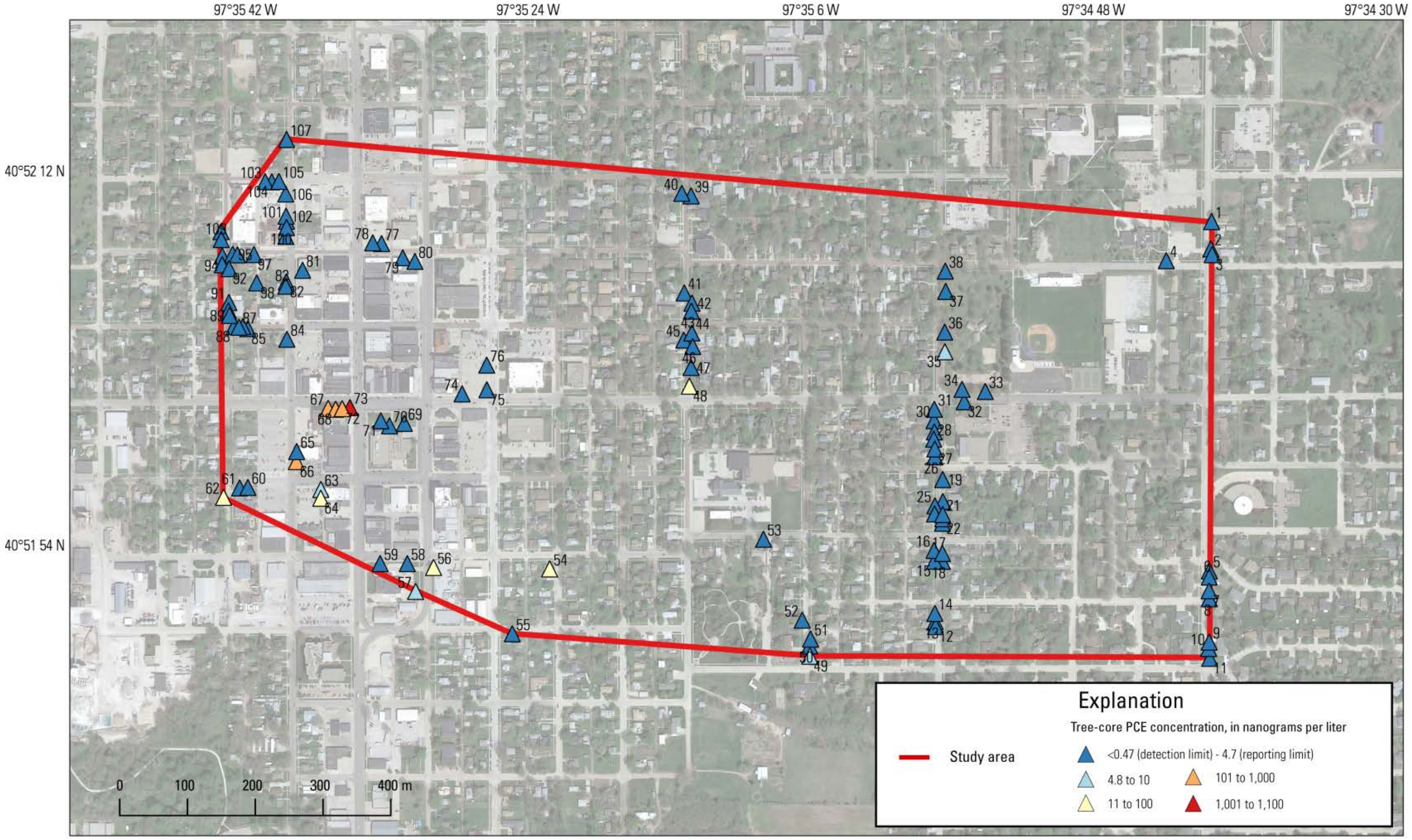
VI sampling

A total of 255 indoor-air samples (Fig 4) and 461 sub-slab samples (S1 Fig) were collected by the EPA in residential and commercial buildings between July 2014 and September 2016. Indoor-air concentrations were determined using TWA concentration over about 20 hours obtained from SUMMA® canisters deployed at the lowest level inside each building. Sub-slab concentrations were determined either as a TWA using SUMMA® canisters or as a discrete concentration (30- to 60-second TWA) using Tedlar® bags and a small pump. All samples were analyzed onsite by the EPA Region 7 mobile laboratory with GC-MS.

Data analysis

Because tree-core samples were not collocated with groundwater, soil, soil-gas, sub-slab, and indoor-air samples, interpolated surfaces for tree-core, soil-gas, and sub-slab PCE concentrations were estimated using a conservative approach by creating a triangulated irregular network (TIN) from the concentration data and interpolating a 1-m raster surface from the TIN using natural neighbors interpolation [20, 21] in ArcMap ® (Environmental Systems Research Institute, Redlands, California) and the Python (Python Software Foundation, Delaware) module ArcPy. In addition to being the most conservative interpolation method, the TIN method resulted in the most realistic surface compared to surfaces developed using kriging and inverse-distance0weighting methods were used. Mean soil-gas and sub-slab PCE concentrations at each location were also interpolated to calculate correlation with indoor-air PCE concentrations. Because of the sparsity of trees in the downtown area, the spatial distribution of tree-core PCE concentration data was non-uniform and the interpolated tree-core PCE concentration surface may not be fully defined in that area and could affect correlations between EPA data and the interpolated tree-core PCE concentration surface.

To correlate groundwater, soil, soil-gas, sub-slab, and indoor-air PCE concentrations with the interpolated tree-core PCE concentration surface and to correlate indoor-air PCE concentrations with the interpolated soil-gas and sub-slab PCE concentration surfaces, the nonparametric Spearman's rank correlation coefficient [22] (ρ) was used at a significance level of 0.05. In this paper, low, moderate, and high values of ρ are defined as less than (<) 0.2, between 0.2 and 0.5, and greater than (>) 0.5. To develop the correlation dataset, PCE concentrations were extracted from the interpolated tree-core, soil-gas, and sub-slab surfaces at each groundwater, soil, soil-gas, sub-slab, or indoor-air sample location. Correlations were calculated for each of the 10 sampling events as well as over multiple sampling events because trees are thought to provide information about subsurface concentrations over a period of time. For correlations over multiple sampling events, averages were calculated and used in correlation analysis for locations with multiple samples. Because there is little spatial variability between sub-



Base map data from Google, 2016
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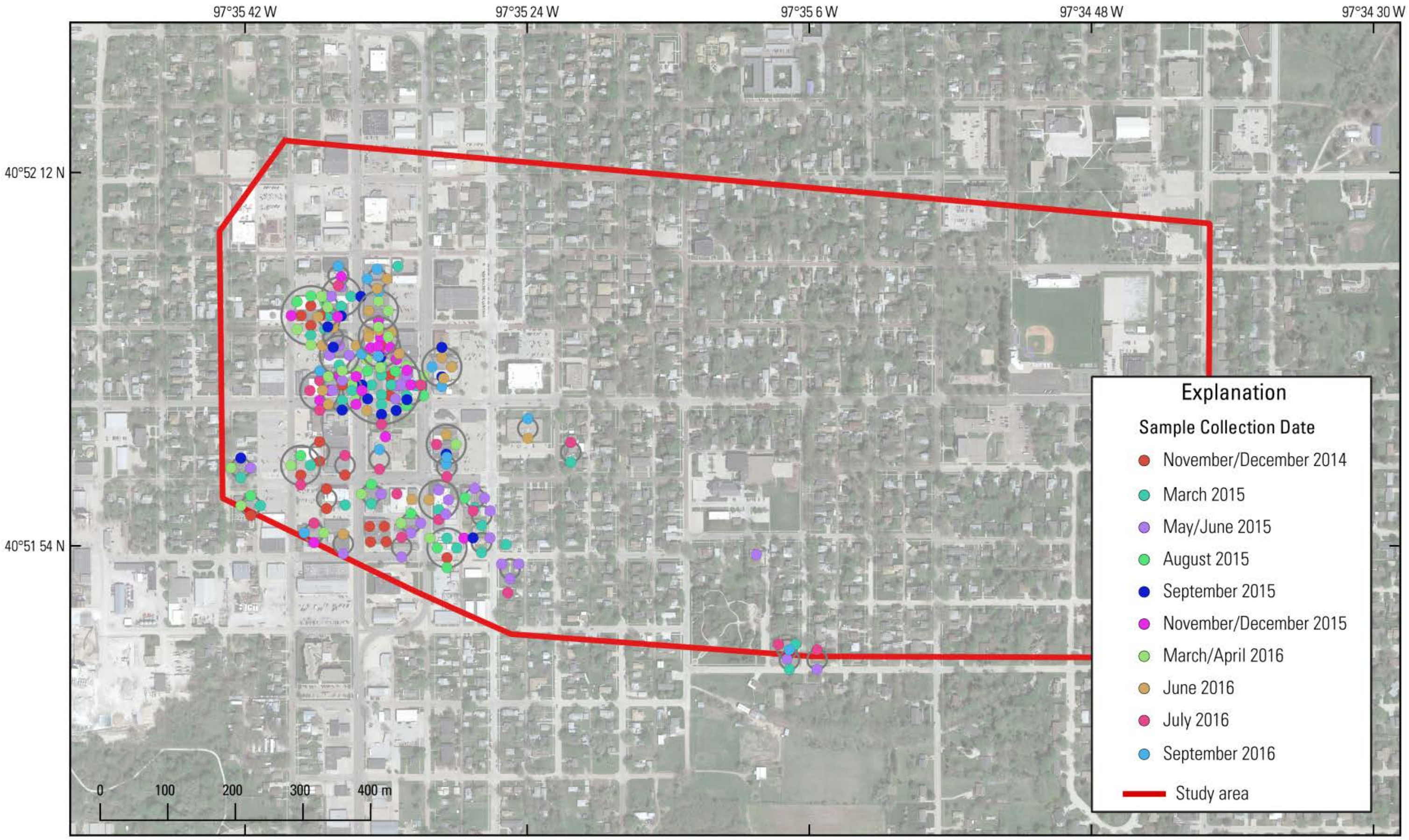
Fig 3. Tree-core tetrachloroethene (PCE) concentrations and corresponding tree numbers in the study area in York, Nebraska, November, 2016.



Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Fig 4. Location and date of indoor-air samples in the study area in York, Nebraska. Each set of points in concentric rings represents multiple samples in one area.

slab and indoor-air sample locations, correlations between paired sub-slab and indoor-air samples collected during the same sampling event were also calculated.

To assess the effect of the non-uniform distribution of samples on the error in the interpolated tree-core PCE surface, groundwater, soil, soil-gas, sub-slab, and indoor-air PCE concentrations were also correlated with tree-core PCE concentrations in tree-core samples located within 31 m. These correlations remove the potential error that may be introduced with non-uniformly distributed tree-core samples and are most representative of the true correlation between tree-core concentrations and nearby vapor intrusion concentrations.

Results and discussion

Trees as indicators

Concentrations of PCE in tree-core samples from the 109 trees sampled were above the detection limit (0.47 ng/L) [11] in 37 trees and above the reporting limit (4.7 ng/L) in 14 trees. Of the 14 trees with PCE concentrations above the reporting limit, 11 were in the vicinity of the downtown area with concentrations as high as 1,100 ng/L (Fig 5). Concentrations of PCE in tree-core samples were also relatively large (250 – 500 ng/L) in samples east and southeast of the downtown area in the direction of the groundwater flow (Fig 2).

Groundwater

Because groundwater PCE concentrations were variable and the distribution of available trees to sample was poor in the downtown area, correlations of groundwater PCE concentrations to the interpolated tree-core PCE concentration surface were poor (Fig 6). When either shallow or all groundwater data was included, no significant correlations existed between groundwater PCE concentrations and the interpolated tree-core PCE concentration surface for any sampling event or period of sampling. Where groundwater PCE concentrations were large, tree-core data were sparse, and as a result, did not allow for full definition of the concentration distribution in those areas (S7 and S9 Figs). Shallow groundwater samples, which were close to the water table surface, had poor correlation with the interpolated tree-core PCE concentration surface. A better assessment of correlation between groundwater PCE and the interpolated tree-core PCE concentration surface would likely result if tree-core samples were more uniformly distributed within the study area. Additionally, many of the groundwater samples were collected greater than 15 m bgs; therefore, trees in some areas might be taking up shallower, infiltrated groundwater from local recharge with smaller PCE concentrations from dilution than the samples at depth.

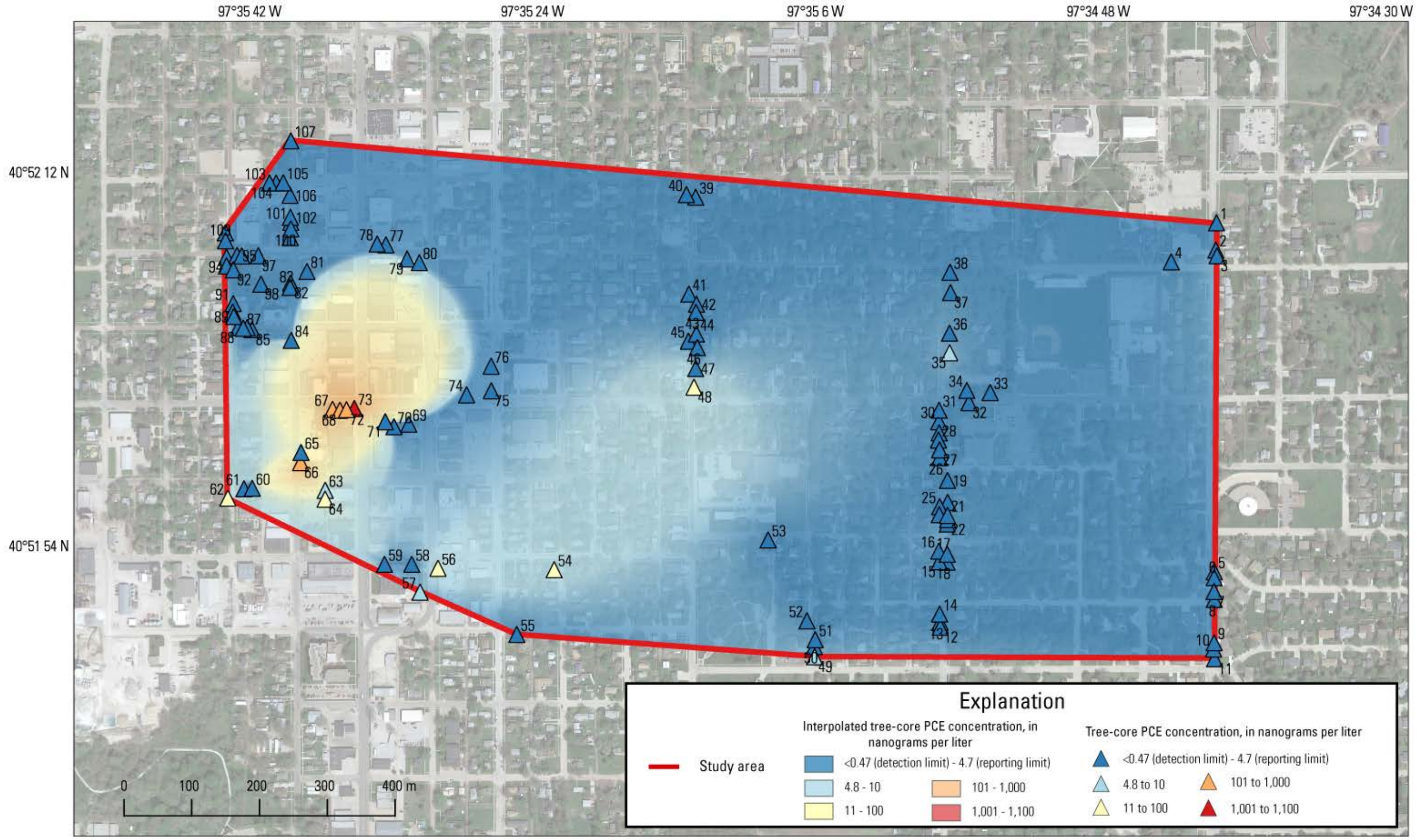
Soil and soil-gas

Because of the scarcity of tree-core data in areas where soil data was collected (S5 Fig), correlations between soil PCE concentrations and the interpolated tree-core PCE concentration surface were poor (Fig 6). Because tree-core PCE concentrations have been shown to correlate well with soil samples [12, 23], tree-core data sparsity and large local variability of soil samples likely resulted in poor correlation between soil PCE concentrations and the interpolated tree-core PCE concentration surface in this study. There was high correlation ($n=15$; $\rho=0.71$) when comparing soil samples collected during March 2015 with the interpolated tree-core PCE concentration surface, likely because the soil samples were located in areas with tree-core samples. Subsequent soil sampling events were focused in the downtown area where tree-core samples were not collected.

