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Matt A. Limmer

Mikhil K. Shetty

Samantha Markus

Ryan Kroeker

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/civarc_enveng_facwork/2432

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Directional Phytoscreening: Contaminant Gradients in Trees for Plume Delineation

Matt A. Limmer,*[,†] Mikhil K. Shetty,[†] Samantha Markus,[†] Ryan Kroeker,[‡] Beth L. Parker,[‡] Camilo Martinez,[§] and Joel G. Burken[†]

[†]Department of Civil, Architectural and Environmental Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States

[‡]G360 Centre for Applied Groundwater Research, School of Engineering, University of Guelph, Guelph, ON, Canada

[§]Ministry of the Environment, Ontario, Canada

Supporting Information

ABSTRACT: Tree sampling methods have been used in phytoscreening applications to delineate contaminated soil and groundwater, augmenting traditional investigative methods that are time-consuming, resource-intensive, invasive, and costly. In the past decade, contaminant concentrations in tree tissues have been shown to reflect the extent and intensity of subsurface contamination. This paper investigates a new phytoscreening tool: directional tree coring, a concept originating from field data that indicated azimuthal concentrations in tree trunks reflected the concentration gradients in the groundwater around the tree.

To experimentally test this hypothesis, large diameter trees were subjected to subsurface contaminant concentration gradients in a greenhouse study. These trees were then analyzed for azimuthal concentration gradients in aboveground tree tissues, revealing contaminant centroids located on the side of the tree nearest the most contaminated groundwater. Tree coring at three field sites revealed sufficiently steep contaminant gradients in trees reflected nearby groundwater contaminant gradients. In practice, trees possessing steep contaminant gradients are indicators of steep subsurface contaminant gradients, providing compass-like information about the contaminant gradient, pointing investigators toward higher concentration regions of the plume.

■ BACKGROUND

Due to widespread use and inadequate handling and disposal standards of past decades, chlorinated compounds are among the most prevalent contaminants of soil and groundwater.[1,2] Additionally, the hydrophobic, recalcitrant nature of these compounds makes them long-lived in the environment and often results in expansive plumes. Due to carcinogenicity concerns of tetrachloroethylene (PCE) and trichloroethylene (TCE),[3] drinking water limits and cleanup standards are low,[4] and high volatility presents vapor intrusion concerns in the built environment.[5]

Detecting and monitoring compounds in the obscured subsurface is time-consuming and resource-intensive. Analyzing contaminant concentrations in plants to understand environmental chemistry, termed phytoforensics,[6] has been demonstrated in the form of phytoscreening as a low-impact supplement to traditional subsurface sampling methods.[7,8] However, application may be limited by many factors, commonly including depth to groundwater and inadequate availability of trees.[9−12] At some sites, these challenges may be overcome by extracting more information from each tree—the focus of this paper.

Water movement in trees is largely passive, flowing from regions of high water potential in the roots to regions of low water potential in the leaves.[13] A majority of the flow occurs through the outermost rings of vessels and tracheids, which are narrow (diameter: 10−500 μm)[14] pipe-like elements in secondary xylem tissue (i.e., wood). These pipe-like elements favor advection of water axially up the trunk, as nonaxial flow through smaller pits in the vessel walls is slowed by greater resistance.[15] The degree of this nonaxial advection is dependent on the degree of xylem sectoriality, which varies across species.[16] Highly sectored species are those which have minimal nonaxial flow, whereas less sectored (i.e., more integrated) species allow for substantial nonaxial flow.[17] Often using different names and approaches,[18] hydraulic sectoriality has been observed for decades by various tracer tests[19−21] and modeling efforts.[22] "Double saw cut" experiments have also demonstrated sectoriality, as staggered, overlapping cuts sever xylem on opposite sides of the trunk,

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requiring nonaxial flow around the cuts to ensure tree survival.[23] More integrated species have exhibit better survival when subjected to a double saw cut,[24] a result also shown by a numerical model.[25] Under more typical growing conditions, sectoriality is thought to protect plants from stressors such as drought[26] and soil erosion[27] by reducing the spread of air embolisms,[28,29] although highly sectored transport may hinder a plant's ability to thrive under patchy light or nutrient conditions.[16] This tissue-level connectivity of xylem and its effect on plant demography is an active area of research, for example, refs 18 and 30.

Much like water (solvent) transport, chemical transport of the chlorinated compounds studied here (solute) is passive,[31] leading to the hypothesis of sectored uptake and transport of dissolved groundwater contaminants as axial advection is thought to exceed radial and azimuthal diffusion in large trees. With diffusivities ca. 10^{-7} cm^2/s for PCE and TCE in wood,[32] axial sap velocities ca. 1 m/h,[33] and minimal nonaxial advection in highly sectored species, sectorial contaminant transport is expected. In highly integrated species, retardation of these hydrophobic contaminants could still result in sectored uptake and distribution of the contaminants, despite substantial, although perhaps transient, nonaxial flow. Regardless of tree physiology, steep gradients in groundwater contaminant concentration across the root zone are needed to observe such sectoriality in contaminant uptake by plants.

Sectored uptake of contaminants has been reported previously at field sites.[7,9,34−36] Vroblesky et al.[9] noted sectored uptake in a 36.5-cm diameter Loblolly pine (*Pinus taeda*) that correlated with a steep groundwater contamination gradient, where TCE concentrations ranged from 10 mg/L (north) to less than 0.1 mg/L (south) across 10 m. Tree cores from southwest and southeast sides of the trunk contained 5087 and 6025 ppbv in the headspace, respectively, whereas analysis of cores from the northwest and northeast sides revealed 1975 and 1925 ppbv, respectively. Schumacher et al.[34] also observed azimuthal variation in two trees (eastern red cedar (*Juniperus virginiana*) and Chinese elm (*Ulmus parvifolia*)) at a field site in New Haven, MO, with subsurface contaminant gradients, but were unable to correlate these concentrations to groundwater concentrations due to anthropogenic subsurface heterogeneities (e.g., adjacent structures). A recent field study did not observe sectored uptake at a field site,[36] although these findings were based on many trees (mostly *Betula alba* and *Salix alba*) that were distant from the most significant groundwater concentration gradients. This study aims to better understand sectored uptake of contaminants to improve the practice of phytoscreening, as additional subsurface information can be gathered from a single tree.

