

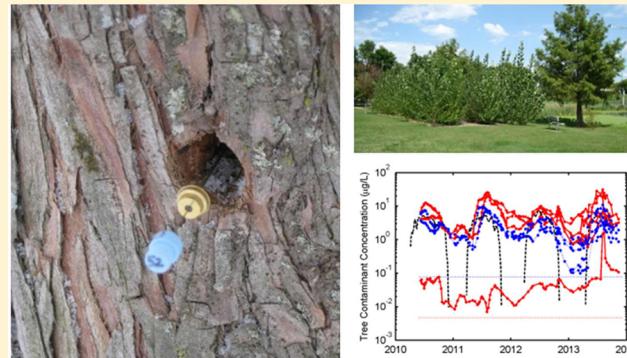
## Phytomonitoring of Chlorinated Ethenes in Trees: A Four-Year Study of Seasonal Chemodynamics *in Planta*

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### Supporting Information

**ABSTRACT:** Long-term monitoring (LTM) of groundwater remedial projects is costly and time-consuming, particularly when using phytoremediation, a long-term remedial approach. The use of trees as sensors of groundwater contamination (i.e., phytoscreening) has been widely described, although the use of trees to provide long-term monitoring of such plumes (phytomonitoring) has been more limited due to unexplained variability of contaminant concentrations in trees. To assess this variability, we developed an *in planta* sampling method to obtain high-frequency measurements of chlorinated ethenes in oak (*Quercus rubra*) and baldcypress (*Taxodium distichum*) trees growing above a contaminated plume during a 4-year trial. The data set revealed that contaminant concentrations increased rapidly with transpiration in the spring and decreased in the fall, resulting in perchloroethene (PCE) and trichloroethene (TCE) sapwood concentrations an order of magnitude higher in late summer as compared to winter. Heartwood PCE and TCE concentrations were more buffered against seasonal effects. Rainfall events caused negligible dilution of contaminant concentrations in trees after precipitation events. Modeling evapotranspiration potential from meteorological data and comparing the modeled uptake and transport with the 4 years of high frequency data provides a foundation to advance the implementation of phytomonitoring and improved understanding of plant contaminant interactions.



### INTRODUCTION

Sites contaminated with volatile organic compounds (VOCs) often require long-term monitoring (LTM), a time-intensive and costly aspect of site cleanup. The U.S. Department of Defense (DoD) estimated their LTM costs at more than \$100 million annually.<sup>1</sup> Although some LTM optimization has occurred, such as passive sampling and monitoring well network optimization,<sup>2</sup> LTM still often relies on labor-intensive active sampling of multiple monitoring wells over years, usually decades. Passive sampling approaches have emerged as a low-energy alternative to active sampling of monitoring wells. Rather than active pumping and collection of groundwater, passive samplers rely on diffusive chemical transport through a polymer and partitioning into a sampling phase. In general, passive sampling has the added benefit of measuring an average concentration over the deployment period in addition to measuring the bioavailable concentration.<sup>3</sup>

Phytoforensics combines plants' ability to pump groundwater, using solar energy to drive transpiration, and plants' inherent ability to sorb organic pollutants, analogous to passive sampling, to understand groundwater contamination by sampling plants growing above plumes.<sup>4</sup> The hydraulic architecture of trees is particularly well suited for the sampling of moderately hydrophobic contaminants. The transpiration stream is conducted through small-diameter tracheary elements

that consist of hydrophobic cell walls. The resulting matrix, wood, has high sorption capacity for many organic contaminants,<sup>5</sup> allowing passive sampling of a tree's transpiration stream over an extended time. Solar-powered groundwater removal by trees makes phytoforensics a relatively sustainable, but indirect, method for groundwater analysis. In one phytoforensic approach, termed phytoscreening, shallow chlorinated solvent (cVOC) plumes have been delineated using cVOC concentrations found in trees.<sup>6–8</sup> While phytoscreening of cVOCs has proven useful at some sites,<sup>6–10</sup> concerns about the effects of seasonality, species, tree diameter, and soil type have yet to be answered.<sup>11,12</sup> Despite limitations in understanding, phytoscreening has been shown to reduce uncertainty in the conceptual site model when combined with traditional groundwater data.<sup>13</sup>