Although no significant correlation existed between soil-gas PCE concentrations and the interpolated tree-core PCE concentration surface for individual sample events, combining the two soil-gas sampling events (March/April 2016 and September 2016) resulted in high correlation ($n=38$; $\rho=0.62$; Fig 6 and S3 Fig). Because the different sampling events were spatially clustered, combining the two sampling events resulted in a more distributed dataset.

Sub-slab

Correlations between sub-slab PCE concentrations and the interpolated tree-core PCE concentration surface were frequently significant, with significant coefficients ranging from 0.43 to 0.70 over all individual sampling events from November 2014 to December 2015 (Figs 6 and 7). Unlike groundwater and soil correlations, correlations

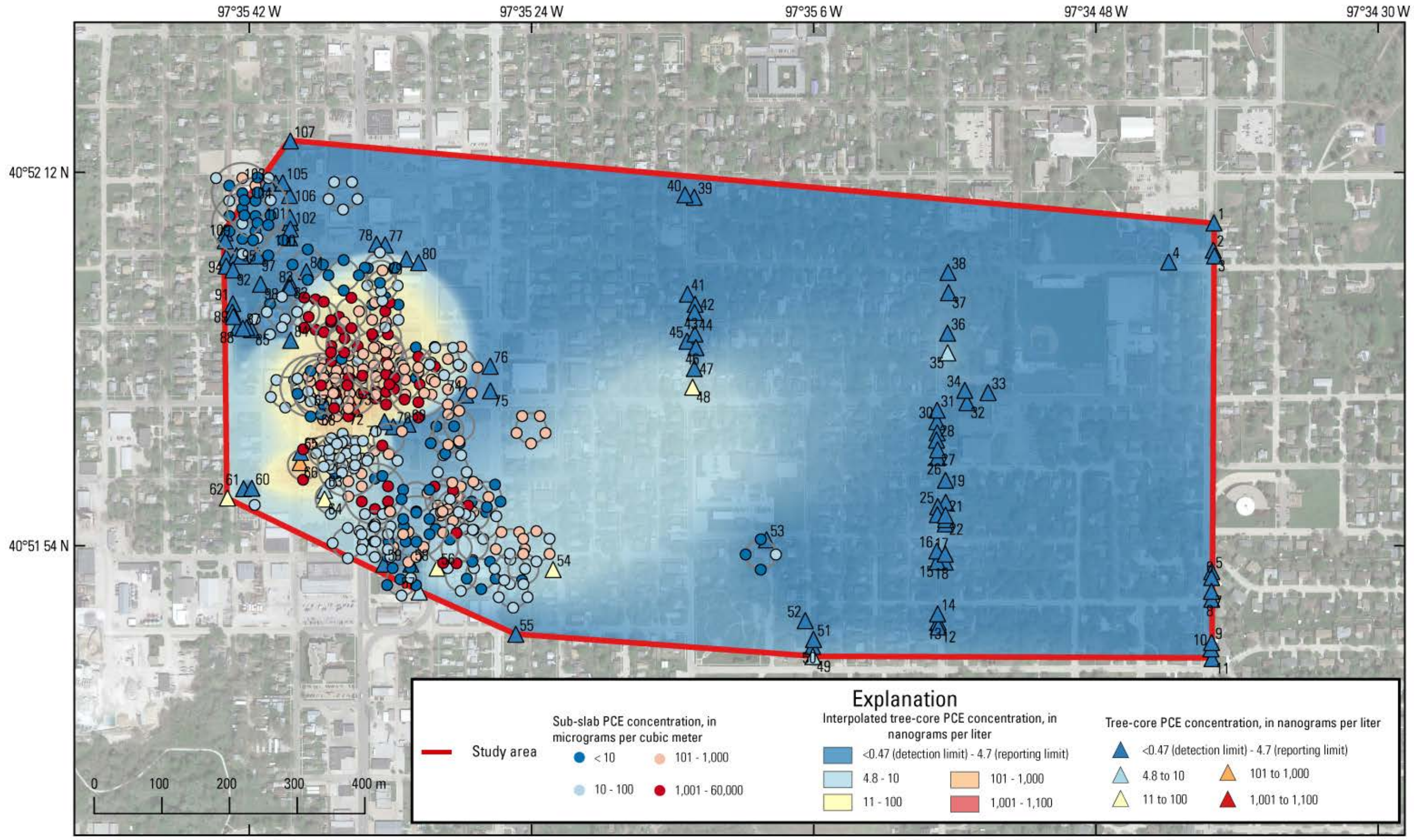


Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Fig 5. Tree-core tetrachloroethene (PCE) concentrations in the study area overlain on the interpolated tree-core PCE concentration surface.

Date			All Groundwater		Shallow (<12 meters) Groundwater		Soil		Soil Gas		Sub-slab		Indoor Air		Indoor Air		Indoor Air	
			ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size
			Correlated with interpolated tree-core surface												Correlated with interpolated soil-gas surface		Correlated with interpolated sub-slab surface	
Individual Sampling Events	More separation in time from tree sampling ↓ Less separation in time from tree sampling	**Nov/Dec 2014**	--	--	--	--	--	1	--	--	**0.62**	**16**	**0.62**	**17**	0.37	10	**0.97**	**16**
		March 2015	--	1	--	--	**0.71**	**15**	--	--	**0.53**	**70**	0.05	30	0.06	22	**0.41**	**29**
		June 2015	-0.36	17	-0.36	13	--	--	--	--	**0.54**	**59**	0.25	24	0.28	20	**0.52**	**24**
		Aug 2015	0.34	28	0.17	19	--	--	--	--	**0.70**	**13**	0.05	15	-0.04	10	0.29	14
		Sept 2015	-0.26	4	--	--	--	--	--	--	**0.43**	**50**	0.21	16	-0.07	15	**0.73**	**15**
		Nov/Dec 2015	-0.24	30	-0.61	12	0.16	21	--	--	**0.53**	**81**	0.34	20	**-0.62**	**17**	0.21	20
		Mar/Apr 2016	--	--	--	--	--	--	0.28	18	0.21	33	0.16	25	-0.25	19	0.26	23
		June 2016	0.74	7	--	--	0.25	13	--	--	--	--	**0.59**	**23**	-0.13	20	**0.71**	**23**
		July 2016	0.01	14	--	--	0.24	8	--	--	0.15	22	0.42	18	-0.01	12	0.27	20
		Sept 2016	--	1	--	--	--	--	-0.26	20	0.14	16	0.41	14	-0.25	9	**0.48**	**15**
Averaging Multiple Sampling Events	Less weight on data collected close in time with tree sampling ↓ More weight on data collected close in time with tree sampling	**Nov/Dec 2014 - Sept 2016**	0.16	100	-0.20	44	0.17	57	**0.62**	**38**	**0.45**	**140**	**0.31**	**117**	-0.11	90	**0.42**	**117**
		March 2015 - Sept 2016	0.18	99			0.21	56			**0.44**	**139**	**0.36**	**103**	-0.18	80	**0.51**	**104**
		June 2015 - Sept 2016					0.16	41			**0.40**	**127**	**0.40**	**94**	-0.19	74	**0.48**	**95**
		Aug 2015 - Sept 2016	0.32	83	-0.16	31					**0.39**	**122**	**0.45**	**81**	-0.16	64	**0.53**	**82**
		Sept 2015 - Sept 2016	0.30	56	-0.53	12					**0.39**	**119**	**0.47**	**77**	-0.12	61	**0.45**	**78**
		Nov/Dec 2015 - Sept 2016	0.26	52							**0.48**	**110**	**0.46**	**69**	-0.15	53	**0.41**	**70**
		Mar/Apr 2016 - Sept 2016	0.49	22	--	--	0.24	20			0.23	57	**0.43**	**64**	-0.10	48	**0.37**	**65**
		June 2016 - Sept 2016			--	--	0.24	20	-0.26	20	0.11	33	**0.53**	**48**	-0.07	37	**0.59**	**51**
		July 2016 - Sept 2016	0.15	15	--	--	0.29	12			0.11	33	**0.45**	**30**	-0.01	21	**0.35**	**33**

Fig 6. Measures of correlation between groundwater, shallow (<12 m) groundwater, soil, soil-gas, sub-slab, and indoor-air PCE concentrations and interpolated tree-core, soil-gas, and sub-slab PCE concentration surfaces. Cells highlighted with color with bold font are significantly correlated. Cells are colored blue, yellow, orange and red if correlation coefficients are <0.40, 0.40-0.49, 0.50-0.59, and >0.59, respectively.



Base map data from Google, 2016
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Horizontal coordinate information references to the North American Datum of 1983

Fig 7. Sub-slab tetrachloroethene (PCE) concentrations in the study area overlain on the interpolated tree-core PCE surface. Each set of points in concentric rings represents multiple samples in one area.

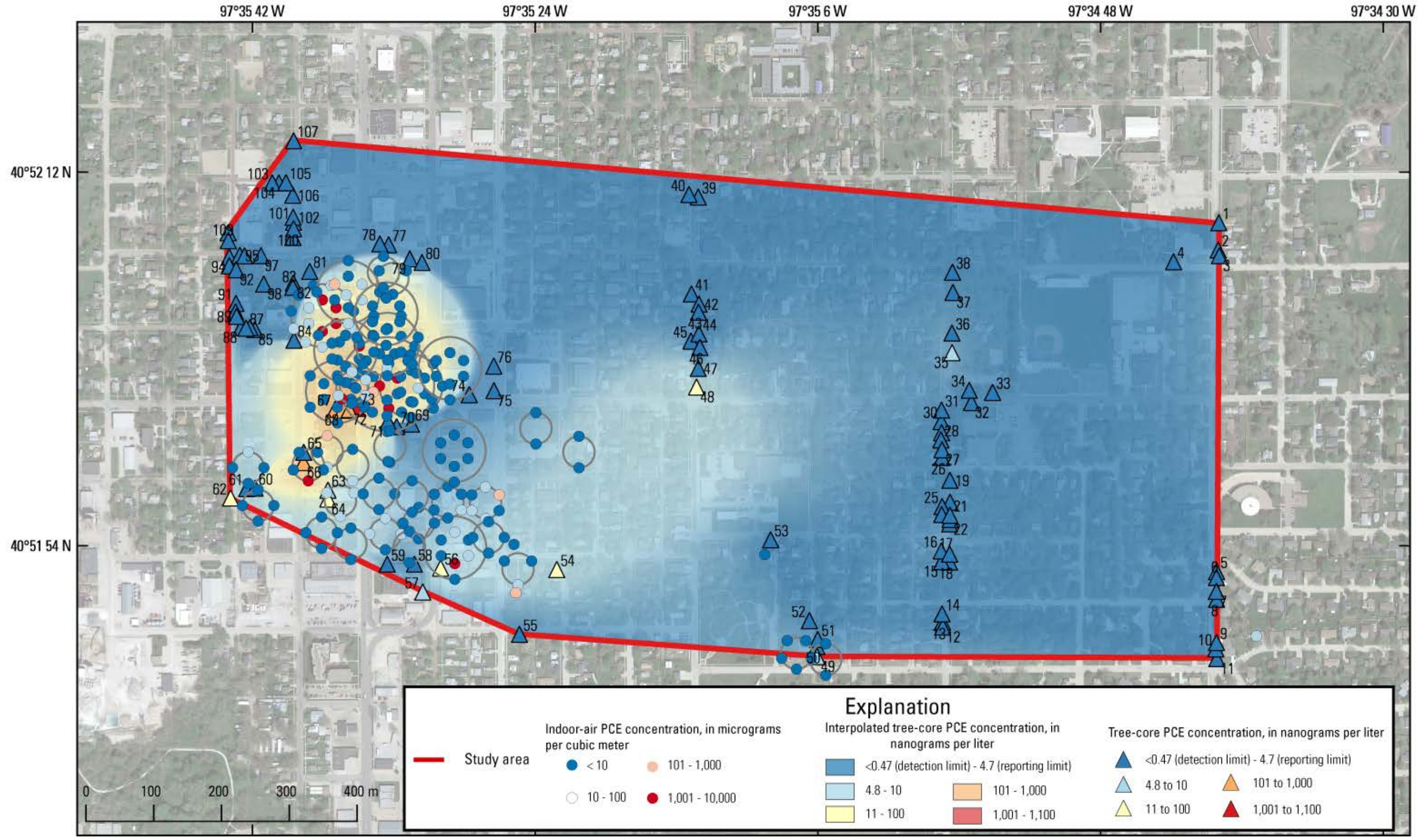
between sub-slab PCE concentrations and the interpolated tree-core PCE concentration surface were consistently correlated over time until March/April 2016 and decreased when the majority of the dataset consisted of more recent data from March/April 2016 to September 2016 sampling events that included samples in areas not well defined by the tree-core sample density (S1 Fig).

Indoor air

Correlation coefficients between indoor-air PCE concentrations and the interpolated tree-core PCE concentration surface were high for the November/December 2014 (ρ=0.62, n=17) and June 2016 (ρ=0.59, n=23) individual sampling events, but were not significant in comparisons for all other individual sampling events across the entire site (Figs 6 and 8). However, when correlating groups of averaged indoor-air sampling events to the interpolated tree-core PCE concentration surface, correlations were significant for all sampling periods, indicating substantial variability between the indoor sampling events likely caused by differences in air-exchange rates. Correlation coefficients ranged from 0.31 to 0.53 and were generally higher for more recent sampling periods. Because aggregating multiple sampling events averages samples from the same location and increases the number of sampled locations through longer time periods, consistently significant and moderate correlations could indicate that the average indoor-air PCE concentrations, rather than the individual indoor-air PCE concentration, are more correlated to the interpolated tree-core PCE surface (i.e., tree sampling is more indicative of a TWA than a “snapshot”), but could also be the result of larger and better distributed sample sizes.

Soil-gas as an indicator of indoor air

Correlations between indoor-air PCE concentrations and the interpolated soil-gas PCE concentration surface (produced from data from two sampling events) for individual sampling events and aggregated sampling events were poor with only one significant correlation coefficient of -0.62, which occurred during the November/December 2015 sampling event (Fig 6 and S10 Fig). Because soil-gas samples were collected along two city streets, soil-gas data was impacted by the same effects of poor spatial distribution of samples that is observed in the tree-core dataset.



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Horizontal coordinate information references to the North American Datum of 1983

Fig 8. Indoor-air tetrachloroethene (PCE) concentrations in the study area and interpolated tree-core PCE concentration surface. Each set of points in concentric rings represents multiple samples in one area.

Sub-slab as an indicator of indoor air

Correlation coefficients between indoor-air PCE concentrations and the interpolated average sub-slab PCE concentration surface (from multiple sampling events) were substantially higher than those between indoor-air PCE concentrations and the interpolated soil-gas PCE concentration surface (Figs 6 and 9). A total of 6 out of 10 individual sampling events had significant correlations. Significant correlation coefficients ranged from 0.41 to 0.97, with the 0.97 coefficient occurring during the November/December 2014 sampling event, and no general trend with time was observed.