■ EXPERIMENTAL METHODOLOGY

Laboratory Setup. To create a realistic field scenario, large-diameter sandbar willow cuttings (*Salix exigua* subsp. *interior*) were grown in mesocosms designed to create an azimuthal concentration gradient in the subsurface and test sectoriality in xylem contaminant transport. The experiment was carried out in two separate stages: a small-scale preliminary experiment and a large-scale experiment. In the preliminary experiment, one 10 cm diameter cutting (Tree A1) was grown in a 20 L reactor (28 cm diameter, 33 cm tall) containing commercially available potting soil. Tree A1 was grown for approximately four months prior to being harvested. In the large-scale experiment, four 5−10 cm diameter cuttings were grown in 200 L reactors (56 cm diameter, 74 cm tall) filled with a loamy soil (Trees B1−B4). All trees were rooted in water until root initials developed (approximately one month). The four trees were allowed to grow for five months prior to harvest, with the exception of tree B3, which grew for only three months, as the original tree did not survive. In both experiments, the willow cuttings were 2−3 m in length, allowing the cutting to reach both the saturated and vadose zones. During the growth period, the tree roots were unlikely to reach the level of complexity and maturity of those in the field; however, this experiment was intended to test the potential of directional transport, rather than root uptake, in the trunk xylem.

Water was fed into the bottom of all reactors through a perforated tube to ensure uniform distribution (see Figure 1).

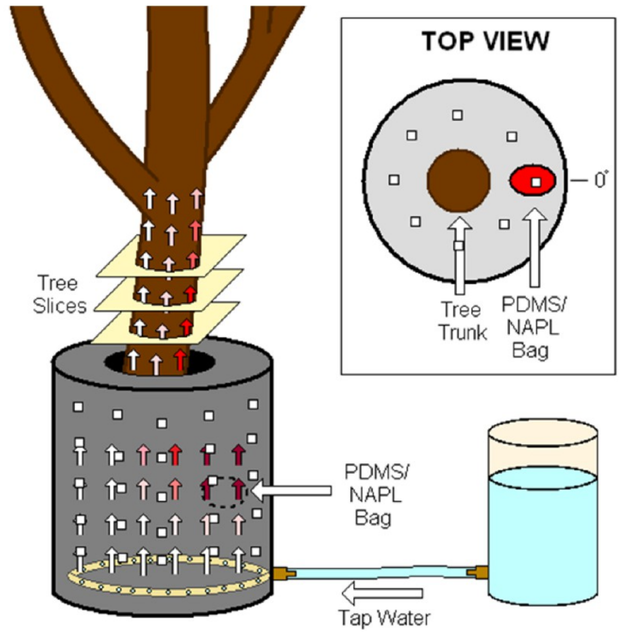

Figure 1. Schematic of reactor setup, where arrows in drum and tree indicate the hypothesized flow of water and the arrow color represents the contaminant concentration. Boxes indicate approximate locations of SPSs.

Water level was checked daily and refilled as needed to maintain a saturated zone approximately half the height of the reactor. To passively measure soil contamination, 40 solid polymer samplers (SPSs)[37] were placed in each of the 200 L reactors, 8 SPSs at five different levels. SPSs were constructed from 0.5 g ± 2% of Tygon tubing (Formulation R-3603, ID: 1.6 mm, OD: 4.8 mm). Prior to deployment, the SPSs were cleaned in methanol for 2 days and dried in a 100 °C oven for 3 days. Stainless steel wire, looped through the tubing, was used to position and hold the SPSs in the soil prior to planting. The SPSs have been shown to equilibrate with the vapor phase in approximately 10 days and were considered to be in equilibrium when removed.[37]

The contaminant source was generated using polydimethylsiloxane (PDMS) oil spiked with PCE and TCE. A zip-top polyethylene bag containing 4 mL of PCE and 6 mL of TCE in 400 mL of PDMS oil was placed at $^1/_3$ the soil depth near the drum wall during planting. The high partitioning coefficient (i.e., low specific activity coefficient) of the contaminants in the PDMS oil limited partitioning and mass transfer to the aqueous phase, generating a dilute plume near the bag. Using PDMS-water partitioning values at 22 °C of 1237 for PCE and 300 for TCE,[38] the equilibrium (i.e., maximum) aqueous concentrations near the source were estimated as 8 mg/L PCE and 50 mg/L TCE.

At the termination of the experiment, the trees were sampled using a destructive method, where cross sections were taken as shown in Figure 1. The thickness of each cross-section was approximately 4 cm. Each slice was then split radially to obtain eight azimuthal segments. Each segment was further split to gather radial information. For each cross-section, between 28 and 57 samples were obtained. A picture of a harvested tree is shown in Figure 2.

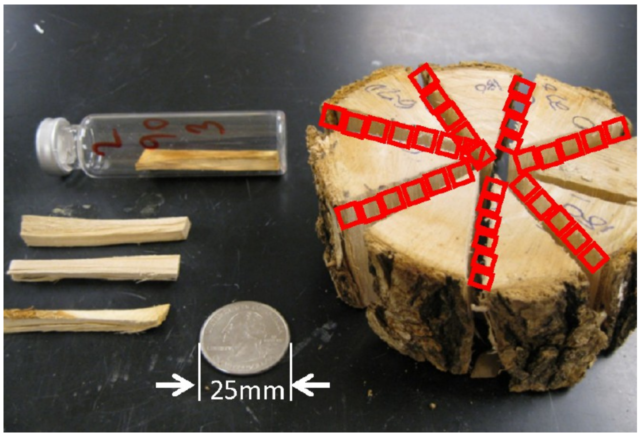

Figure 2. Destructive sampling of willow trees, with the red boxes indicating the approximate location of excised samples.