Similar to phytoscreening, phytomonitoring is a phytoforensic approach to LTM. Concentrations in trees can be monitored yearly by taking tree cores or inserting a passive sampling device into the tree.<sup>14,15</sup> Such a practice would be ideal for sites employing phytoremediation, as LTM requires

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ments may be longer in duration and sampling points are readily available. Contrasted with traditional techniques, phytomonitoring also provides direct evidence of phytoremediation efficacy. As trees directly remove more water than contaminant (i.e., transpiration stream concentration factor  $<1$ ),<sup>16</sup> groundwater concentrations of cVOCs could theoretically increase despite contaminant mass removal. The tree's removal of the solvent at a rate greater than removal of the solute implies that groundwater concentrations are poor measures of phytoremediation efficacy.

Previous studies have suggested phytomonitoring as a low-impact alternative to traditional LTM methods at phytoscreening sites but have also highlighted potential limitations.<sup>11</sup> Recent rainfall is one limitation that has been reported to decrease contaminant concentrations in the tree due to uptake of uncontaminated surface water.<sup>11,17</sup> Contaminant concentrations in trees have also been shown to fluctuate seasonally,<sup>18</sup> as uptake of cVOCs from the groundwater is dependent on the amount of transpired water and on the fraction of groundwater transpired, while the losses of contaminants include diffusion from the bark and leaves and phytodegradation.<sup>19,20</sup> Both of these loss mechanism rates will vary seasonally, potentially preventing any steady state conditions.

The effect of seasonality on tree cVOC concentrations has been investigated at field sites, albeit at low temporal resolution. Sorek et al. observed TCE concentrations approximately 1 order of magnitude greater in the summer than in the winter for rosewood (*Dalbergia sisso*, 46 cm in diameter) and laurel fig (*Ficus microcarpa*, 37 cm in diameter) sampled during five different months.<sup>6</sup> Such seasonal variations have been reported for baldcypress (*Taxodium distichum*),<sup>8</sup> cottonwood (*Populus deltoides*),<sup>21</sup> and Russian olive (*Elaeagnus angustifolia*).<sup>21</sup> However, TCE concentrations in an oak (*Quercus* sp., 40 cm in diameter) and pine (*Pinus* sp., 68 cm in diameter) tree were largely unchanged between August and November.<sup>12,22</sup> The dynamic relationship between subsurface and tree cVOC concentrations may depend on species-specific variables such as wood morphology and site-specific variables such as precipitation, groundwater levels, and soil type.

Temporal variability in tree cVOC concentrations has also hindered phytoscreening using data sets collected over time. At a phytoscreening site where sampling occurred during a summer event and a fall event, Wahyudi et al. noted that temporal variability accounted for 83% of the total variability in tree core chloroethene concentrations.<sup>23</sup> Despite measurement of such temporal variability, no statistically significant differences were found between growing and non-growing season tree core chloroethene concentrations. The authors attributed the apparent randomness of seasonal effects to active remediation at the site.<sup>24</sup>

To better understand the effects of such variables described above, a larger, high-frequency data set is needed. Previous work has consisted of at most 12 temporal measurements, always taken from slightly different locations on the tree. cVOC concentrations in trees have been shown to vary in all three dimensions of the wood, potentially introducing additional variability.<sup>25,26</sup> Here we detail the collection of a much larger data set taken from stationary locations in multiple trees. We then use these data to describe the effect of explanatory variables, such as transpiration rate and precipitation, on *in planta* cVOC concentrations. Without detailed understanding of these variables' effects on tree cVOC concentrations, substantial uncertainty will limit the value of phytoforensic

data. Once understood, these effects can help to better explain and predict contaminant removal rates for phytoremediation systems.