Because one of the current best available and most accepted methods for screening for vapor intrusion risk is sub-slab sampling, a pairwise correlation test was conducted on all paired indoor-air and sub-slab samples collected during the same sampling event and location and indicated a significant correlation coefficient of 0.55 (n=89), which is comparable to the correlation between indoor-air and the interpolated tree-core PCE concentration surface.

Effect of non-uniform tree-core sample distribution on correlations

Correlations between indoor-air and sub-slab PCE concentrations and tree-core samples collected within 31 m (Fig 10) generally agreed with the correlations between indoor-air and sub-slab PCE concentrations and the interpolated tree-core PCE surface (Fig 6). All significant correlation coefficients were moderate or high with values ranging from 0.54 to 0.83. Although correlations were insignificant for many individual sampling events and sampling periods, correlation significance is limited in part by small sample sizes. In contrast, significant correlations between groundwater, soil, and soil-gas PCE concentrations and tree-core samples collected within 31 m (Fig 10) were negatively correlated with high values ranging from -0.74 to -0.94. This is likely explained by the large amount of heterogeneity in the subsurface over small distances, especially near the source areas downtown where most of the groundwater, soil, and soil-gas samples in these correlations are located. Future should be focused on collecting tree-core samples closely paired with vapor intrusion samples in order to better evaluate correlations between vapor intrusion and tree-core samples without the potential error associated with non-uniform distributions of tree-core samples. The use of a diameter-dependent buffer

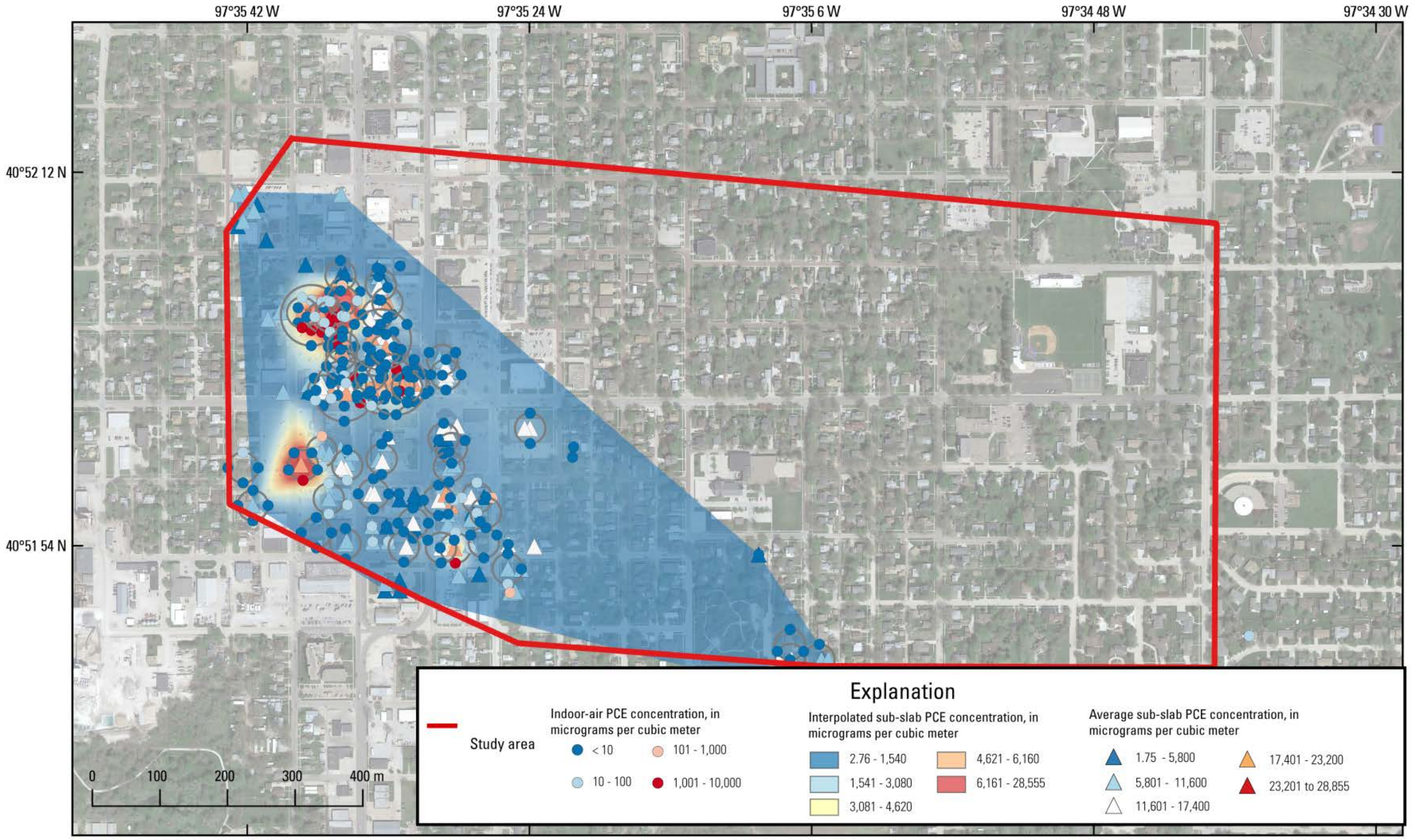

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Fig 9. Indoor-air tetrachloroethene (PCE) concentrations in the study area overlain on the interpolated sub-slab PCE concentration surface. Points in each concentric ring represent multiple sampling events at one location.

Date			All Groundwater		Shallow (<12 meters) Groundwater		Soil		Soil Gas		Sub-slab		Indoor Air	
			ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size	ρ	Sample Size
			Correlated with tree-core samples within 31 m											
Individual Sampling Events	More separation in time from tree sampling	**Nov/Dec 2014**	--	--	--	--	--	--	--	--	--	--	0.53	5
		March 2015	--	--	--	--	--	--	--	--	**0.73**	**16**	0.26	10
	↓	**June 2015**	-0.24	10	-0.06	10	--	--	--	--	**0.79**	**13**	**0.73**	**9**
		Aug 2015	-0.58	8	-0.56	6	--	--	--	--	--	--	0.89	4
		Sept 2015	--	--	--	--	--	--	--	--	0.35	10	--	--
		Nov/Dec 2015	**-0.77**	**10**	--	--	**-0.94**	**6**	--	--	**0.54**	**15**	0.80	6
	Less separation in time from tree sampling	**Mar/Apr 2016**	--	--	--	--	--	--	**-0.85**	**6**	-0.41	5	0.58	7
		June 2016	0.87	3	--	--	0.87	3	--	--	--	--	--	--
		July 2016	-0.41	22	--	--	--	--	--	--	--	--	0.52	6
		Sept 2016	--	--	--	--	--	--	--	--	--	--	--	--
Averaging Multiple Sampling Events	Less weight on data collected close in time with tree sampling	**Nov/Dec 2014 - Sept 2016**	--	--	--	--	--	--	--	--	--	--	0.53	5
		March 2015 - Sept 2016	--	--	--	--	--	--	--	--	**0.75**	**18**	0.15	11
	↓	**June 2015 - Sept 2016**	-0.36	13	-0.24	13	--	--	--	--	**0.74**	**19**	**0.80**	**10**
		Aug 2015 - Sept 2016	**-0.74**	**11**	-0.64	8	--	--	--	--	--	--	0.89	4
		Sept 2015 - Sept 2016	--	--	--	--	--	--	--	--	0.44	15	--	3
		Nov/Dec 2015 - Sept 2016	**-0.75**	**17**	--	--	**-0.80**	**7**	--	--	**0.69**	**19**	**0.83**	**7**
	More weight on data collected close in time with tree sampling	**Mar/Apr 2016 - Sept 2016**	--	--	--	--	--	--	0.03	13	-0.41	5	0.55	8
		June 2016 - Sept 2016	0.56	5	--	--	0.56	5	--	--	--	--	0.54	4
		July 2016 - Sept 2016	-0.41	22	--	--	--	--	--	--	--	--	0.60	7

Fig 10. Measures of correlation between groundwater, shallow (<12 m) groundwater, soil, soil-gas, sub-slab, and indoor-air PCE concentrations and tree-core concentrations in tree-core samples collected within 31 m. Cell highlighted with color with bold font are significantly correlated. Cells are colored orange and red if correlation coefficients are 0.50-0.59, and >0.59, respectively.

may also be useful in correlations as it has been shown that trees represent a subsurface volume proportionate to their trunk diameter [24].

Conclusions and site implications

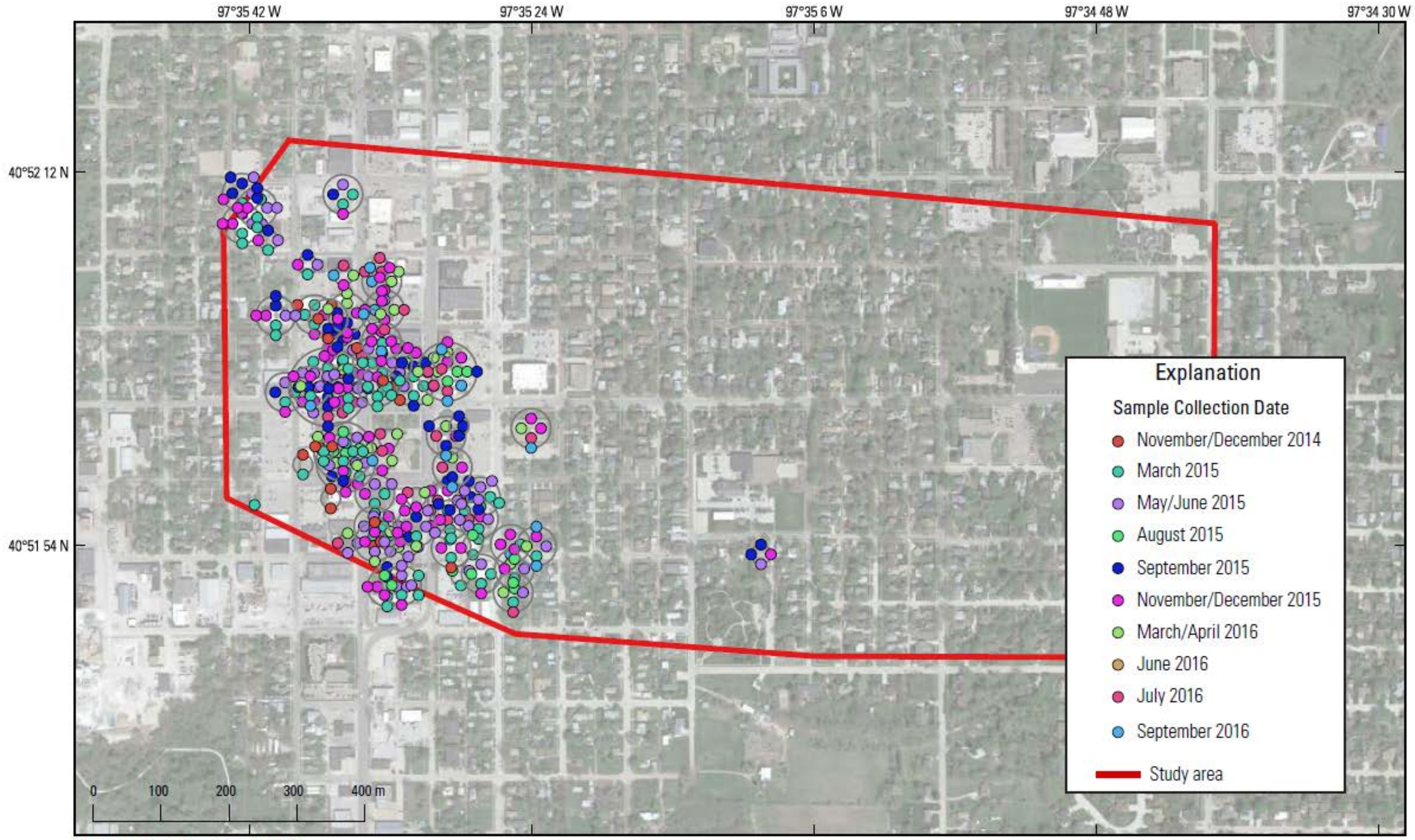
Tree-coring is best utilized as an initial screening tool to determine the general areas of interest and specific hot spots to focus future VI sampling. Because of the cost- and time-efficient nature of tree-coring, several hundred tree-core samples can be collected in a week’s time depending on the required permissions on individual properties, a potential limiting factors in phytoforensic studies and all methods requiring private-property access; however, if trees are located in a city right-of-way and permission is granted by the city, tree-core samples can be collected simply by walking along city streets with approximately 5 minutes per sample required.

As VI transport involves multi-media environmental transport and the heterogeneities inherent in urban environments, multiple sampling approaches of various media are commonly applied, such as groundwater, soil-gas, sub-slab, and indoor-air applied at this site in conjunction with the tree core sampling. Phytoforensic sampling has been shown offer a blending or composite of these multiple environmental media. [12, 23, 24] Findings shown here indicate that PCE concentrations in trees can be highly correlated with multiple VI investigative methods, including soil-gas and VI samples (sub-slab and indoor-air samples), especially when comparing to indoor-air concentrations over long periods, and are comparable to sub-slab samples. Indoor-air PCE concentrations in this study collected within two months and, to a lesser extent, with average indoor-air concentrations over years, were highly correlated with the interpolated tree-core PCE concentration surface. Although this is only one case study, these findings and previous studies suggest that trees are valid indicators of VI potential over long temporal periods.

The non-uniform distribution of tree-core samples in this specific study left spatial gaps in the dataset, especially in the residential area, and likely resulted in poor definition of the interpolated tree-core PCE concentration surface. Ideally, the collection of tree-core samples should be in a more uniformly distributed pattern over the study area to avoid spatial gaps in tree-core data and to better define the tree-core PCE concentration distribution.