PCE and TCE concentrations were determined in the transect samples via analysis outlined below. The PCE and TCE distribution in the trees were mapped in Surfer 9 (Golden Software, Golden, Colorado) using point kriging with a linear variogram. The coordinates were obtained by assuming a uniform thickness per radial slice at the corresponding azimuthal angle. No outer boundary conditions were imposed when kriging the concentration data.

Analytics. All *in vitro* tree samples and SPSs were analyzed using negligible depletion solid-phase microextraction (nd-SPME) of the vial headspace coupled with gas chromatography (GC) following methods detailed elsewhere.[39] The SPME fiber was calibrated against water standards to give soil water and xylem-water concentrations. Depletion of contaminant mass due to partitioning to the headspace was corrected using mass balance approaches described previously,[39−41] requiring wood-air partitioning values from literature.[41,42] Using this methodology, the reported concentrations reflect the contaminant concentration in the xylem water at the time of harvesting.

Field Sites. To test sectoriality in contaminant uptake and transport, directional samples were collected from trees at two sites in Ontario, Canada and one site in Missouri. The well documented experimental research site for studying chlorinated compound source and plume behavior at the Canadian Forces Base Borden north of Alliston, ON[43−45] was sampled along with the Shanley Street site, a closed manufacturing plant with an aged chlorinated compound source zone and plume studied in detail in Kitchener, ON.[46,47] Groundwater data from the Borden site was collected in September 2008, using approximately 250 multilevel sampler (MLS) locations with 12−15 ports, each at depths from 1.05 to 3.15 m below ground surface (bgs), allowing high-resolution plume mapping. To map the plume, concentrations were averaged across all depths of the multilevel wells. At the Shanley Street site, seven groundwater sampling trips have been performed, dating to May 1992, with the most recent occurring in June 2009. Samples were taken from several monitoring wells and 27 MLS, each with 4−9 ports ranging from 0.3 to 5.5 m bgs. Phytoscreening occurred at both Canadian sites during September 2009 and May 2010 using tree coring, as destructive sampling was undesirable. The Front Street site in New Haven, MO (OU1) was sampled on October 12, 2010. This site has been previously been delineated using phytoscreening and traditional methods.[34,42] Approximately 140 soil samples and 28 groundwater samples were taken from the site in 2003 during the remedial investigation (RI).[34] Groundwater at the site is approximately 6−8 m bgs.[34]

Tree cores were obtained using a 0.5-cm increment borer at the three sites. Methods are described in detail in Vroblesky[8] and are briefly summarized here. Radial cores were approximately 8 cm in length and were taken at breast height (approximately 1.5 m above ground surface). Immediately after sample removal, the cores were transferred to 20 mL vials and sealed with Teflon septa. After sampling, vials were stored on ice until analyzed by SPME-GC.

■ RESULTS AND DISCUSSION

Laboratory Results. The laboratory experiment was effective at generating a subsurface gradient and a corresponding azimuthal gradient was observed in trees. The cross-sectional PCE data for tree B3 are shown in Figure 3, where '+' indicates an individual sample. The source zone was located between the first and fourth quadrants. The left side shows SPS soil concentrations in $\log_{10}$ μg/L while the tree concentrations are not $\log_{10}$ transformed for clarity. Soil data show stronger gradients than the tree data, but the gradient direction remains similar for both. The tree data exhibit decreasing concentrations with height, which is consistent with retardation or diffusional loss of VOCs from the xylem flow to the atmosphere, likely through the lenticels.[48]

The azimuthal data for Tree A1 are shown in Supporting Information (SI) Figure SI1. PCE and TCE concentrations were largest in the first and fourth quadrants. Azimuthal gradients appeared least noticeable for PCE in the lower slice, perhaps due to high azimuthal diffusion or advection. Given previous modeling work, low PCE concentrations in the center of the tree are unlikely.[49] Instead, this observation may be a transient effect, where PCE was retarded more than TCE as it diffused into the trunk due to higher partitioning and lower diffusion coefficients.[32]

The azimuthal gradient in trees A1 and B3 revealed high contaminant concentrations in quadrants I and IV adjacent to the source location, providing strong evidence of sectored uptake. In contrast, the transient radial effect observed in tree A1 was not observed in tree B3. Tree B2 exhibited severe leaf curl throughout the experiment, limiting its water usage (see SI). For this reason, tree B2 is not considered further. Trees B1 and B4 did not show strong azimuthal contaminant distribution. Instead, the contaminant mass was largely located at the center of the tree, with only a slight bias toward the source zone. Figure SI2 shows a typical concentration profile observed in these two trees.

Given this observed contaminant profile and the one month longer experimental time, the contaminant profile in trees B1