## METHODS

**Field Site.** Schuman Park in Rolla, MO was used as the field site for this research. The park is immediately down-gradient from a former dry cleaning site contaminated with tetrachloroethylene (PCE) and trichloroethylene (TCE). The reductive dechlorination product, *cis*-1,2-dichloroethylene (cDCE), is also present at the site. The park contains a number of baldcypress (*Taxodium distichum*) and northern red oak (*Quercus rubra*) trees. Additionally, the site is approximately one-quarter mile from the Missouri S&T Environmental Research Center analytical laboratories, allowing field sampling without use of a portable GC. Groundwater at the site is shallow,  $<2$  m below ground surface near the trees, and is contaminated with low, but steady, levels of PCE and TCE. In the nearest monitoring well (see Figure 1), quarterly groundwater monitoring data



**Figure 1.** Plan view of the field site showing the five sampled trees. The red ellipse denotes the likely source area. Groundwater flow is toward the park to the east.

revealed that concentrations of PCE ranged from 0.17 to 0.96 mg/L and those of TCE ranged from 29 to 158 µg/L (Table 1). For comparison, the maximum contaminant level for these compounds in drinking water is 5 µg/L.<sup>27</sup> The soil is clayey with 2% organic matter and occasional fill, particularly closer to the lake. The clay is underlain by a dolomite layer ~3 m below ground surface that is fractured in some locations.

**Table 1. Concentrations of cVOCs (mg/L) in Groundwater Monitoring Well Nearest Measured Trees**

date	PCE	TCE	cDCE
4/23/2009	0.230	0.039	0.021
9/22/2009	0.175	0.029	0.018
3/30/2010	0.283	0.048	0.027
8/16/2010	0.554	0.058	0.050
12/02/2010	0.955	0.067	0.043
5/4/2011	0.680	0.158	0.177
8/15/2011	0.573	0.129	0.143

**In Planta SPME.** Traditional methods of tree sampling for cVOCs remove a small core sample from the tree, which is later analyzed by gas chromatography (GC) (for example, see ref 12). This sampling approach is unsuitable for the LTM performed here, as an excessive number of cores would be removed from the tree to obtain high frequency (i.e., weekly–monthly) temporal data. Removing a large number of cores would severely damage the tree and introduce substantial variability in tree response. To address this concern, *in planta* solid-phase microextraction (SPME) was utilized to repeatedly sample individual trees without additional damage to the tree.<sup>28</sup> SPME is a solvent-less extraction technique that easily interfaces with GC<sup>29</sup> and is particularly appropriate for headspace sampling of VOCs,<sup>30</sup> as high diffusion coefficients in air lead to rapid equilibrium. For comparison to the *in planta* SPME method, tree cores were taken approximately 1–2 per year and analyzed using headspace SPME.

*In planta* sampling required construction of a resealable sampling port. The sampling port was constructed from a brass pipe fitting, a 3/8-in. hex plug, with a 70-gauge hole (0.71 mm diameter) drilled through. The hole was plugged with 22-gauge stainless steel wire (0.64 mm diameter) when not in use (see Figure 2). This small amount of clearance restricted diffusive

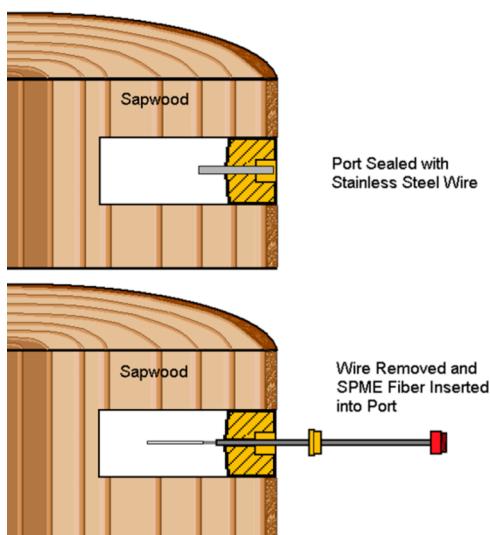
were drilled to a depth of 1/3 the tree radius. The ports were approximately 1 m above the ground surface.