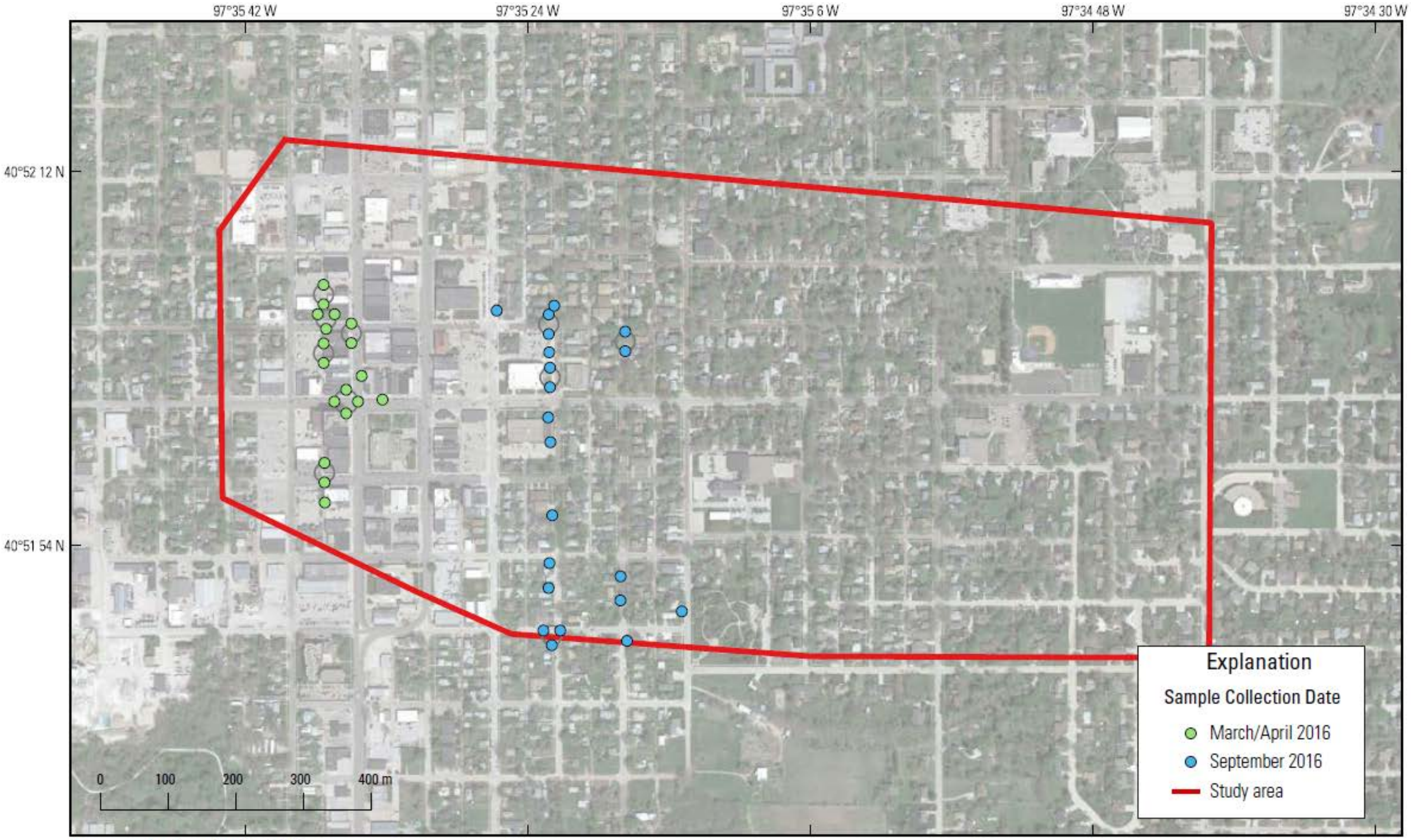
Like all geospatial datasets, collecting uniformly distributed tree-core data of sufficient density over the entire project area is vital to fully describe the tree-core concentration surface. Prior knowledge of the local hydrogeology and potential source areas can also be used to direct sample density in certain areas as tree-core samples can be collected in greater densities in the vicinity of the source areas with decreasing spatial density in the downgradient direction. This approach is relatively easy to accomplish, however, because tree-coring is an exceptionally rapid and inexpensive practice compared to traditional methods. With each sample taking less than 5 minutes to collect, a large study area on the order of square kilometers of can be sampled in days compared to the weeks and months required from traditional methods. In this study of approximately 1 km^2 with less than 60 trees in the vicinity of the source area, roughly 12 hours of tree-core sampling with minimal equipment was sufficient to delineate the vapor intrusion potential and offered comparable delineation to traditional sub-slab sampling performed at 140 properties over a period of approximately 2 years with multiple mobilizations of large, vehicle-mounted equipment.

Supporting information



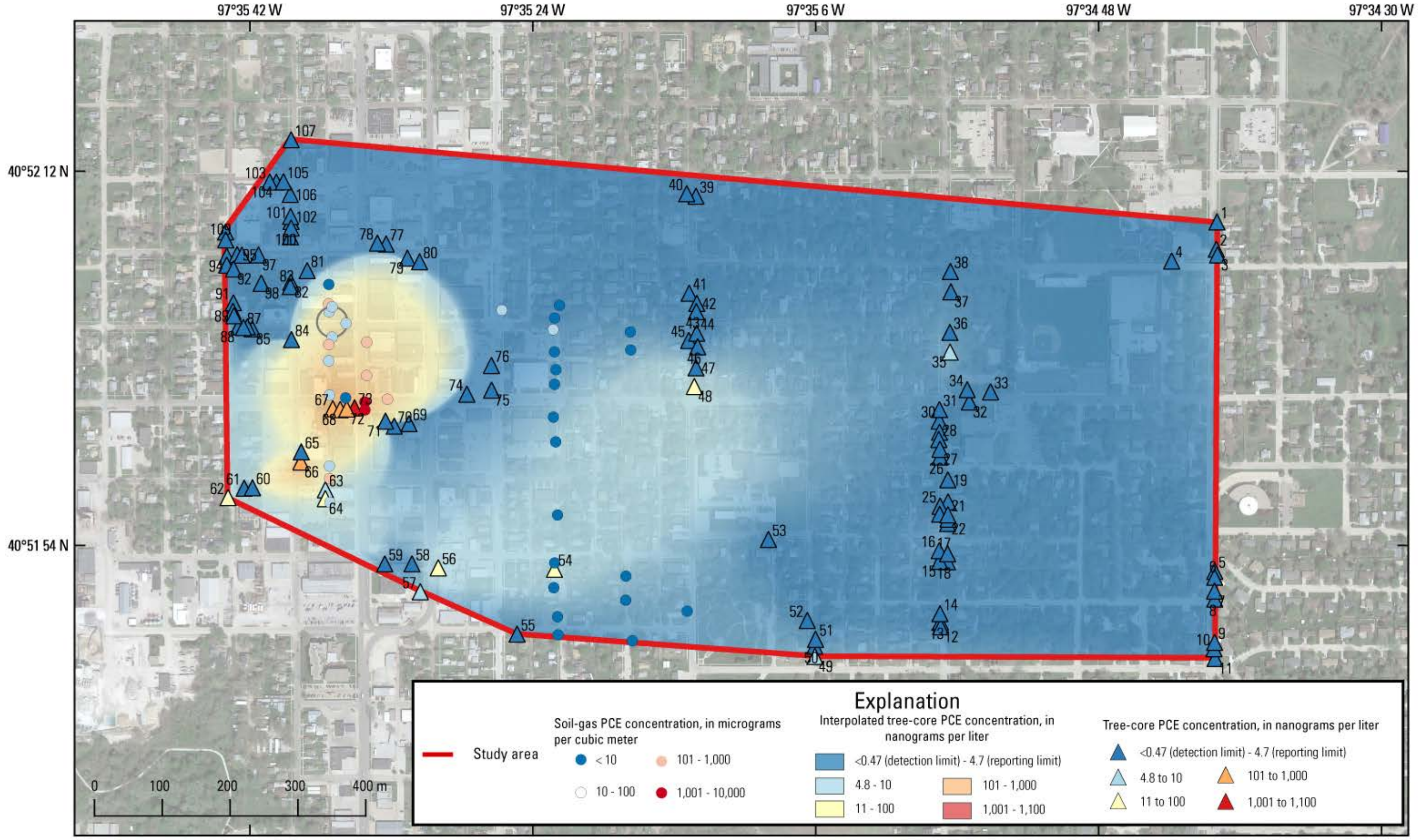
Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Figure S1. Location and date of sub-slab samples in the York, Nebraska study area. Each set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Figure S2. Location and date of soil-gas samples in the York, Nebraska study area. Each set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
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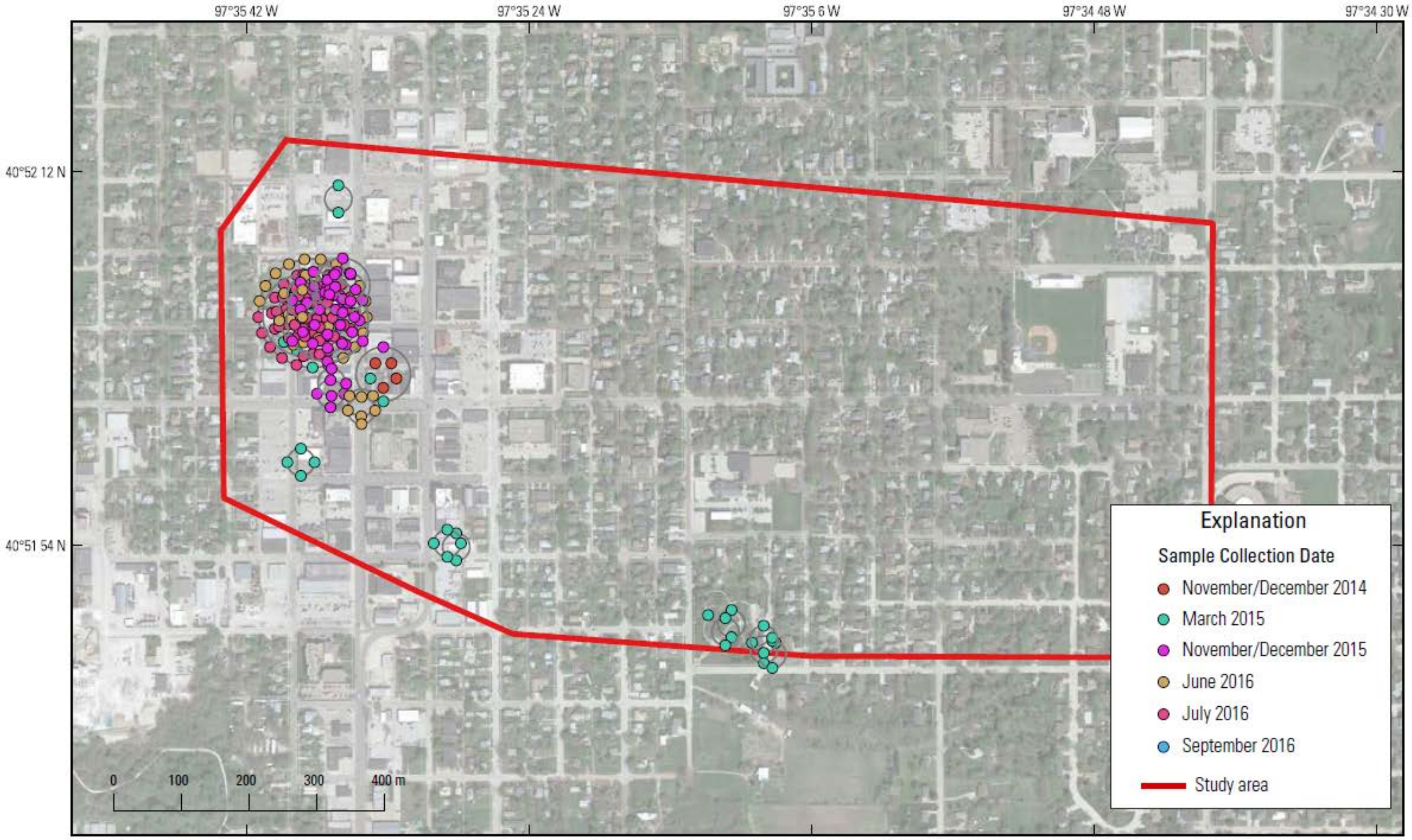
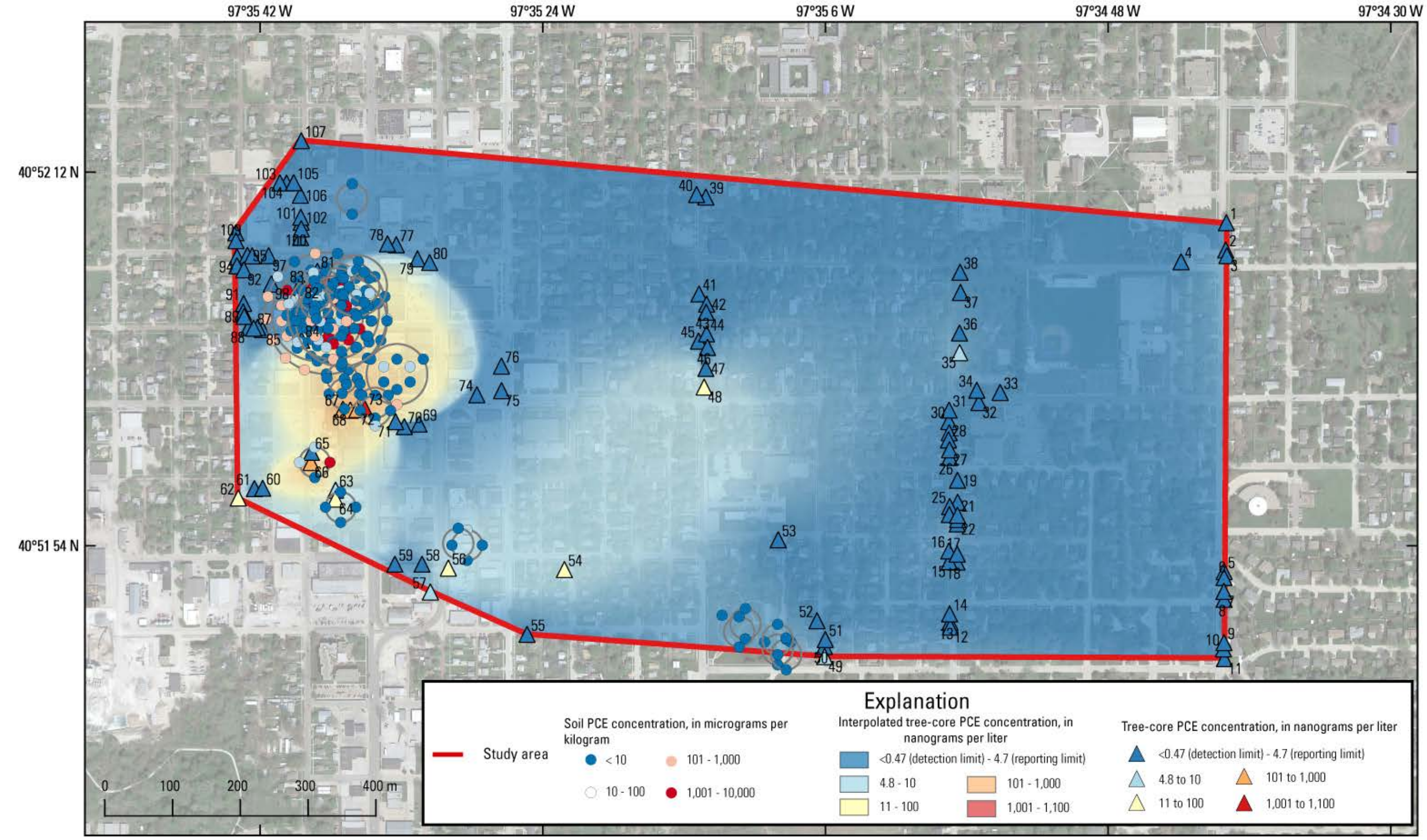
Figure S3. Soil-gas tetrachloroethene (PCE) concentrations in the study area overlain on the interpolated tree-core PCE concentration surfaceEach set of points in concentric rings represents multiple samples in one area.