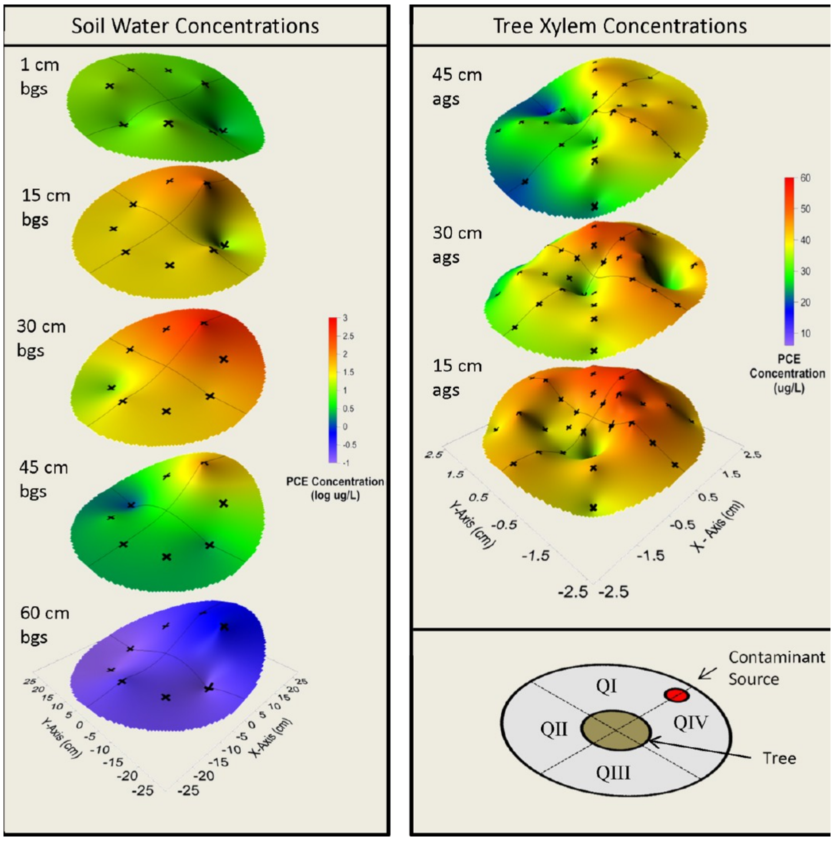

Figure 3. PCE concentration profiles for Tree B3 (Left: soil slices below ground surface (bgs), Right: tree slices above ground surface (ags)). For reference, the approximate location of the contaminant is shown in the lower right. Note that the soil and tree diameters differ.

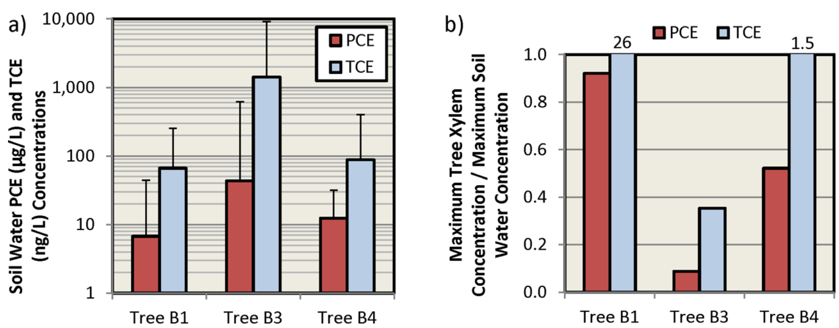

Figure 4. (a) Average soil water concentrations (positive error bars denote maximum) (b) Maximum tree xylem concentrations relative to maximum soil water concentrations.

and B4 is hypothesized to be a result of contaminant source depletion in the reactor. Figure 4a shows the average and maximum soil water concentration for trees B1, B3, and B4. Note that B3 soil shows the highest concentrations of PCE and TCE and all concentrations are below the maximum possible concentrations of 8 mg/L and 50 mg/L PCE and TCE, respectively. Plant-contaminant kinetics can be envisioned as a tree loading phase, where soil contaminants are translocated in the trunk xylem water. The contaminants diffuse and partition into the trunk xylem tissue (e.g., heartwood) until pseudo steady state is reached with the transpiration stream. As contaminants are removed from the subsurface, the subsurface NAPL reservoir is being depleted of contaminant, so less contaminant is translocated to the shoots. Correspondingly, concentrations in the outer trunk tissues decrease as the compounds diffuse out of the trunk and transfer to the atmosphere. The center of the tree, being farthest from the bark will have the highest remaining concentrations during this "unloading" phase, leaving a peak as shown in Figure SI3.

The hypothesis of soil depletion and "unloading" in the tree is also supported by the ratio of the maximum tree concentration to the maximum soil concentration (Figure 4b). This idea is similar to the transpiration stream concentration factor (TSCF),[31,50] but only considers maximum concentration, which should be less than 1 for PCE and TCE. TSCFs for these compounds have been reported between 0.1 and 0.75 in laboratory studies involving trees.[31,51−53] In field studies, concentrations of PCE and TCE in tree xylem water have been found to be 1−3 orders of magnitude lower than groundwater concentrations.[39] While inherent heterogeneities in soil concentrations prevent accurate determination of a TSCF, the observation of a TSCF greater than 1 indicates a

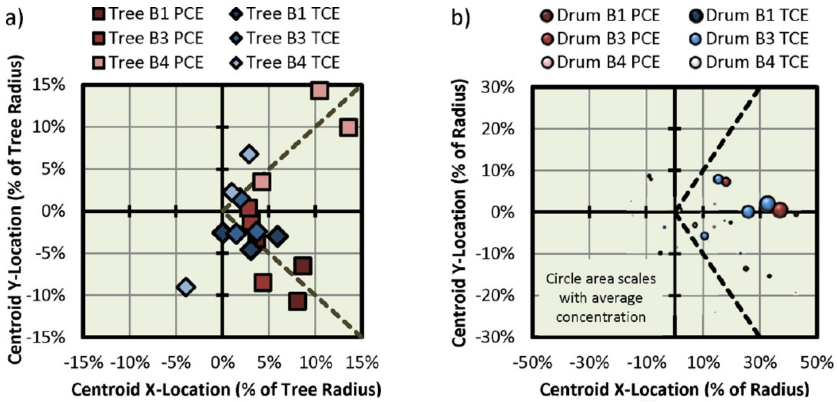

Figure 5. Radius normalized centroids for contaminant concentrations; (a) trees data, (b) soil data.

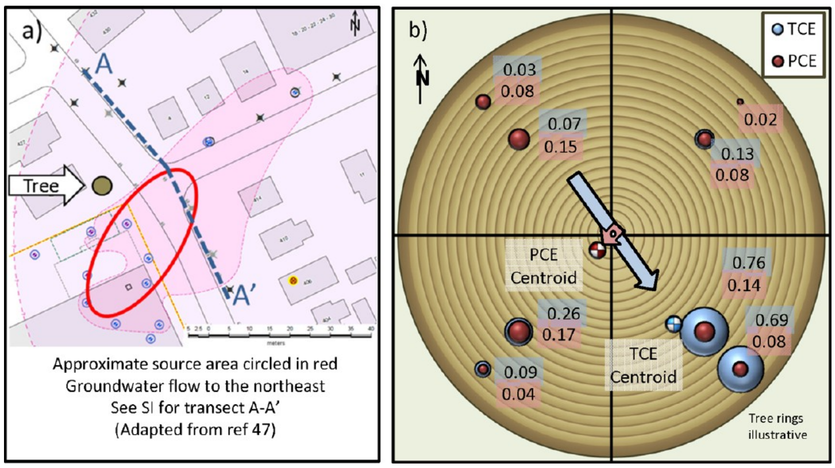

Figure 6. (a) Shanley Street site plume and location of sampled tree, (b) Azimuthal concentrations found in tree (μg/L), May 2010.

highly transient situation, as tree concentrations exceeding soil concentrations imply contaminant depletion in the soil for these contaminants.