**Analytics.** For *in planta* SPME sampling, a 100-μm poly(dimethylsiloxane) (PDMS) fiber was used. PDMS has high affinity for nonpolar compounds<sup>32</sup> and has been used previously to measure cVOC concentrations in trees.<sup>7,33</sup> Five-minute headspace extraction periods were sufficient to reach equilibrium at typical sampling temperatures, although when the air temperature dropped below 5 °C the extraction time was extended to 6 min.

The SPME fiber was desorbed into a 7890 Agilent GC with a VOCOL column (Supelco) and electron capture detector.<sup>7</sup> The fiber was desorbed at 230 °C for 3 min. The oven was held at 40 °C for 0.75 min and then ramped at 20 °C/min to 160 °C, which terminated the run. Prior to field sampling, the PDMS fiber was desorbed in the GC inlet for 3 min to ensure the fiber was clean. The equilibrium-based sampling technique allowed detection limits for PCE and TCE of 0.5 and 7 ng/L, respectively. Air blanks were taken onsite every 1–2 months to ensure no background contamination was detectable. Calibrations were performed approximately monthly using 10 mL water standards in 20 mL vials spiked with cVOCs with partitioning in the vial assessed using Henry's constants.<sup>34</sup> Collectively, the relative standard deviation of calibration parameters was ~5%, demonstrating good reproducibility across time and between different PDMS fibers. Using an equilibrium SPME sampling method allowed direct calculation of cVOCs in the transpiration stream assuming a local equilibrium existed for wood-water-vapor in the *in planta* sampling port.

cVOC PDMS:air partitioning coefficients are highly dependent on temperature, potentially complicating field sampling. Partitioning into the fiber is an exothermic process, leading to increased PDMS:air partitioning coefficients at lower temperatures. However, a majority of the heat of partitioning results from the heat of condensation as compared to the heat of mixing.<sup>35</sup> Therefore, if the enthalpy of mixing is neglected, the effect of temperature on water-fiber partitioning is negligible, which was the approach taken here by reporting water concentrations.

**Evapotranspiration (ET).** To estimate tree transpiration, daily reference evapotranspiration ( $ET_0$ ) was calculated using the procedure described by the Food and Agriculture Organization (FAO) of the United Nations.<sup>36</sup>  $ET_0$  estimates the amount of water evapotranspired by a hypothetical grass reference crop and has been shown to be directly proportional to sap flux in isolated trees.<sup>37</sup>  $ET_0$  is calculated from solar radiation and other factors such as vapor pressure deficit, wind, humidity, temperature, and pressure. Meteorological data were



**Figure 2.** Schematic of SPME sampling port and *in planta* sampling process (not to scale).

flux through the port to the same order of magnitude of diffusive flux escaping from a similar area of the tree.<sup>31</sup> To create sealed headspace in the tree, 19/32-in. (15 mm) holes

**Table 2. Ports and Trees Sampled at Field Site**

port no.	tree no.	tree type	diameter (cm)	depth of port (cm) <sup>a</sup>	sampling period	total samples
1	1	baldcypress	48	N/A	6/2010–10/2012	48
2W				3.9	6/2010–7/2014	122
2N	2	baldcypress	51	6.8	6/2010–7/2014	120
2E				3.2	12/2012–7/2014	34
3	3	northern red oak	44	N/A	6/2010–11/2012	37
4	4	northern red oak	36	5.6	6/2010–7/2014	111
5S	5	baldcypress	48	4.1	10/2011–7/2014	63
5N				2.7	1/2013–7/2014	33

<sup>a</sup>Distance, measured on 8/1/2014, from outer edge of bark to outer face of sampling port. Note that this distance was initially zero.

obtained from nearby weather stations,<sup>38,39</sup> and calculation details are described further in the Supporting Information and FAO document.<sup>36</sup>