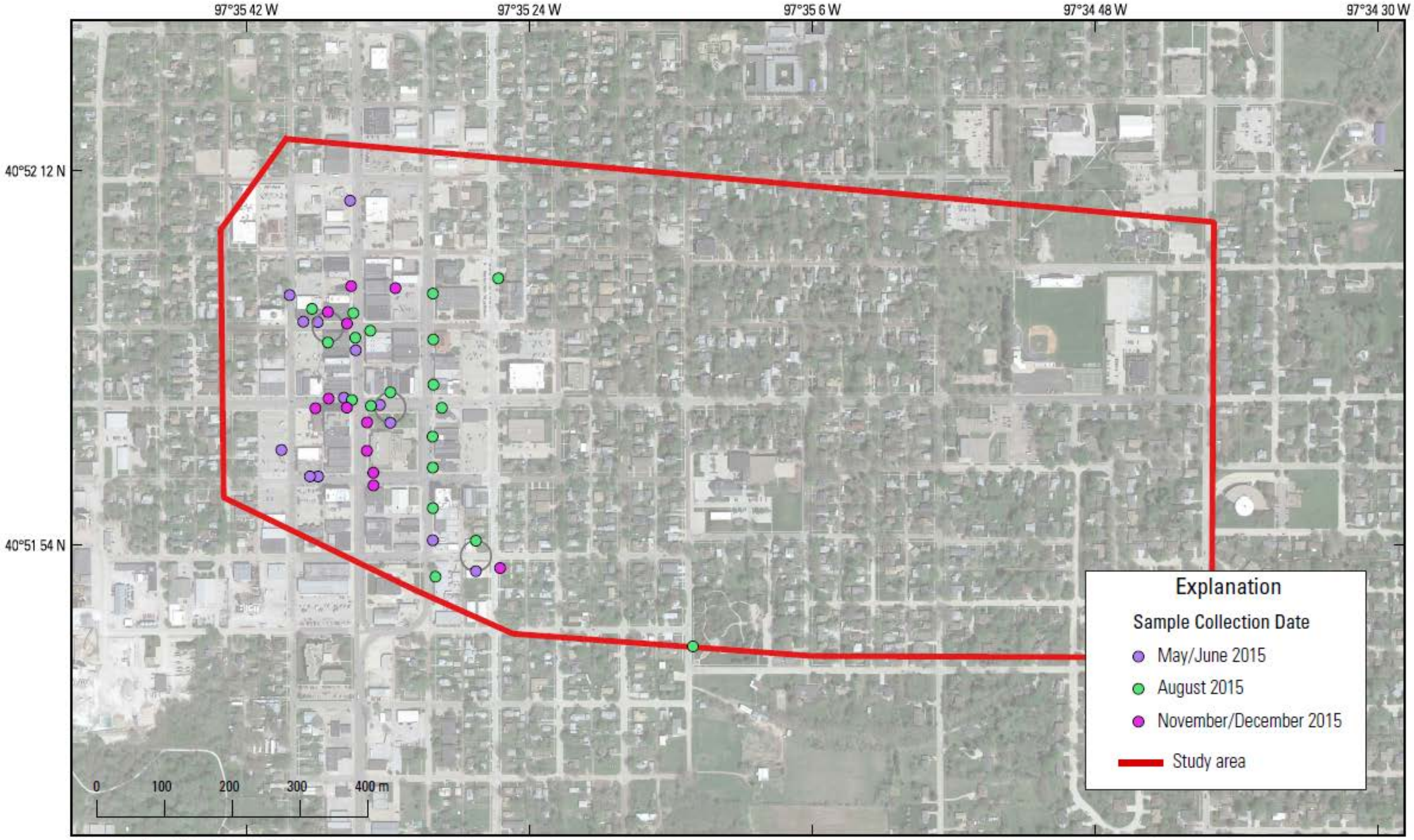
Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Figure S4. Location and date of soil samples in the York, Nebraska study areaEach set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Figure S5. Soil tetrachloroethene (PCE) concentrations in the study area overlain on the interpolated tree-core PCE concentration surfaceEach set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
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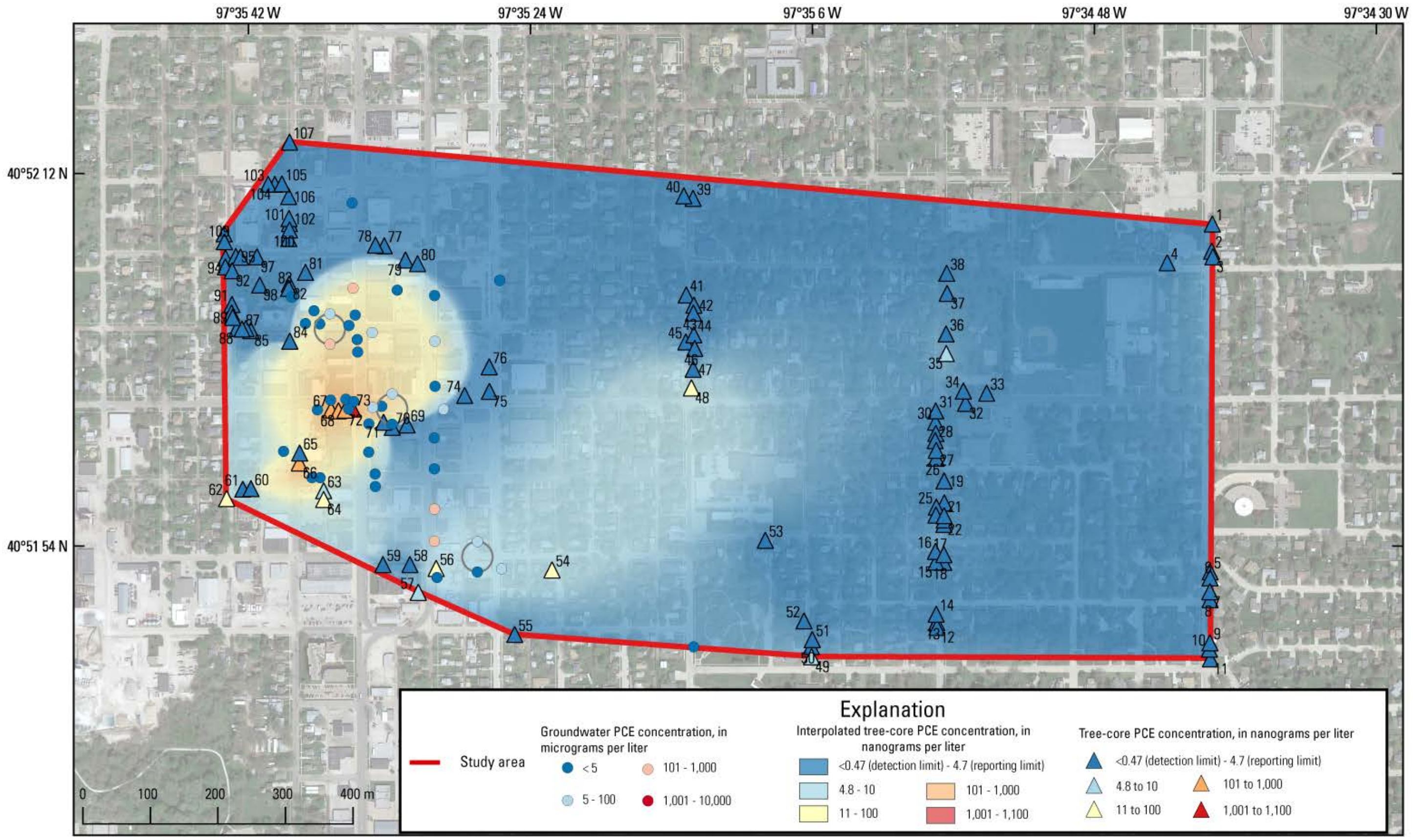
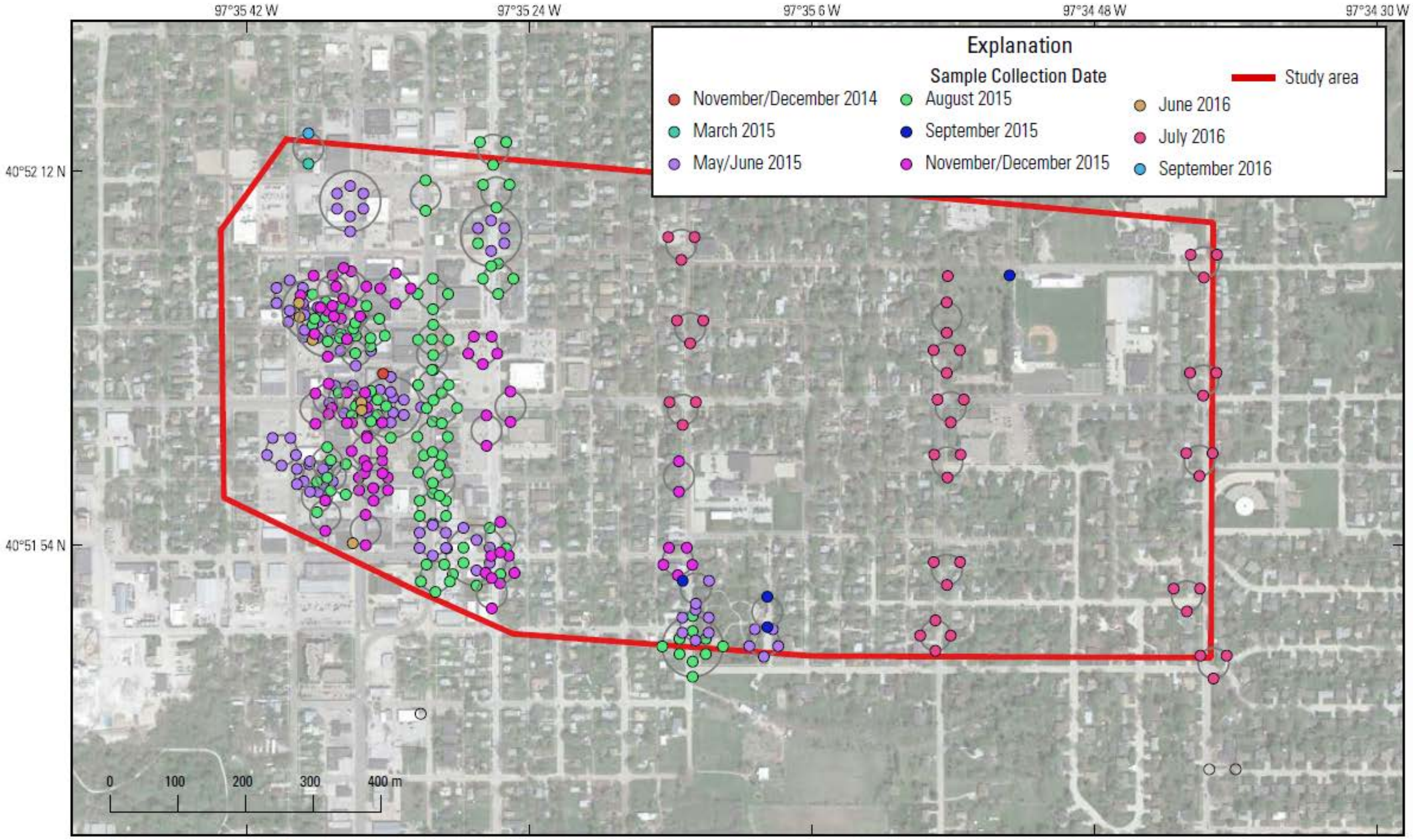
Horizontal coordinate information references to the North American Datum of 1983

Figure S6. Location and date of shallow (<12 m) groundwater samples, York, Nebraska in the study area. Each set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
Universal Transverse Mercator projection zone 14
Horizontal coordinate information references to the North American Datum of 1983

Figure S7. Groundwater tetrachloroethene (PCE) concentrations in shallow (< 12 m) groundwater samples in the study area overlain on the interpolated tree-core PCE concentration surface. Each set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
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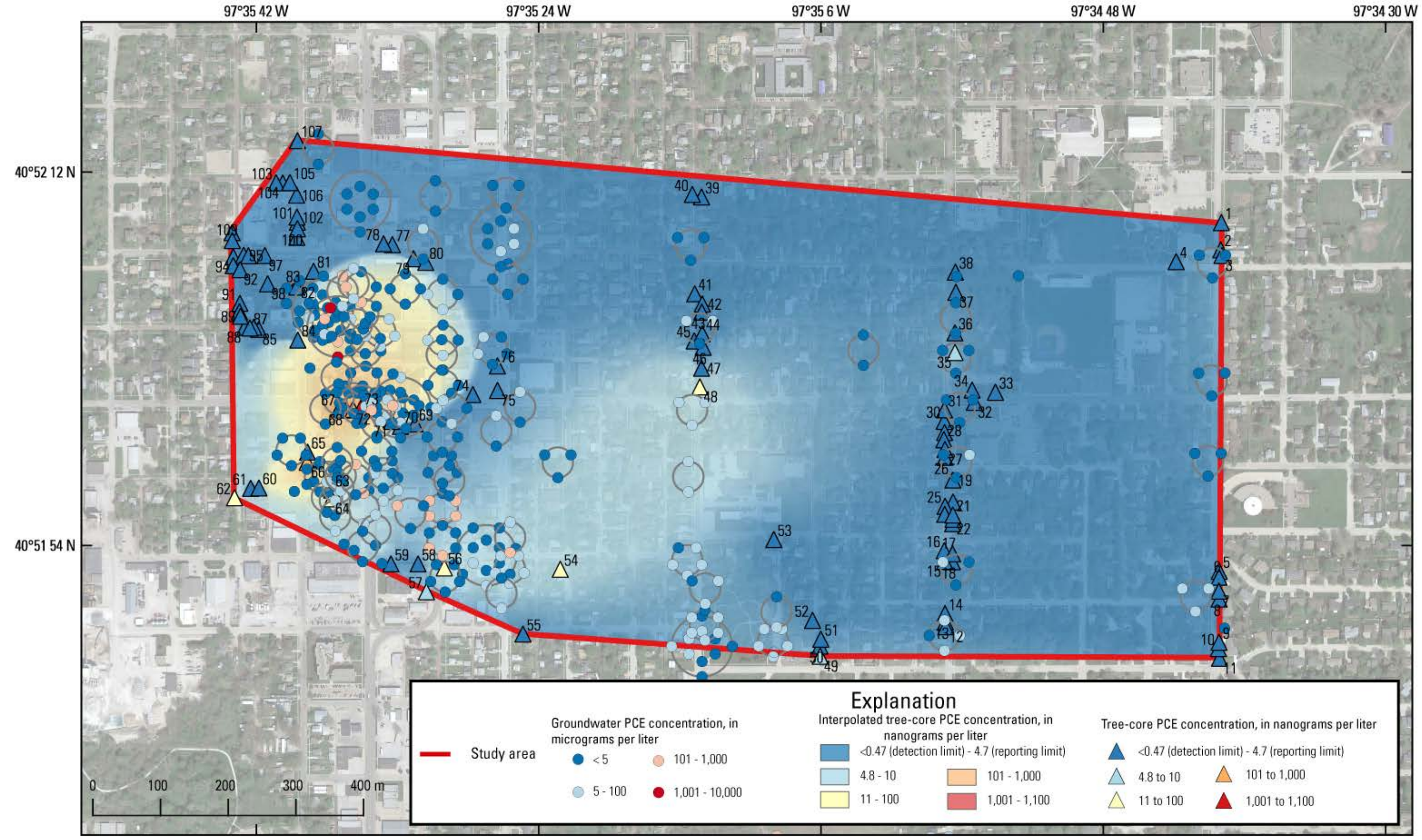
Figure S8. Location and date of all groundwater samples in the York, Nebraska study area. Each set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
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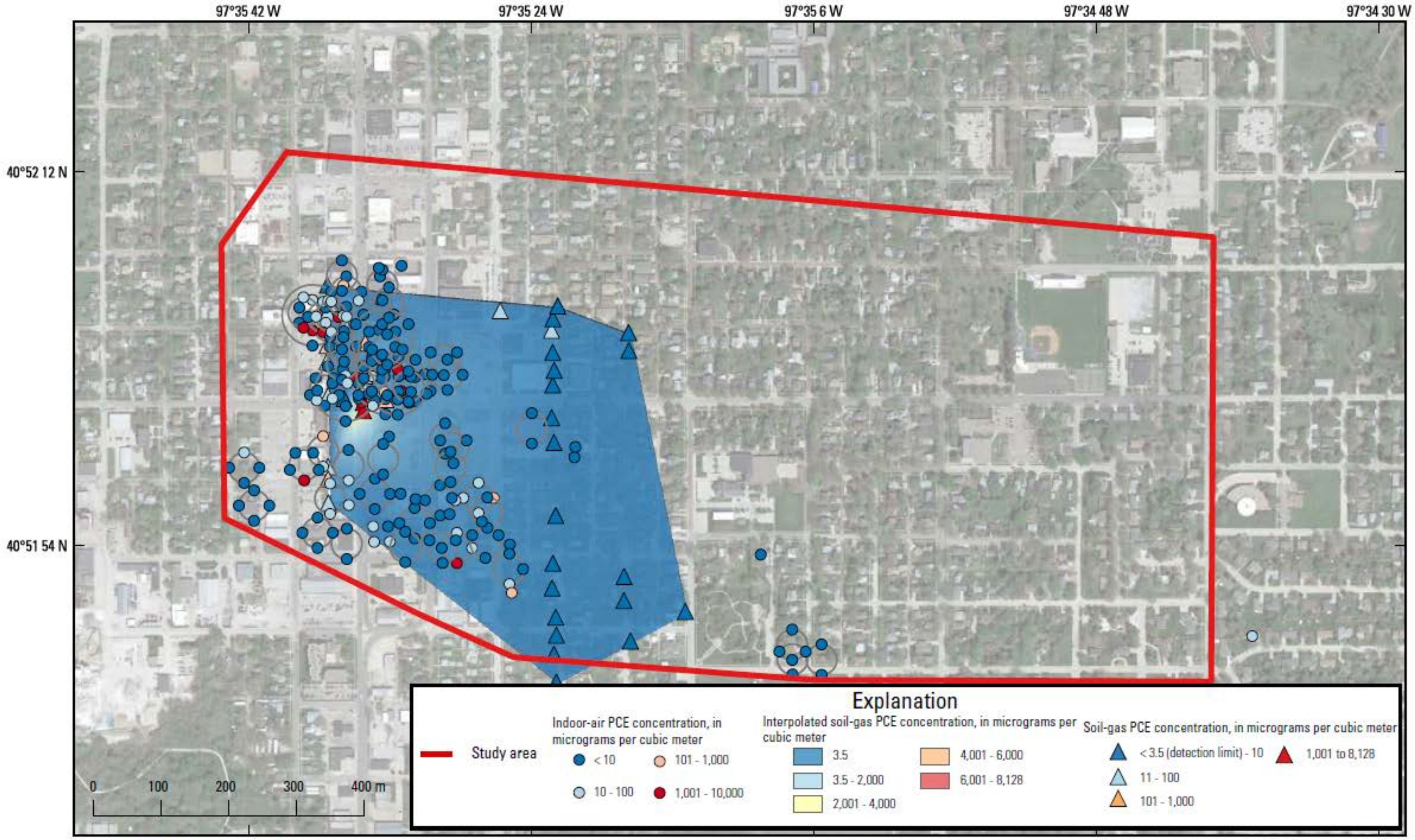
Figure S9. Groundwater tetrachloroethene (PCE) concentrations in all groundwater samples in the study area overlain on the interpolated tree-core PCE concentration surface. Each set of points in concentric rings represents multiple samples in one area.