Despite apparent depletion of the contaminant source in the reactor, trends can be observed in the data. To quantify sectored uptake, the cross-sectional contaminant centroid was calculated using eq 1.

$$(x_C, y_C) = \left(\frac{\sum x_i \cdot C_i}{\sum C_i}, \frac{\sum y_i \cdot C_i}{\sum C_i} \right) \tag{1}$$

Where (x_c, y_c) is the centroid coordinates and (x_i, y_i) are the coordinates for concentration c_i

For comparison, each centroid was normalized by the radius, with the results shown in Figure 5.

Seventeen of eighteen tree centroids have positive x-coordinates, with no clear pattern of y-coordinates showing the highest tree concentrations in quadrants I and IV, providing further evidence of sectored uptake of contaminants in all experiments conducted. The average centroid for PCE was (7%, 0%) and for TCE was (2%, −2%). Both the x-centroids were significantly greater than zero, using a one-sided t test (PCE: p = 0.0004; TCE: p = 0.043), while neither y-centroid was significantly different from zero (PCE: p = 0.93; TCE: p = 0.34). The stronger x-coordinate bias of the PCE centroid may result from the greater retardation of PCE during transient periods of nonaxial flow or lower diffusivity of the larger molecule.

The soil data revealed more scatter (Figure 5b), which is expected given the variation in depth. Regardless, the soil centroids generally have positive x-coordinates. One important observation is that the soil centroids have a stronger azimuthal bias, as the centroid x-location approaches 40% of the drum radius, indicating a more pronounced gradient in the drum than in the tree.

Field Studies. At the Shanley site, seven trees were cored directionally (minimum two sides). PCE was detected in two of the trees, although PCE groundwater data were variable at the site preventing comparison. TCE was only detected in a large (57 cm diameter) Norway maple (*Acer platanoides*) near the source zone, cored on four sides at two radial depths into the xylem tissue. The concentrations observed in the tree cores are shown in Figure 6b, where the absence of a data point indicates the contaminant was not detected in that sample. The highest concentrations of TCE were found in the southeast side of the trunk, which matches well with the documented plume gradient in this area (see Figure 6a). A groundwater sample to the southeast of the tree in June 2009 found 23.5 mg/L TCE, while a sample just north of the tree found 3.2 mg/L TCE. PCE concentrations in the tree showed less azimuthal variability, suggesting that the PCE plume gradient was less steep in this location. However, PCE groundwater concentrations were much lower (<50 μg/L) and highly variable at the site, hindering any definitive conclusion regarding the PCE concentration gradient. The location of the contaminant centroid is also shown in Figure 6 for PCE and TCE. For

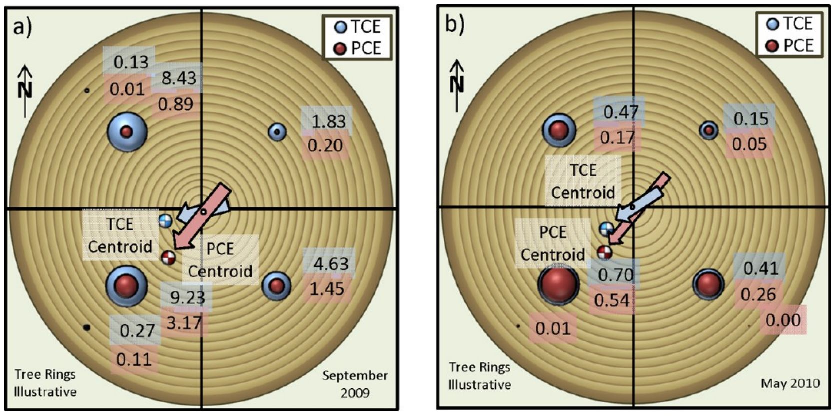

Figure 7. Tree 22 core concentrations (μg/L) at Borden site (a): Sept. 2009, (b): May 2010).

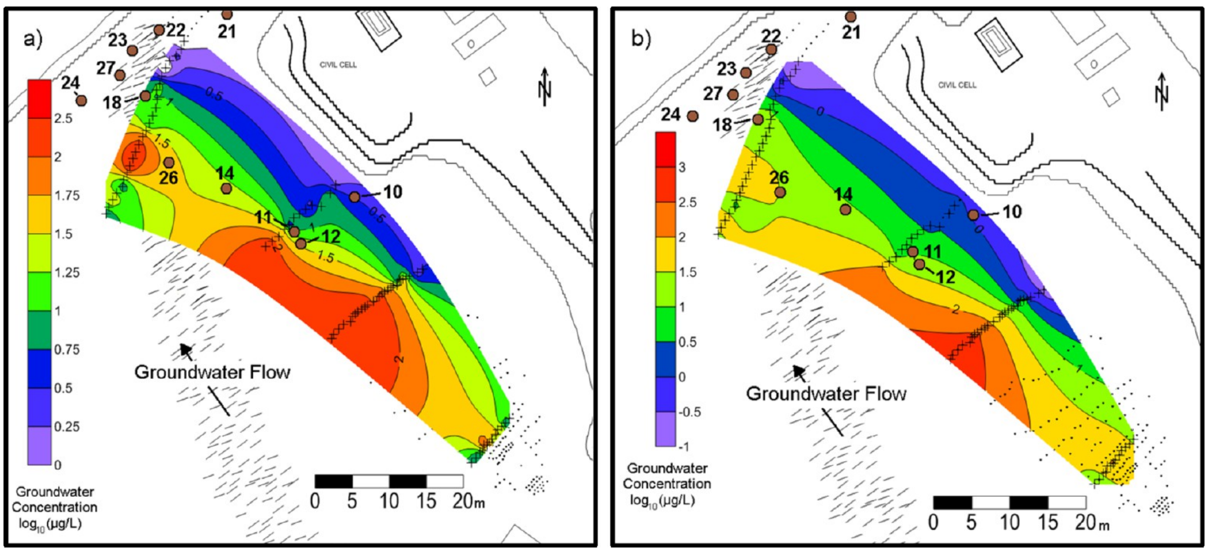

Figure 8. Borden site directionally sampled tree and groundwater plumes ($\log_{10}$ μg/L); (a) TCE, (b) PCE.