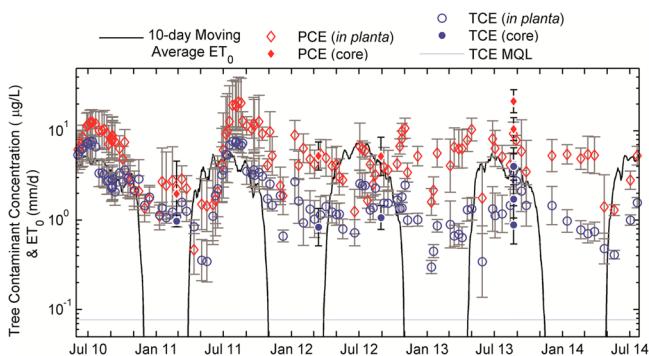
Calculated ET is realized only if sufficient water is available for uptake and functioning leaves can evaporate the water. At this study's field site, groundwater was 1–2 m below the ground surface, so the trees were assumed to have ample water supply. However, 2012 was the hottest summer on record and a severe drought year, and several trees exhibited water stress. During the period of leaf drop or leaf emergence, ET was linearly scaled from 100% to 0% of ET<sub>0</sub> by visual inspection of the trees' leaf coverage and health.

**Sampling Procedure.** *In planta* SPME sampling at the field site occurred weekly to monthly beginning June 2010 and is reported here through January 2014. Note that some trees contained additional ports for replication purposes. Ports were occasionally retired due to a continual presence of sap filling the port. The likelihood of a port filling with sap appeared to be individual-specific. Every several months tree tissue was drilled away from the surface of the port to prevent the tree from healing over the embedded port and obscuring sampling ports. Ports were not moved within the xylem, allowing the port to gradually sample deeper into the xylem as the tree diameter increased. Details regarding the sampled trees can be found in Table 2.

Sampling and analysis of any single port could be accomplished in approximately 20 min. After sampling, the SPME fiber was retracted and capped with Teflon during the 5 min transport to the GC. While transporting the capped SPME fiber, losses were reduced by placing the capped SPME fiber into a cooler containing ice. A preliminary test using spiked water showed the capped SPME fiber lost 1% of measured PCE and TCE after 10 min of storage at 20 °C.

## RESULTS AND DISCUSSION

Concentrations of cVOCs in the trees varied in a seasonal manner. cVOC seasonal variability in port 2W is illustrated in Figure 3. Also shown is the method quantitation limit (MQL)



**Figure 3.** Seasonal variation in port 2W *in planta* and tree core sap cVOC concentrations. Error bars denote the 95% prediction interval resulting from error in the calibration curve. ET<sub>0</sub> is also plotted over the experimental period.

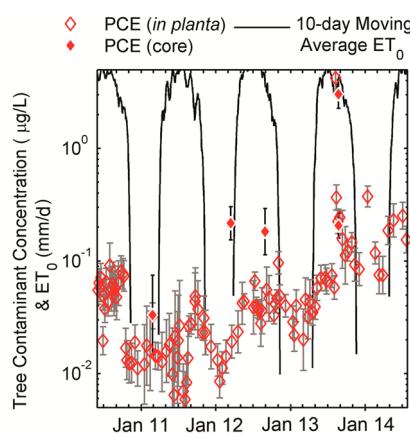
for TCE, defined as 10 times the method detection limit (MDL). The MQL for PCE is 5 ng/L, approximately an order of magnitude lower than the MQL for TCE, and does not appear on the figure. Concentrations of cDCE *in planta* remained near the MQL throughout the experiment and are not discussed further. For visual comparison, evapotranspira-

tion potential is displayed as a 10-day centered moving average of calculated ET<sub>0</sub>. The filled circles denote concentrations measured in tree core samples collected through the 4-year period.

The data shown in Figure 3 reveal a strong increase in PCE and TCE *in planta* concentrations following the commencement of transpiration as estimated by ET<sub>0</sub>. The increase in contaminant concentration was less pronounced during the summer of 2012, thought to be a result of a severe drought that year. Total precipitation in 2012 was 42 cm less than the annual average of 122 cm. Such an effect may also result from the port's location in the tree. Sampling ports were not moved but rather sampled the same xylem, which progressed from sapwood-dominated to heartwood-dominated over the 4-year study. Note the variability in core concentrations from August 2013 when three cores were taken from depths of 0–11 cm into the trunk. Concentrations of PCE and TCE increased approximately 5× from the outermost sample to the innermost sample.