Base map data from Google, 2016
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Figure S10. Indoor-air tetrachloroethene (PCE) concentrations in the study area overlain on the interpolated soil-gas PCE concentration surfaceEach set of points in concentric rings represents multiple samples in one area.

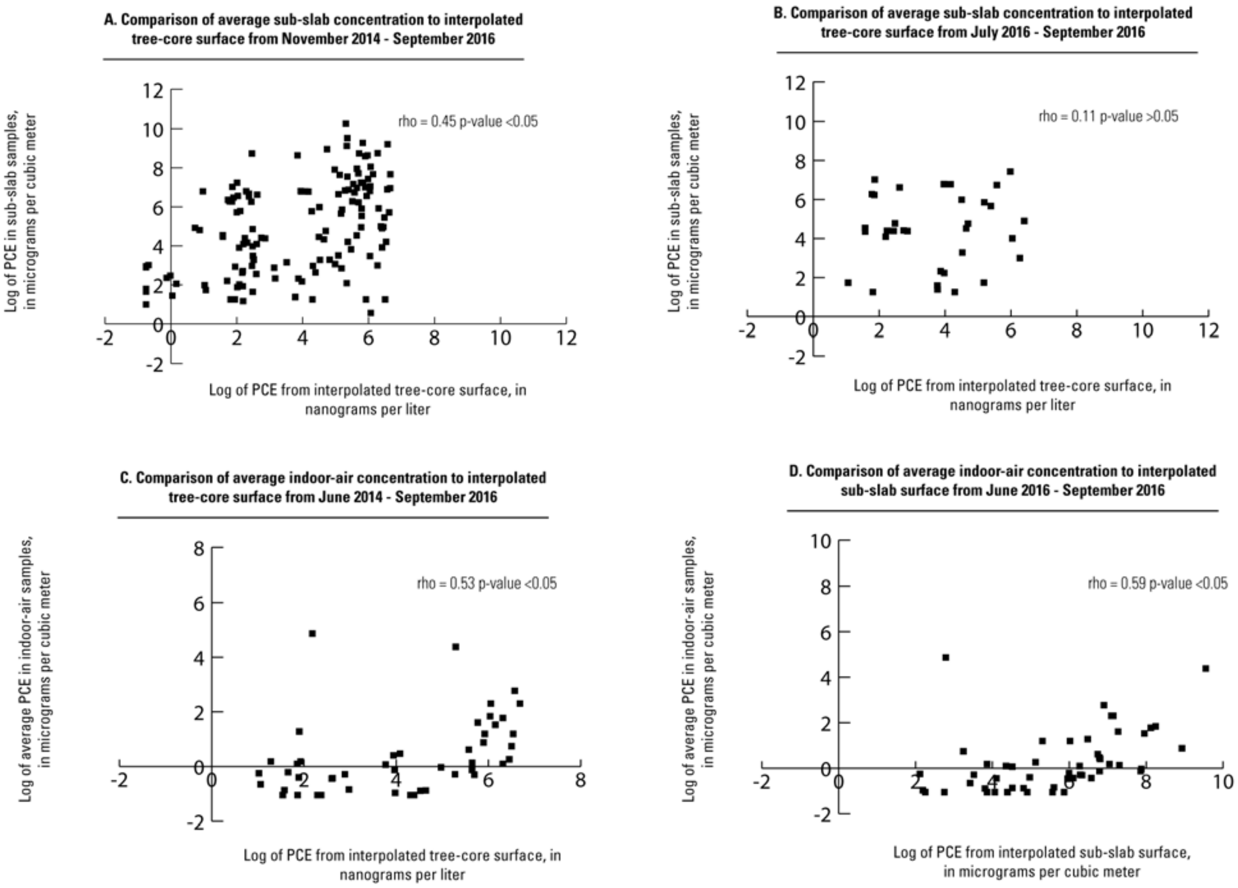

Figure S11. Average concentrations of tetrachloroethylene (PCE) in sub-slab versus interpolated tree-core surface a) from November 2014 to September 2016 and b) from July 2016 to September 2016 as well as average concentrations of tetrachloroethylene (PCE) in indoor-air samples from June 2016 to September 2016 versus c) the interpolated PCE tree-core surface and d) the interpolated PCE sub-slab surface. Rho is the spearman's rank correlation coefficient.

Acknowledgments

Special thanks to Owens Hull of the EPA Region 7 who provided all EPA data at the site and who was extremely helpful in supporting this research. The authors also thank Mitch Doht and the City of York, Nebraska for permitting right-of-way access. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References

1. Bennett DH, McKone TE, Evans JS, Nazaroff WW, Margni MD, Jolliet O, et al. Peer reviewed: defining intake fraction. Environmental Science & Technology. 2002;36(9):206A-11A.

2. USEPA. Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air. In: Office of Solid Waste and Emergency Response, editor. 2015. p. 267.

3. Fitzgerald J. One regulatory perspective on the vapor intrusion pathway. Groundwater Monitoring & Remediation. 2009;29(1):51-2. doi: 10.1111/j.1745-6592.2008.01213.x.

4. McAlary T, Ettinger R, Johnson P, Eklund B, Hayes H, Chadwick D, et al. Review of Best Practices, Knowledge and Data Gaps, and Research Opportunities for the US Department of Navy Vapor Intrusion Focus Areas. DTIC Document, 2009.

5. Johnson PC, Ettinger RA. Heuristic model for predicting the intrusion rate of contaminant vapors into buildings. Environmental Science & Technology. 1991;25(8):1445-52.

6. Burken JG, Schnoor JL. Predictive Relationships for Uptake of Organic Contaminants by Hybrid Poplar Trees. Environmental Science & Technology. 1998;32(21):3379-85. doi: 10.1021/es9706817.

7. Briggs GG, Bromilow RH, Evans AA. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. Pesticide Science. 1982;13(5):495-504. doi: 10.1002/ps.2780130506.

8. Larsen M, Burken J, Machackova J, Karlson UG, Trapp S. Using Tree Core Samples to Monitor Natural Attenuation and Plume Distribution After a PCE Spill. Environmental Science & Technology. 2008;42(5):1711-7. doi: 10.1021/es0717055.

9. Schumacher JG, Struckhoff GC, Burken JG. Assessment of Subsurface Chlorinated Solvent Contamination Using Tree Cores at the Front Street Site and a Former Dry Cleaning Facility at the River-front Superfund Site, New Haven, Missouri, 1999-2003: US Department of the Interior, US Geological Survey; 2004. 41 p.

10. Wahyudi A, Bogaert P, Trapp S, Macháčková J. Pollutant plume delineation from tree core sampling using standardized ranks. Environmental Pollution. 2012;162:120-8. doi: http://dx.doi.org/10.1016/j.envpol.2011.11.010.

11. Limmer MA, Balouet J-C, Karg F, Vroblesky DA, Burken JG. Phytoscreening for Chlorinated Solvents Using Rapid in Vitro SPME Sampling: Application to Urban Plume in Verl, Germany. Environmental Science & Technology. 2011;45(19):8276-82. doi: 10.1021/es201704v.

12. Struckhoff GC, Burken JG, Schumacher JG. Vapor-Phase Exchange of Perchloroethene between Soil and Plants. Environmental Science & Technology. 2005;39(6):1563-8. doi: 10.1021/es049411w.

13. Ma X, Burken J. Modeling of TCE Diffusion to the Atmosphere and Distribution in Plant Stems. Environmental Science & Technology. 2004;38(17):4580-6. doi: 10.1021/es035435b.

14. Sorek A, Atzmon N, Dahan O, Gerstl Z, Kushisin L, Laor Y, et al. “Phytoscreening”: The Use of Trees for Discovering Subsurface Contamination by VOCs. Environmental Science & Technology. 2007;42(2):536-42. doi: 10.1021/es072014b.

15. Dobson MC, Moffat AJ. A Re-Evaluation of Objections to Tree Planting On Containment Landfills. Waste Management & Research. 1995;13(6):579-600. doi: 10.1177/0734242X9501300607.

16. MacKay AA, Gschwend PM. Sorption of Monoaromatic Hydrocarbons to Wood. Environmental Science & Technology. 2000;34(5):839-45. doi: 10.1021/es9900858.

17. Trapp S, Miglioranza KSB. Sorption of Lipophilic Organic Compounds to Wood and Implications for Their Environmental Fate. Environmental Science & Technology. 2001;35(8):1561-6. doi: 10.1021/es000204f.

18. Vroblesky DA. User’s Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds2008. 59 p.

19. Luo H, Dahlen P, Johnson PC, Peargin T, Creamer T. Spatial Variability of Soil-Gas Concentrations near and beneath a Building Overlying Shallow Petroleum Hydrocarbon–Impacted Soils. Groundwater Monitoring & Remediation. 2009;29(1):81-91.

20. Sibson R. A Brief Description of Natural Neighbor Interpolation. Interpolating Multivaritate Data. New York: John Wiley & Sons; 1981. p. 21-36.

21. Watson D. Contouring: a guide to the analysis and display of spatial data: Elsevier; 2013.

22. Fieller EC, Hartley HO, Pearson ES. Tests for Rank Correlation Coefficients. I. Biometrika. 1957;44(3/4):470-81. doi: 10.2307/2332878.

23. Algreen M, Trapp S, Jensen PR, Broholm MM. Tree Coring as a Complement to Soil Gas Screening to Locate PCE and TCE Source Zones and Hot Spots. Groundwater Monitoring & Remediation. 2015;35(4):57-66. doi: 10.1111/gwmr.12133.

24. Wilson JL, Limmer MA, Samaranayake VA, Schumacher JG, Burken JG. Tree Sampling as a Method to Assess Vapor Intrusion Potential at a Site Characterized by VOC-Contaminated Groundwater and Soil. Environmental Science & Technology. 2017. doi: 10.1021/acs.est.7b02667.

SECTION

3. CONCLUSIONS

The objectives of this work were carried out and the overall goal of improving vapor intrusion assessment through the use of plant sampling was achieved. This work improves the knowledge of how trees interact with multiple contaminated media in the subsurface and relates that knowledge to the field of vapor intrusion assessment. The research carried out as part of this project further establishes and validates the use of tree sampling as a screening tool for vapor intrusion potential, but the approach is not without caveats and limitations that were also elucidated in this research to offer knowledge on limitations and possible pitfalls in using plant sampling.

This work demonstrates that trees are most representative of the shallow subsurface, and that the volume sampled by a tree is directly related to the size of the tree, measured as tree-trunk diameter in this work. For example, using a root-to-trunk diameter ratio of 1 m/cm shown to have the best model fit in this work, a commonly sized tree (30-cm diameter) is representative of a large area similar to the footprint of a residential building. However, sampled trees are often not located immediately adjacent to homes or buildings, therefore some interpretation must be made when extrapolating tree-core concentrations to the subsurface below homes because of the large heterogeneity of soil-gas in urban areas overall and specifically around built structures. Trees were demonstrated to sample large subsurface volumes in this work and therefore can minimize concerns of subsurface heterogeneity and pitfalls of traditional methods that gather relatively small sample volumes.

Tree sampling was also demonstrated to have a significant directional component that can be used to delineate the spatial distribution of shallow subsurface contamination, center around the tree, around homes by sampling a single tree. Provided *in-planta* concentration gradients are present, the multi-directional sampling of a single tree can indicate if a home is at increased potential for VI relative to the average *in-planta* concentration. Where *in-planta* concentrations gradients are small, the resulting direction of subsurface contamination distribution has higher uncertainty, and the subsurface should be interpreted as more uniform (i.e., less heterogeneous distribution of pollutants). Directional tree sampling was also shown to be correlated with shallow subsurface soil-gas contamination, an imperative characteristic of a VI assessment tool. Revealing the directionality of tree coring in this work greatly increases the potential application of phytoforensics for VI assessment by turning a single large tree into a multidirectional sampling point that can provide a 360-degree assessment from that single location with just minutes of sampling. The indication of a subsurface pollutant gradient is also valuable in assessing the heterogeneity of a site with increased sampling density near homes.

Tree sampling was also shown in this work to be correlated with soil-gas, sub-slab, and indoor-air samples, especially when averaging soil-gas, sub-slab, and indoor-air samples over months and years; however, the non-uniform distribution of tree-core samples in this study left spatial gaps in the specific dataset, and likely did not represent the true tree-core concentration surface in those gaps well. Collection of tree-core samples should be in an evenly distributed pattern if possible, like all geospatial data, to avoid spatial gaps in tree-core data and to reduce interpolation error. Although these findings demonstrate that tree sampling fills information gaps left by traditional VI assessment methods, tree sampling is best applied as a screening tool and to augment traditional sampling because of the many parameters, and their associate uncertainties, that control mass transfer of contaminants in the subsurface and built environment. The time-weighting characteristic of tree-coring also provides insight into potential long-term VI exposure, rather than a snap-shot in time and the temporal variability of indoor-air sampling or shallow soil sampling. Phytoforensics adds a new tool in assessing VI potential and predicting possible exposure.

Tree sampling is an addition to the vapor intrusion assessment toolkit that complements traditional VI methods. Tree sampling is a cost- and time- effective method for screening and enhancing delineation of a site, costing on the order of hundreds of dollars per sample versus the thousands to hundreds of thousands of dollars associated with traditional methods that are applied at sites. The collection of tree-core samples can be conducted in less than five minutes per sample by a single person. Trees are essentially preinstalled and place-bound “samplers” that actively and intimately interactive with the subsurface soil, vapor, and groundwater. Tree sampling is less invasive than VI and traditional sampling, eliminating concerns and problems of disrupting underground utilities or concerns of theft or disruption of sampling canisters and increasing the overall data density through the increased likelihood of obtaining permissions from home or business owners.

Directional tree sampling can be used during the initial screening to pinpoint the direction and relative magnitude of shallow subsurface contaminant plumes associated with vapor intrusion. This novel “one plant, multiple samples” finding is highly valuable in informing traditional analyses. These beneficial qualities of tree sampling fill the current and growing need for more noninvasive, representative, and cost-effective methods in vapor intrusion assessment, as vapor intrusion is noted as a primary pathway for subsurface pollutants to impact human health.