TCE, the centroid is clearly on the side of the tree toward the more concentrated region of the plume as determined from the groundwater data.

At the Borden site, 12 trees were sampled directionally. Eight of the trees sampled contained measurable amounts of chlorinated compounds. Results from these trees were used to estimate the minimum concentration gradient in a tree representative of a groundwater contaminant gradient (see SI). One of these trees that exhibited strong directionality, a 47 cm diameter Ash (*Fraxinus* sp.), was cored on four different sides, each at two different distances into the xylem tissue (Tree 22). Figure 7 shows the resulting tree core data from two sampling trips. The highest concentrations were observed in the southwest, inner core. The less obvious detection of contaminants in the southwest, outer core also implies the most concentrated region of the plume lies to the southwest. Figure 8 shows the plume maps for the Borden site. Detailed spatial groundwater concentration data along the transect show the position of the plume centerline remains to the southwest of the sampled tree.

Data from both trips have similar PCE and TCE centroids, despite differences in absolute concentrations between the two trips. Plant PCE and TCE concentrations have been shown to vary seasonally and to be affected by recent rainfall,[9,35,54,55] which may explain some or all of the variation in these concentrations. These concentration profiles bear semblance to tree B3, where the highest concentrations were found approximately halfway to the center of the tree.

At the New Haven, MO site, two Eastern Cottonwood (*Populus deltoides*) trees were cored on four sides. Tree 1 was 45 cm in diameter, while tree 2 was 38 cm in diameter. Tree cores, 7 cm long, were taken from the trunk surface and 7 cm in from the trunk surface. Figure SI5 shows the PCE vadose zone soil plume for the site along with the tree concentrations for two trees cored at the site. Both trees are located near the northeastern edge of the plume, and directional sampling shows evidence of the plume to the southwest.

While these findings show contaminant gradients in trees can be indicative of subsurface contaminant gradients, the question remains as to how steep of a groundwater contaminant gradient can be reliably measured by phytoscreening techniques. Data from the Borden site suggest a groundwater contaminant concentration gradient of approximately 1 order of magnitude per ten meters is measurable by directional phytoscreening. However, a lack of additional data prevents further assessment, although insufficiently steep subsurface contaminant gradients will not yield steep contaminant gradients in the tree.

A variety of additional factors may prevent effective application of directional phytoscreening, such as the physiology of the vascular tissue. Observation of sectored uptake is aided by a large ratio of axial transport to nonaxial transport, which is shown to vary between species and within a particular plant due to variations in hydraulic sectoriality.[56] Of the trees studied here, both *Acer* and *Populus* have exhibited sectoriality,[17] although the degree of sectoriality is not widely available for most species. As the tissue-level distribution and connectivity of xylem is better understood for various trees, the development of a sectoriality index by species, for example, ref 16, may lead to a better understanding of tree genera that are most appropriate for directional phytoscreening. Spiraling of xylem is another complicating phenomena observed in some trees,[57] but its effect can be minimized by taking core samples near the ground surface. Patchy water distribution can also lead to nonaxial transport, as demonstrated by hydraulic redistribution (HR) of water,[15,58] where water is transported from wetter to drier portions of the soil via xylem conduits. To overcome these limitations and reduce false positives, several tree cores should be taken azimuthally from a tree at a consistent height to estimate contaminant variability within an individual tree. Through such a sampling technique, this study demonstrates the potential of contaminant gradients in trees of different genera to capture azimuthal groundwater data, making directional tree coring a valuable phytoforensic tool for indicating steep subsurface contaminant gradients, areas often of particular concern. This tool can be used to provide compass-like information, pointing phytoscreening investigators toward more concentrated regions of the plume.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional greenhouse data, Borden directional results and the Shanley site groundwater transect are available. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Corresponding author: malqn3@mst.edu.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Doherty, R. E. A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane in the United States: Part 1; Historical background; carbon tetrachloride and tetrachloroethylene. *Environ. Forensics* **2000**, *1* (2), 69−81, DOI: 10.1006/enfo.2000.0010.

(2) Stroo, H. F.; Ward, C. H., *In Situ Remediation of Chlorinated Solvent Plumes*; Springer Science, 2010.

(3) NTP. *Report on Carcinogens*, 12th ed.; United States Department of Health and Human Services, National Toxicology Program, 2011.

(4) EPA. *National Primary Drinking Water Regulations*, 2009.

(5) Atteia, O.; Höhener, P. Semianalytical model predicting transfer of volatile pollutants from groundwater to the soil surface. *Environ. Sci. Technol.* **2010**, *44* (16), 6228−6232, DOI: 10.1021/es903477f.

(6) Burken, J. G.; Vroblesky, D. A.; Balouet, J. C. Phytoforensics, dendrochemistry, and phytoscreening: New green tools for delineating contaminants from past and present. *Environ. Sci. Technol.* **2011**, *45* (15), 6218−6226, DOI: 10.1021/es2005286.

(7) Vroblesky, D. A.; Nietch, C. T.; Morris, J. T. Chlorinated ethenes from groundwater in tree trunks. *Environ. Sci. Technol.* **1999**, *33* (3), 510−515, DOI: 10.1021/es980848b.