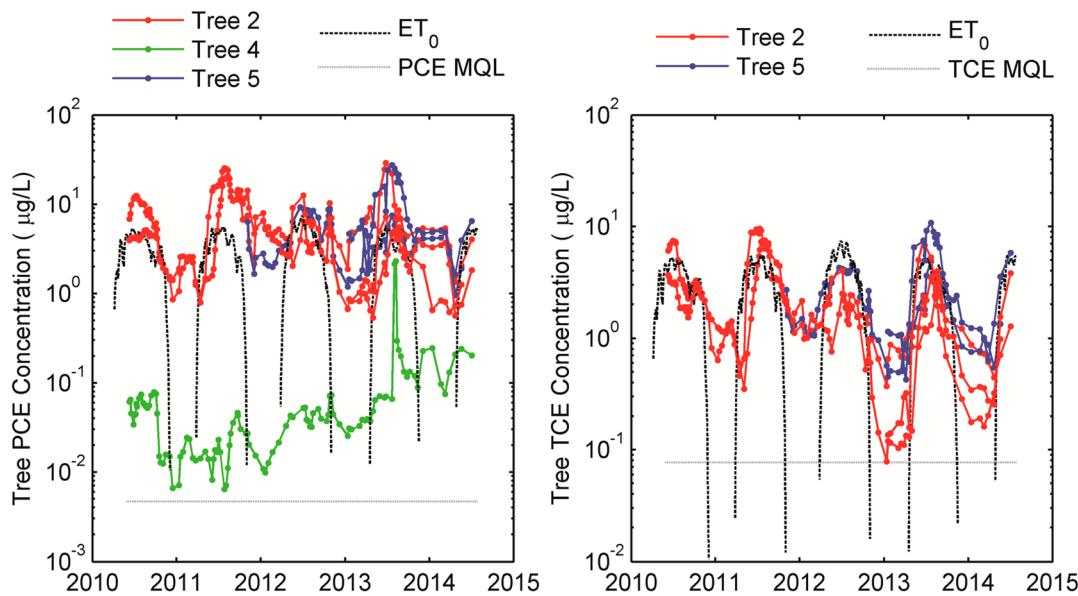
Sampling ports 2N, 2E, 5S, and 5N revealed a very similar trend to the trend shown in Figure 3 (see Supporting Information). *In planta* concentrations of PCE and TCE increased as ET<sub>0</sub> increased during leaf emergence in the spring. Contaminant concentrations increased until ET<sub>0</sub> dropped in late summer. As ET<sub>0</sub> dropped, contaminant concentrations reduced during fall, while remaining nearly constant over winter. Some variability was observed between replicate ports in the same trees, consistent with previously documented variability.<sup>25</sup>

Concentrations of cVOCs in trees 1, 3, and 4 were much lower, making identification of clear trends more difficult. Figure 4 shows the seasonal variation of PCE in port 4 (TCE



**Figure 4.** Seasonal variation in port 4 sap cVOC concentrations. Error bars denote the 95% prediction interval resulting from error in the calibration curve. Note the spike in PCE late in 2013.

not detected). Fluctuations in concentrations were less pronounced than in Tree 2, but a similar trend is observed. Concentrations of PCE were highest in the summer and corresponded to periods of peak ET<sub>0</sub>. Figure 4 also shows a unique spike in PCE concentration on 8/9/2013, which occurred after a period of unusually heavy rain. Between the measurements on 8/3/2013 and 8/9/2013, 21 cm of rain fell, with 12 cm falling on 8/7/2013. The substantial rainfall led to widespread flooding across much of the field site, with water levels approximately 1/2 m above ground surface near the lake.



**Figure 5.** Concentrations of PCE and TCE in tree sap for 6 ports installed in 3 trees. Data are a running average spanning 3 measurements.