4. RECOMMENDATIONS FOR FUTURE RESEARCH

4.1. ROBUST PREDICTIVE MODELING OF VAPOR INTRUSION USING TREES

While this work is the first demonstration of positive correlation between tree sampling and VI occurrence and potential, the development of a robust predictive model for VI risk and potential as a function of tree-core data would be beneficial to assess the predictive potential of tree sampling. Because simple interpolation techniques were used in this work to correlate VI risk, and VI risk is likely a function of more than tree-core concentration alone, findings from Papers I and II should be used to create a predictive model that incorporates both the effective subsurface sampling volume and directional information of each tree with site-specific properties (e.g., geology and hydrology).

One possible method for developing a predictive model is with more robust statistical approaches such as decision tree learning.[55] Decision tree learning is a data-mining approach that provides insight into which model parameters under what conditions provide the best model fits as subsets of data are modeled (e.g., models incorporating only trees with diameters larger than 6 inches; Figure 4.1).

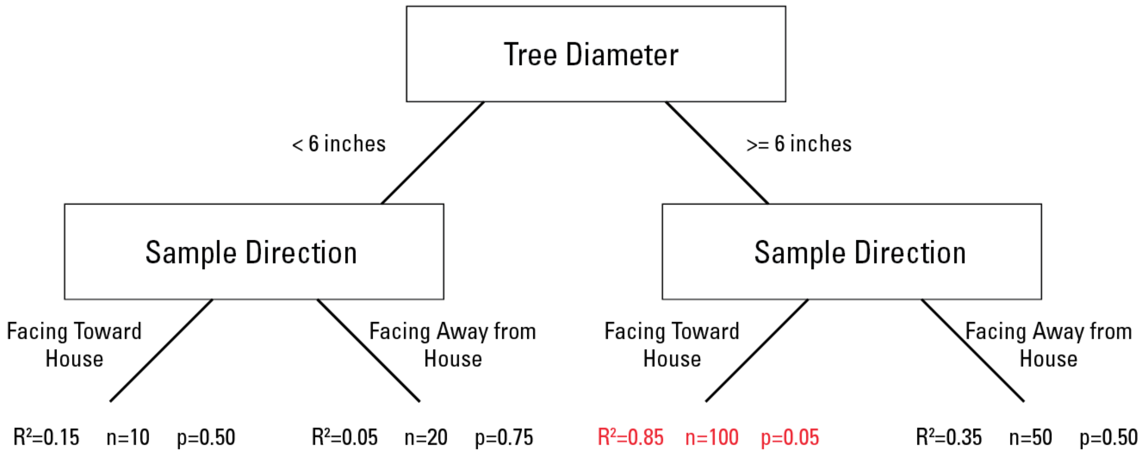

Figure 4.1. Depiction of regression tree analysis incorporating information on tree diameter and sample direction. Each end member is a regression from data fulfilling the conditional hierarchy.

Using the data from the PCE Southeast Contamination Site, *K*-fold cross-validation could be used to develop the model by randomly removing 10% of the data (test dataset), building the decision tree using the remaining 90% of the data (training set), then validating the model with the test dataset.[56] Diameter will be used in the decision tree regression as a proxy for subsurface sampling volume, and each sample will be categorized as either facing toward or away from the building with indoor-air or sub-slab data. Because trees closer to VI samples are likely more related than trees distant from VI samples, the distance between the tree-core sample and the VI sample will also be incorporated into the decision tree regression. Additionally, tree species will be included in the regression. Known site-specific properties including depth to groundwater and building age and estimates of other site-specific properties including soil porosity and soil organic carbon fraction will also be included in the decision tree regression.

4.2. TRANSLATION OF EFFECTIVE ROOT VOLUME TO A FIELD-APPLICABLE TOOL

Geophysical methods such as electrical resistivity tomography (ERT) and ground-penetrating radar (GPR) have been used successfully to delineate root morphology of trees to varying degrees.[57-61] With ERT, soils are differentiated by the electrical properties of different subsurface regions, and ERT is particularly useful in showing differences in water content and porosity. With GPR, electromagnetic radiation is emitted from a source and reflects on features in the subsurface (e.g. pipes, septic tanks, roots, etc) producing characteristic inflection points. A higher frequency source provides better object resolution although with greater signal attenuation. GPR is particularly useful in defining individual roots to a high resolution (e.g. 1mm); however, at this resolution the presence of water content, commonly found in clay-rich soils, restricts signal penetration to a few inches into the subsurface.

Geophysical assessments are quick and non-invasive and might be used to delineate the effective subsurface sampling volume of trees when calibrated with other sampling volume data, such as from Paper I. Once a calibrated model is developed, geophysical surveys could be conducted at other sites to measure the effective sampling volumes of trees.

In order to assess root morphology, several geophysical surveys will be conducted on trees at the Vienna Wells site in Paper I. Multiple trees will be surveyed, and multiple geophysical techniques will be applied at each tree. Trees of various sizes will be selected with minimal overlapping of root systems with other trees (i.e. maximum distance from other trees). For ERT surveys, three parallel transects consisting of 112 electrodes each at 1-ft spacings will be placed at 3 tree-crown distances on either side of the trunk and through the trunk. Results from all transects will be used to create a pseudo-three-dimensional model of subsurface electrical resistivity. For GPR surveys, a 1GHz antenna will be used to measure root structure. The survey will consist of transects running from 3 tree-crown distances on one side of the trunk to the other side (6 tree-crown distances total). Spacings between transects will be 10 cm to obtain high resolution images of root structures. After transects have been made in one direction, the same number of transects will be made in the perpendicular direction, producing a gridded area around the trunk extending 3 tree-crown distances in four directions. Results from the GPR survey will be post-processed and three-dimensional maps of root structure will be produced. For each survey, geophysical results will be related to the effective subsurface root volumes measured in Paper I. In addition, the geophysical models will be validated using cross-validation as well as through implementation of field-validation methods such as trenching with two 112-ft trenches per tree located between the ERT survey lines at 1.5 tree-crown distances.

Figure 4.2 shows preliminary results of an ERT survey at Schuman Park in Rolla, MO. A total of 112 electrodes spaced at 1-ft intervals were placed on a transect intersecting a 16-inch (40-cm) oak tree and extending out approximately 2.5 times the crown width (Figure 4.2), resulting in a total survey depth of approximately 20 ft. A 1-ft spacing was selected to optimize data resolution in the shallow subsurface. These preliminary results indicate a zone of large resistivity near the surface and down to approximately 3 ft below ground surface and extending out about 2 crown widths, both of which are within typical values for the extend of root systems.[62] Based on the findings from Paper I of a footprint of approximately 1 m/cm, the subsurface sampling footprint should be approximately 130 ft in diameter, which compares relatively well with the observed zone of large resistivity that extends approximately 90 ft in diameter. Although these preliminary results suggest that a relationship between the subsurface sampling volume in Paper I and ERT surveys is likely viable, this single transect at one tree is not sufficient enough to establish the relationship.

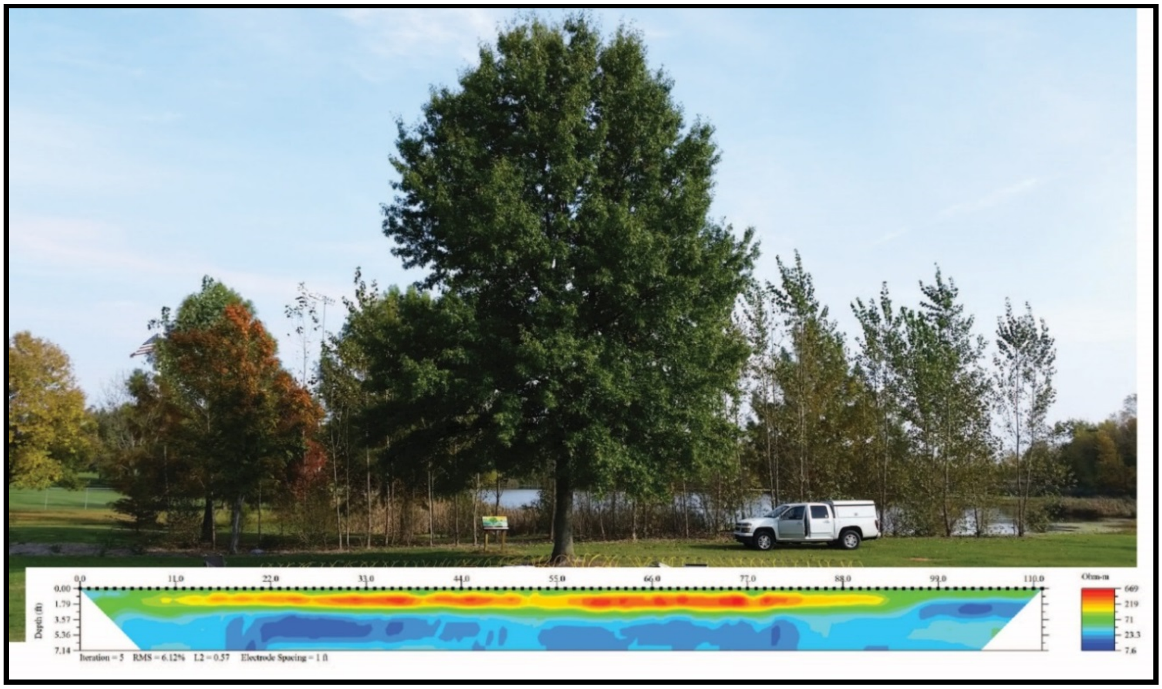

Figure 4.2. Preliminary electrical resistivity data outlining the hypothesized effective root volume (zone of large resistivity) of a large oak tree at Schuman Park in Rolla, MO.

4.3. SUBSURFACE DIRECTIONAL UPTAKE OF CONTAMINANTS IN ROOT BIOMASS

Directional tree sampling has been studied strictly above-ground in this and previous work,[34, 54, 63, 64] and above-ground tree tissues have been shown in this work to indicate the direction of subsurface contamination based on *in-planta* concentration gradients, but three-dimensional directional uptake and transport of contaminants in the subsurface, into below-ground tree tissues, and then into above-ground tree tissue, has not been shown in the field setting. Initial results of tree-core samples collected below ground surface from tree 29 in Paper II indicate a large concentration 0.05 m below ground surface on the west side of the tree (facing the general direction of the subsurface contaminant plume); however, all other directional tree samples collected at 0.05 m below ground surface were below the detection limit, suggesting that PCE tree-core concentrations above ground may be the result of PCE transport through a small section of lateral root tissue at the base of the tree or possibly the result of PCE transport into the central part of the trunk from greater depths (Figure 4.3). Because contaminant concentrations diffuse radially with height up the tree trunk, directionality in tree-core samples is likely slowly lost. This loss of directionality could also be caused by the structure of xylem tissue, as lateral roots assimilate into the outer-most xylem tissues of the tree trunk, and deeper roots (e.g., tap roots) assimilate into the central part of the trunk. An assessment of contaminant transport from subsurface contamination into below-ground tissues and into above-ground tissues would provide insight into interpretation of directional tree sampling that would have direct benefit to VI assessment as well as the general field of phytoforensics and phytoremediation.

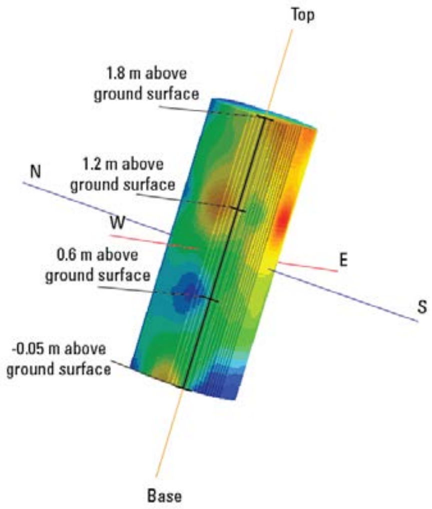

Figure 4.3. Spatial distribution of tetrachloroethylene (PCE) in tree 29 in Paper II including tree-cores collected below ground surface at a 45-degree angle.

To assess the transport of contaminants from the subsurface into below-ground and above-ground tree tissues, soil, soil-gas, root, and tree-core samples will be collected. Contaminant characterization of subsurface soil-gas, soil, and groundwater concentrations will include the installation of solid phase samplers (SPSs) in concentric rings around an isolated tree with radii spaced at 1, 2, 3, and 4 crown widths and at locations corresponding to the 8 cardinal and ordinal directions. At each location, SPSs will be installed at 1, 2, 3, and 4-ft below ground surface to characterize contaminant concentrations in soil-gas. Soil samples collocated with SPS samples will be collected using direct-push methods and temporary monitoring wells will be installed to characterize contaminant concentrations in groundwater. Root and tree-core samples will be collected after the subsurface has been characterized. The tree's roots will be excavated and samples will be collected near the locations of the SPSs as well as in concentric rings around the base of the trunk to fully characterize any potential transport of contaminants via deep roots. Tree-core samples will be collected similar to tree 29 in Paper II. Each dataset will be interpolated over three-dimensional space in order to interpret whether a) the majority of contaminants are transported via lateral roots and diffuse with height, b) the majority of contaminants enter through the base of the trunk and diffuse out radially, or c) a combination of lateral root and tap root transport contaminants.

4.4. REGULATORY ACCEPTANCE OF PHYTOFORENSICS FOR VAPOR INTRUSION ASSESSMENT

Although this work demonstrates the use of tree sampling as a screening tool for vapor intrusion potential, the transfer of this knowledge to the practice of vapor intrusion assessment will likely stagnate and meet opposition from state and federal regulatory institutions. Because the adoption of novel techniques is slow in general because of reluctance to implement technologies without numerous case studies, future research should be focused on building a body of field-based knowledge that further establishes the connection between tree sampling and vapor intrusion potential under a variety of hydrogeological conditions and that further investigates potential limitations of this novel method. Because phytoforensics is currently building momentum as a screening tool for general delineation of subsurface contamination in EPA Region 7, future research would primarily be carried out through piggy-backing current and potential phytoforensic investigations at recently discovered contaminated sites with probable vapor intrusion potential. Besides the obvious value of method validation through comparison with vapor intrusion samples, this experimental design would provide immediate value to the EPA through initial screening of subsurface contamination. Thorough, detailed research at the field scale to further demonstrate the phytoforensic sampling validation is critical to future acceptance.

An important aspect of establishing this body of field-based knowledge is developing a diverse group of stakeholders including partners from federal and state science and regulatory agencies, private consulting firms, and academia. The benefits and limitations of phytoforensics for vapor intrusion assessment would be best evaluated through this diverse group of stakeholders, with each able to convey concerns and questions from their unique viewpoint. Working in concert with multiple stakeholders will have the largest probability of advancing broad acceptance and becoming a method that is suitable and fully embraced for vapor intrusion assessment by the general scientific and public-health community.

BIBLIOGRAPHY

1. USEPA Superfund: National Priorities List (NPL). https://www.epa.gov/superfund/superfund-national-priorities-list-npl (4/1/2017).

2. Panagos, P.; Van Liedekerke, M.; Yigini, Y.; Montanarella, L., Contaminated Sites in Europe: Review of the Current Situation Based on Data Collected through a European Network. *Journal of Environmental and Public Health* **2013,** *2013*, 11. DOI: 10.1155/2013/158764.

3. Khattak, S.; G, K. M.; McMartin, K.; Barrera, M.; Kennedy, D.; Koren, G., Pregnancy outcome following gestational exposure to organic solvents: A prospective controlled study. *JAMA* **1999,** *281*, (12), 1106-1109. DOI: 10.1001/jama.281.12.1106.

4. McGreevey, J. E.; Lacy, C. R.; Commissioner, G., Case-control Study of Childhood Cancers in Dover Township (Ocean County), New Jersey. **2003**.