(8) Vroblesky, D. A. *User's Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds*, USGS Report 2008−5088. 2008; p 72.

(9) 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 Monit. Rem.* **2004**, *24* (3), 124−138, DOI: 10.1111/j.1745-6592.2004.tb01299.x.

(10) Larsen, M.; Burken, J.; Machackova, J. i.; Karlson, U. G.; Trapp, S. Using tree core samples to monitor natural attenuation and plume distribution after a PCE spill. *Environ. Sci. Technol.* **2008**, *42* (5), 1711−1717, DOI: 10.1021/es0717055.

(11) Gopalakrishnan, G.; Negri, M. C.; Minsker, B. S.; Werth, C. J. Monitoring subsurface contamination using tree branches. *Ground Water Monit. Rem.* **2007**, *27*, 65−74.

(12) Wahyudi, A.; Bogaert, P.; Trapp, S.; Macháčková, J. Pollutant plume delineation from tree core sampling using standardized ranks. *Environ. Pollut.* **2012**, *162*, 120−128.

(13) Meinzer, F. C.; Clearwater, M. J.; Goldstein, G. Water transport in trees: Current perspectives, new insights and some controversies. *Environ. Exp. Bot.* **2001**, *45* (3), 239−262.

(14) Hopkins, W. G. *Introduction to Plant Physiology*; John Wiley & Sons, 1995.

(15) Burgess, S.; Bleby, T. Redistribution of soil water by lateral roots mediated by stem tissues. *J. Exp. Bot.* **2006**, *57* (12), 3283−3291, DOI: 10.1093/jxb/erl085.

(16) Zanne, A. E.; Sweeney, K.; Sharma, M.; Orians, C. M. Patterns and consequences of differential vascular sectoriality in 18 temperate tree and shrub species. *Funct. Ecol.* **2006**, *20* (2), 200−206.

(17) Orians, C. M.; van Vuuren, M. M. I.; Harris, N. L.; Babst, B. A.; Ellmore, G. S. Differential sectoriality in long-distance transport in temperate tree species: Evidence from dye flow, ^{15}N transport, and vessel element pitting. *Trees—Struct. Funct.* **2004**, *18* (5), 501−509, DOI: 10.1007/s00468-004-0326-y.

(18) Martínez-Vilalta, J.; Mencuccini, M.; Álvarez, X.; Camacho, J.; Loepfe, L.; Piñol, J. Spatial distribution and packing of xylem conduits. *Am. J. Bot.* **2012**, *99* (7), 1189−1196.

(19) Schulte, P. J.; Brooks, J. R. Branch junctions and the flow of water through xylem in douglas-fir and ponderosa pine stems. *J. Exp. Bot.* **2003**, *54* (387), 1597−1605.

(20) 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. *J. Exp. Bot.* **2003**, *54* (386), 1399−1405.

(21) Orians, C. M.; Ardón, M.; Mohammad, B. A. Vascular architecture and patchy nutrient availability generate within-plant heterogeneity in plant traits important to herbivores. *Am. J. Bot.* **2002**, *89* (2), 270−278.

(22) Thorn, A.; Orians, C. Modeling the influence of differential sectoriality on the photosynthetic responses of understory saplings to patchy light and water availability. *Trees—Struct. Funct.* **2011**, *25* (5), 833−845, DOI: 10.1007/s00468-011-0559-5.

(23) Tyree, M. T.; Zimmermann, M. H., *Xylem Structure and the Ascent of Sap*, 2nd ed.; Springer, 2002.

(24) Sperry, J. S.; Alder, N. N.; Eastlack, S. E. The effect of reduced hydraulic conductance on stomatal conductance and xylem cavitation. *J. Exp. Bot.* **1993**, *44* (6), 1075−1082.