5. Cohn, P.; Klotz, J.; Bove, F.; Berkowitz, M.; Fagliano, J., Drinking Water Contamination and the Incidence of Leukemia and Non-Hodgkin's Lymphoma. *Environmental health perspectives* **1994,** *102*, (6-7), 556.

6. Costas, K.; Knorr, R. S.; Condon, S. K., A case–control study of childhood leukemia in Woburn, Massachusetts: the relationship between leukemia incidence and exposure to public drinking water. *Science of the Total Environment* **2002,** *300*, (1), 23-35.

7. Forand, S. P.; Lewis-Michl, E. L.; Gomez, M. I., Adverse birth outcomes and maternal exposure to trichloroethylene and tetrachloroethylene through soil vapor intrusion in New York State. *Environ Health Perspect* **2012,** *120*, (4), 616-21. DOI: 10.1289/ehp.1103884.

8. USEPA Table of Regulated Drinking Water Contaminants. (December).

9. USEPA, Regional Screening Level (RSL) Resident Ambient Air Table In 2015.

10. USEPA Superfund Enterprise Management System (SEMS). http://cumulis.epa.gov/supercpad/cursites/srchsites.cfm (July 2017).

11. Little, J. C.; Daisey, J. M.; Nazaroff, W. W., Transport of subsurface contaminants into buildings. *Environmental Science & Technology* **1992,** *26*, (11), 2058-2066. DOI: 10.1021/es00035a001.

12. Moseley, C. L.; Meyer, M. R., Petroleum contamination of an elementary school: a case history involving air, soil-gas, and groundwater monitoring. *Environmental Science & Technology* **1992,** *26*, (1), 185-192. DOI: 10.1021/es00025a023.

13. Bennett, D. H.; McKone, T. E.; Evans, J. S.; Nazaroff, W. W.; Margni, M. D.; Jolliet, O.; Smith, K. R., Peer reviewed: defining intake fraction. *Environmental Science & Technology* **2002,** *36*, (9), 206A-211A.

14. USEPA, Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air. In Office of Solid Waste and Emergency Response, Ed. 2015; p 267.

15. McAlary, T.; Ettinger, R.; Johnson, P.; Eklund, B.; Hayes, H.; Chadwick, D.; Rivera-Duarte, I. *Review of Best Practices, Knowledge and Data Gaps, and Research Opportunities for the US Department of Navy Vapor Intrusion Focus Areas*; DTIC Document: 2009.

16. Fitzgerald, J., One regulatory perspective on the vapor intrusion pathway. *Groundwater Monitoring & Remediation* **2009,** *29*, (1), 51-52. DOI: 10.1111/j.1745-6592.2008.01213.x.

17. Kuehster, T.; Folkes, D.; Wannamaker, E. In *Seasonal Variation of Observed Indoor Air Concentrations due to Vapor Intrusion*, Midwestern States Risk Assessment Symposium, Indianapolis.(www. envirogroup. com), 2004; 2004.

18. McAlary, T.; Dollar, P.; de Haven, P.; Moss, R.; Wilkinson, G.; Llewellyn, J.; Crump, D. In *Assessment of Subsurface Vapour Transport Through Triassic Sandstone and Quarry Fill into Indoor Air in Weston Village, Runcorn*, Indoor Air, 2002; 2002.

19. USEPA, Comparison of Geoprobe® PRT and AMS GVP Soil-Gas Sampling Systems withDedicated Vapor Probes in Sandy Soils at the Raymark Superfund Site. In DEVELOPMENT, O. O. R. A., Ed. 2006; p 79.

20. Luo, H.; Dahlen, P.; Johnson, P. C.; Peargin, T.; Creamer, T., Spatial Variability of Soil-Gas Concentrations near and beneath a Building Overlying Shallow Petroleum Hydrocarbon–Impacted Soils. *Groundwater Monitoring & Remediation* **2009,** *29*, (1), 81-91. DOI:

21. McAlary, T. In *Lessons from petroleum hydrocarbon and chlorinated solvent sites extensively monitored for vapor intrusion*, Platform Presentation at the USEPA Workshop on Vapor Intrusion at the Association for Environmental Health and Sciences 18th Annual West Coast Conference on Soils, Sediment and Water, San Diego, 2008; 2008.

22. McAlary, T.; Nicholson, P.; Bertrand, D.; Abreu, L.; Ettinger, R. In *A case study on the influence of aerobic biodegradation on vapor intrusion at a former refinery property*, Platform Presentation at the Air and Waste Management Association's Specialty Conference on Vapor Intrusion, Providence, RI, 2007; 2007.

23. DiGiulio, D.; Paul, C.; Cody, R.; Willey, R.; Clifford, S.; Kahn, P.; Mosley, R.; Lee, A.; Christensen, K. *Assessment of vapor intrusion in homes near the Raymark Superfund site using basement and sub-slab air samples*; EPA/600/R-05/147: 2006.

24. Tillman Jr, F. D.; Weaver, J. W., Temporal moisture content variability beneath and external to a building and the potential effects on vapor intrusion risk assessment. *Science of the Total Environment* **2007,** *379,* (1), 1-15. DOI: https://doi.org/10.1016/j.scitotenv.2007.02.003.

25. Tillman Jr, F. D.; Weaver, J. W., Uncertainty from synergistic effects of multiple parameters in the Johnson and Ettinger (1991) vapor intrusion model. *Atmospheric Environment* **2006,** *40,* (22), 4098-4112. DOI: https://doi.org/10.1016/j.atmosenv.2006.03.011.

26. USEPA Vapor Intrusion Screening Level (VISL) Calculator https://www.epa.gov/vaporintrusion/vapor-intrusion-screening-levels-visls (April 2017).

27. California Environmental Protection Agency Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air (Vapor Intrusion Guidance). http://www.dtsc.ca.gov/AssessingRisk/upload/Final_VIG_Oct_2011.pdf (2011).

28. Struckhoff, G. C.; Burken, J. G.; Schumacher, J. G., Vapor-Phase Exchange of Perchloroethene between Soil and Plants. *Environmental Science & Technology* **2005,** *39,* (6), 1563-1568. DOI: 10.1021/es049411w.

29. Bromilow, R. H.; Chamberlain, K., *Principles governing uptake and transport of chemicals*. Lewis Publishers: London: 1995.

30. Nietch, C. T.; Morris, J. T.; Vroblesky, D. A., Biophysical Mechanisms of Trichloroethene Uptake and Loss in Baldcypress Growing in Shallow Contaminated Groundwater. *Environmental Science & Technology* **1999,** *33,* (17), 2899-2904. DOI: 10.1021/es981183g.

31. Landmeyer, J. E., *Introduction to phytoremediation of contaminated groundwater: Historical foundation, hydrologic control, and contaminant remediation*. Springer Science & Business Media: 2011.

32. Burken, J.; Schnoor, J. L., Distribution and Volatilization of Organic Compounds Following Uptake by Hybrid Poplar Trees. *International journal of phytoremediation* **1999,** *1*, (2), 139-151. DOI: 10.1080/15226519908500012.

33. Larsen, M.; Burken, J.; Machackova, J.; Karlson, U. G.; Trapp, S., Using Tree Core Samples to Monitor Natural Attenuation and Plume Distribution After a PCE Spill. *Environmental Science & Technology* **2008,** *42*, (5), 1711-1717. DOI: 10.1021/es0717055.

34. Schumacher, J. G.; Struckhoff, G. C.; Burken, J. G., *Assessment of Subsurface Chlorinated Solvent Contamination Using Tree Cores at the Front Street Site and a Former Dry Cleaning Facility at the River-front Superfund Site, New Haven, Missouri, 1999-2003*. US Department of the Interior, US Geological Survey: 2004; p 41.

35. Wahyudi, A.; Bogaert, P.; Trapp, S.; Macháčková, J., Pollutant plume delineation from tree core sampling using standardized ranks. *Environmental Pollution* **2012,** *162*, 120-128. DOI: http://dx.doi.org/10.1016/j.envpol.2011.11.010.

36. Limmer, M. A.; Balouet, J.-C.; Karg, F.; Vroblesky, D. A.; Burken, J. G., Phytoscreening for Chlorinated Solvents Using Rapid in Vitro SPME Sampling: Application to Urban Plume in Verl, Germany. *Environmental Science & Technology* **2011,** *45*, (19), 8276-8282. DOI: 10.1021/es201704v.

37. Ma, X.; Burken, J. G., TCE Diffusion to the Atmosphere in Phytoremediation Applications. *Environmental Science & Technology* **2003,** *37*, (11), 2534-2539. DOI: 10.1021/es026055d.

38. Dettenmaier, E. M.; Doucette, W. J.; Bugbee, B., Chemical Hydrophobicity and Uptake by Plant Roots. *Environmental Science & Technology* **2009,** *43*, (2), 324-329. DOI: 10.1021/es801751x.

39. Limmer, M. A.; Burken, J. G., Plant Translocation of Organic Compounds: Molecular and Physicochemical Predictors. *Environmental Science & Technology Letters* **2014,** *1*, (2), 156-161. DOI: 10.1021/ez400214q.

40. Briggs, G. G.; Bromilow, R. H.; Evans, A. A., Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pesticide Science* **1982,** *13*, (5), 495-504. DOI: 10.1002/ps.2780130506.

41. Burken, J. G.; Schnoor, J. L., Predictive Relationships for Uptake of Organic Contaminants by Hybrid Poplar Trees. *Environmental Science & Technology* **1998,** *32*, (21), 3379-3385. DOI: 10.1021/es9706817.

42. Dobson, M. C.; Moffat, A. J., A Re-Evaluation of Objections to Tree Planting On Containment Landfills. *Waste Management & Research* **1995,** *13*, (6), 579-600. DOI: 10.1177/0734242X9501300607.

43. Sorek, A.; Atzmon, N.; Dahan, O.; Gerstl, Z.; Kushisin, L.; Laor, Y.; Mingelgrin, U.; Nasser, A.; Ronen, D.; Tsechansky, L.; Weisbrod, N.; Graber, E. R., "Phytoscreening": The Use of Trees for Discovering Subsurface Contamination by VOCs. *Environmental Science & Technology* **2007,** *42*, (2), 536-542. DOI: 10.1021/es072014b.

44. MacKay, A. A.; Gschwend, P. M., Sorption of Monoaromatic Hydrocarbons to Wood. *Environmental Science & Technology* **2000,** *34*, (5), 839-845. DOI: 10.1021/es9900858.

45. Trapp, S.; Miglioranza, K. S. B., Sorption of Lipophilic Organic Compounds to Wood and Implications for Their Environmental Fate. *Environmental Science & Technology* **2001,** *35*, (8), 1561-1566. DOI: 10.1021/es000204f.

46. Limmer, M. A.; Martin, G. D.; Watson, C. J.; Martinez, C.; Burken, J. G., Phytoscreening: A Comparison of In Planta Portable GC-MS and In Vitro Analyses. *Groundwater Monitoring & Remediation* **2014,** *34*, (1), 49-56.

47. Limmer, M. A.; West, D. M.; Mu, R.; Shi, H.; Whitlock, K.; Burken, J. G., Phytoscreening for perchlorate: rapid analysis of tree sap. *Environmental Science: Water Research & Technology* **2015,** *1*, (2), 138-145.

48. Burken, J. G.; Vroblesky, D. A.; Balouet, J. C., Phytoforensics, Dendrochemistry, and Phytoscreening: New Green Tools for Delineating Contaminants from Past and Present. *Environmental Science & Technology* **2011,** *45*, (15), 6218-6226. DOI: 10.1021/es2005286.

49. Ma, X.; Burken, J. G., VOCs fate and partitioning in vegetation: Use of tree cores in groundwater analysis. *Environmental science & technology* **2002,** *36*, (21), 4663-4668.

50. Stone, E. L.; Kalisz, P. J., On the maximum extent of tree roots. *Forest Ecology and Management* **1991,** *46*, (1), 59-102.

51. Wilson, J.; Bartz, R.; Limmer, M.; Burken, J., Plants as bio-indicators of subsurface conditions: impact of groundwater level on BTEX concentrations in trees. *International journal of phytoremediation* **2013,** *15*, (9), 900-910.

52. Weishaar, J. A.; Tsao, D.; Burken, J. G., PHYTOREMEDIATION OF BTEX HYDROCARBONS: POTENTIAL IMPACTS OF DIURNAL GROUNDWATER FLUCTUATION ON MICROBIAL DEGRADATION. *International Journal of Phytoremediation* **2009,** *11*, (5), 509-523. DOI: 10.1080/15226510802656326.

53. Vroblesky, D. A.; Clinton, B. D.; Vose, J. M.; Casey, C. C.; Harvey, G. J.; Bradley, P. M., Ground water chlorinated ethenes in tree trunks: Case studies, influence of recharge, and potential degradation mechanism. *Groundwater Monitoring & Remediation* **2004,** *24*, (3), 124-138.

54. Sorek, A.; Atzmon, N.; Dahan, O.; Gerstl, Z.; Kushisin, L.; Laor, Y.; Mingelgrin, U.; Nasser, A.; Ronen, D.; Tsechansky, L.; Weisbrod, N.; Graber, E. R., “Phytoscreening”: The Use of Trees for Discovering Subsurface Contamination by VOCs. *Environmental Science & Technology* **2008,** *42*, (2), 536-542. DOI: 10.1021/es072014b.

55. Loh, W.-Y., Classification and regression trees. *Wiley Interdisciplinary Reviews: Data Mining and Knowledge Discovery* **2011,** *1*, (1), 14-23. DOI: 10.1002/widm.8.

56. Kohavi, R. In *A study of cross-validation and bootstrap for accuracy estimation and model selection*.

57. al Hagrey, S. A., Geophysical imaging of root-zone, trunk, and moisture heterogeneity. *Journal of Experimental Botany* **2007,** *58*, (4), 839-854. DOI:

58. Amato, M.; Basso, B.; Celano, G.; Bitella, G.; Morelli, G.; Rossi, R., In situ detection of tree root distribution and biomass by multi-electrode resistivity imaging. *Tree Physiology* **2008,** *28*, (10), 1441-1448. DOI: 10.1093/treephys/28.10.1441.

59. Hruska, J.; Čermák, J.; Šustek, S., Mapping tree root systems with ground-penetrating radar. *Tree Physiology* **1999,** *19*, (2), 125-130. DOI: 10.1093/treephys/19.2.125.

60. Morelli, G.; Zenone, T.; Teobaldelli, M.; Fischanger, F.; Matteucci, M.; Seufert, G., Use of ground-penetrating radar (GPR) and electrical resistivity tomography (ERT) to study tree roots volume in pine forest and poplar plantation. *Napier, New Zealand* **2007,** *21*, 1-4.

61. Zenone, T.; Morelli, G.; Teobaldelli, M.; Fischanger, F.; Matteucci, M.; Sordini, M.; Armani, A.; Ferrè, C.; Chiti, T.; Seufert, G., Preliminary use of ground-penetrating radar and electrical resistivity tomography to study tree roots in pine forests and poplar plantations. *Functional Plant Biology* **2008,** *35*, (10), 1047-1058. DOI: http://dx.doi.org/10.1071/FP08062.

62. Perry, T. O., Tree roots: Facts and fallacies. *Arnoldia* **1989,** *49,* (4), 3-24.

63. Vroblesky, D. A.; Clinton, B. D.; Vose, J. M.; Casey, C. C.; Harvey, G. J.; Bradley, P. M., Ground Water Chlorinated Ethenes in Tree Trunks: Case Studies, Influence of Recharge, and Potential Degradation Mechanism. *Ground Water Monitoring & Remediation* **2004,** *24*, (3), 124-138. DOI: 10.1111/j.1745-6592.2004.tb01299.x.

64. Vroblesky, D. A.; Nietch, C. T.; Morris, J. T., Chlorinated Ethenes from Groundwater in Tree Trunks. *Environmental Science & Technology* **1999,** *33,* (3), 510-515. DOI: 10.1021/es980848b.

VITA

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