(25) Schulte, P. J.; Costa, D. G. Xylem anisotropy and water transport—a model for the double sawcut experiment. *Tree Physiol.* **2010**, *30* (7), 901−913, DOI: 10.1093/treephys/tpq034.
(26) Schenk, H. J.; Espino, S.; Goedhart, C. M.; Nordenstahl, M.; Cabrera, H. I. M.; Jones, C. S. Hydraulic integration and shrub growth form linked across continental aridity gradients. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105* (32), 11248−11253.
(27) Lanner, R. M. Why do trees live so long? *Ageing Res. Rev.* **2002**, *1* (4), 653−671, DOI: 10.1016/s1568-1637(02)00025-9.
(28) Sprugel, D. G.; Hinckley, T. M.; Schaap, W. The Theory and Practice of Branch Autonomy. *Annu. Rev. Ecol. Syst.* **1991**, *22*, 309−334.
(29) Loepfe, L.; Martinez-Vilalta, J.; Piñol, J.; Mencuccini, M. The relevance of xylem network structure for plant hydraulic efficiency and safety. *J. Theor. Biol.* **2007**, *247* (4), 788−803, DOI: 10.1016/j.jtbi.2007.03.036.
(30) Salguero-Gómez, R.; Casper, B. B. A hydraulic explanation for size-specific plant shrinkage: Developmental hydraulic sectoriality. *New Phytol.* **2011**, *189* (1), 229−240.
(31) Burken, J. G.; Schnoor, J. L. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. *Environ. Sci. Technol.* **1998**, *32* (21), 3379−3385, DOI: 10.1021/es9706817.
(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. *Environ. Sci. Technol.* **2008**, *42* (4), 1268−1275, DOI: 10.1021/es071552l.
(33) James, S. A.; Meinzer, F. C.; Goldstein, G.; Woodruff, D.; Jones, T.; Restom, T.; Mejia, M.; Clearwater, M.; Campanello, P. Axial and radial water transport and internal water storage in tropical forest canopy trees. *Oecologia* **2003**, *134* (1), 37−45.
(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 Riverfront Superfund Site, New Haven, Missouri, 1999−2003*, USGS Report 2004−5049, 2004, p 41.
(35) 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. *Environ. Sci. Technol.* **2008**, *42* (2), 536−542, DOI: 10.1021/es072014b.
(36) 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. *Environ. Sci. Technol.* **2011**, *45* (22), 9604−9610, DOI: 10.1021/es202014h.
(37) Shetty, M.; Limmer, M.; Waltermire, K.; Morrison, G. C.; Burken, J. G., *In planta* passive sampling devices for assessing subsurface chlorinated solvents. *Chemosphere*. In review.
(38) Avila, M.; Breiter, R. Estimating the PDMS-Coated, SPME-fibre/water- and fibre/gas-partition coefficients of chlorinated ethenes by headspace-SPME. *Chromatographia* **2007**, *66* (5), 369−376, DOI: 10.1365/s10337-007-0332-5.
(39) 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. *Environ. Sci. Technol.* **2011**, *45* (19), 8276−8282, DOI: 10.1021/es201704v.
(40) Legind, C. N.; Karlson, U.; Burken, J. G.; Reichenberg, F.; Mayer, P. Determining chemical activity of (semi)volatile compounds by headspace solid-phase microextraction. *Anal. Chem.* **2007**, *79* (7), 2869−2876, DOI: 10.1021/ac061880o.
(41) Ma, X.; Burken, J. G. VOCs Fate and partitioning in vegetation: Use of tree cores in groundwater analysis. *Environ. Sci. Technol.* **2002**, *36* (21), 4663−4668, DOI: 10.1021/es025795j.
(42) Struckhoff, G. C.; Burken, J. G.; Schumacher, J. G. Vapor-phase exchange of perchloroethene between soil and plants. *Environ. Sci. Technol.* **2005**, *39* (6), 1563−1568, DOI: 10.1021/es049411w.
(43) Hartog, N.; Cho, J.; Parker, B. L.; Annable, M. D. Characterization of a heterogeneous DNAPL source zone in the Borden aquifer using partitioning and interfacial tracers: Residual morphologies and background sorption. *J. Contam. Hydrol.* **2010**, *115* (1−4), 79−89, DOI: 10.1016/j.jconhyd.2010.04.004.
(44) Laukonen, K. A.; Parker, B. L.; Cherry, J. A. Internal characteristics of a bromide tracer zone during natural flow in the Borden aquifer, Ontario, Canada. *IAHS-AISH Publ.* **2000**, *262*, 227−233.
(45) Hunkeler, D.; Aravena, R.; Parker, B. L.; Cherry, J. A.; Diao, X. Monitoring Oxidation of Chlorinated ethenes by permanganate in groundwater using stable isotopes: Laboratory and field studies. *Environ. Sci. Technol.* **2003**, *37* (4), 798−804, DOI: 10.1021/es020073d.
(46) Hunkeler, D.; Chollet, N.; Pittet, X.; Aravena, R.; Cherry, J. A.; Parker, B. L. Effect of source variability and transport processes on carbon isotope ratios of TCE and PCE in two sandy aquifers. *J. Contam. Hydrol.* **2004**, *74* (1−4), 265−282.
(47) Franz Environmental Inc.. *Final Report on Environmental Assessment Activities at 152/153 Shanley Street, Kitchener ON*; Ministry of the Environment: Guelph, 2010.
(48) Ma, X.; Burken, J. G. TCE diffusion to the atmosphere in phytoremediation applications. *Environ. Sci. Technol.* **2003**, *37* (11), 2534−2539, DOI: 10.1021/es026055d.
(49) Ma, X.; Burken, J. Modeling of TCE diffusion to the atmosphere and distribution in plant stems. *Environ. Sci. Technol.* **2004**, *38* (17), 4580−4586, DOI: 10.1021/es035435b.
(50) Briggs, G. G.; Bromilow, R. H.; Evans, A. A. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pestic. Sci.* **1982**, *13* (5), 495−504, DOI: 10.1002/ps.2780130506.
(51) Davis, L. C.; Vanderhoof, S.; Dana, J.; Selk, K.; Smith, K.; Goplen, B.; Erickson, L. E. Movement of chlorinated solvents and other volatile organics through plants monitored by fourier transform infrared (FT-IR) spectrometry. *J. Hazard. Subst. Res.* **1998**, *1* (4), 1−26.
(52) Orchard, B. J.; Doucette, W. J.; Chard, J. K.; Bugbee, B. Uptake of trichloroethylene by hybrid poplar trees grown hydroponically in flow-through plant growth chambers. *Environ. Toxicol. Chem.* **2000**, *19* (4), 895−903, DOI: 10.1002/etc.5620190416.
(53) Dettenmaier, E. M.; Doucette, W. J.; Bugbee, B. Chemical hydrophobicity and uptake by plant roots. *Environ. Sci. Technol.* **2009**, *43* (2), 324−329, DOI: 10.1021/es801751x.
(54) Nietch, C. T.; Morris, J. T.; Vroblesky, D. A. Biophysical mechanisms of trichloroethene uptake and loss in baldcypress growing in shallow contaminated groundwater. *Environ. Sci. Technol.* **1999**, *33* (17), 2899−2904, DOI: 10.1021/es981183g.
(55) Doucette, W. J.; Bugbee, B. G.; Smith, S. C.; Pajak, C. J.; Ginn, J. S., Uptake, metabolism, and phytovolatilization of trichloroethylene by indigenous vegetation: Impact of precipitation. In *Phytoremediation: Transformation and Control of Contaminants*; McCutcheon, S. C., Schnoor, J. L., Eds.; John Wiley & Sons, Inc., 2004; pp 561−588.
(56) Pate, J. S.; Jeschke, W. D.; Aylward, M. J. Hydraulic architecture and xylem structure of the dimorphic root systems of South-West Australian species of Proteaceae. *J. Exp. Bot.* **1995**, *46* (8), 907−915.
(57) Herrick, E. H. Further Notes on Twisted Trees. *Science* **1932**, *76* (1975), 406−407.
(58) Burgess, S. S. O.; Adams, M. A.; Turner, N. C.; Ong, C. K. The redistribution of soil water by tree root systems. *Oecologia* **1998**, *115* (3), 306−311, DOI: 10.1007/s004420050521.