Heavy rainfall is hypothesized to have displaced an area of highly contaminated water or non-aqueous phase liquid (NAPL) into the root zone of tree 4, resulting in the substantial spike in PCE *in planta* observed only in this individual tree. To ensure the spike was actual concentration increases, cores were collected and *in planta* sampling frequency was increased. Core and *in planta* sampling confirmed the increased concentration following the flood, and *in planta* sampling revealed a steady decline to near pre-flood concentrations. As there are no groundwater monitoring wells in this section of Schuman park, further details other than the tree sampling are not available, and the event would have gone undetected.

The collective data set is shown in Figure 5, which includes all ports in trees 2, 4, and 5. For clarity, a 3-point centered moving average of measured concentration data is shown for both PCE and TCE, while  $ET_0$  is a 10-day centered moving average. The baldcypress data (trees 2 and 5) show a similar seasonal pattern, with cVOC concentrations climbing during summer. This climb appears to coincide relatively close to or slightly after the annual onset of transpiration. A slight retardation was expected due to the hydrophobicity of the contaminants. However, a more likely explanation may be errors in approximating actual transpiration for each tree by modeling the site-specific  $ET_0$ . The oak PCE response (tree 4) deviates substantially from the baldcypress response. A number of plausible explanations exist, such as an inability of the port to accurately measure cVOC concentrations in ring-porous oak. The ring-porosity of the oak may also affect the seasonal fluctuations in cVOC concentration, as the wood has considerable anisotropy and water is largely conducted in the outermost ring(s).<sup>40</sup> The effect of wood type is difficult to elucidate at a field site where wood type is confounded with other factors such as root structure. However, wood type can affect partitioning due to differences in xylem composition.<sup>41</sup>

The general correlation between transpiration and concentration was anticipated given previous experimental and field work. For example, Nietch et al. used a mesocosm experiment to demonstrate that baldcypress tree transpiration was correlated to TCE flux from the system.<sup>18</sup> As described in

the Introduction, tree cores collected seasonally from contaminated field sites have exhibited similar seasonal trends as the data presented here, with contaminant concentrations highest during seasons of greatest transpiration.<sup>12</sup>

**Diffusive Losses.** The loss of cVOCs during fall and winter has been widely attributed to volatilization from the trunk.<sup>8,19,26,42,43</sup> Contaminant degradation *in planta* also represents a potential loss mechanism,<sup>20,44</sup> although degradation rates have not been measured at field scale. Several authors have estimated diffusional loss rates. For a 40 cm diameter tree contaminated with TCE, half-life due to volatilization was calculated to be 37 days at 20 °C using the Fruit Tree model, which assumes contaminants in the trunk are well-mixed.<sup>24,45</sup> At a temperature of 0 °C, the half-life increased to 102 days due to increased TCE partitioning to condensed phases. An alternative approach models diffusional losses during the winter using a cylindrical model, initially at a uniform concentration diffusing out to a clean atmosphere. This model is appropriate when  $ET_0$  is minimal during the winter, resulting in a diffusion-dominated process. This diffusion problem was solved by Crank, resulting in the following equation:<sup>46</sup>

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) \cdot J_0(r\alpha_n)}{\alpha_n \cdot J_1(a\alpha_n)}$$

where  $C$  is the concentration at radius  $r$ ;  $C_1$  is the initial concentration;  $C_0$  is the ambient concentration;  $a$  is the cylinder radius;  $D$  is the analyte diffusivity in the cylinder;  $\alpha_n$ 's are the roots of  $J_0(a\alpha_n) = 0$ , the Bessel function of the first kind and order zero.

Assuming the port measures the contaminant concentration at 90% of the tree radius (i.e., nearer the bark) and using wood diffusion coefficients from literature,<sup>31</sup> diffusional losses are estimated to be minimal during the winter (half-life of ~1 year for TCE), which agrees well with the measured data. However, this calculation is quite sensitive to the chosen radius and diffusivity.

In the observed data, cVOC concentrations drop more rapidly in early fall, indicative of higher diffusion out of the tree, possibly from warmer temperatures, higher trunk permeability,

changes in wood air content, or the presence of convection. Recent research has shown that tree trunk permeability increases due to structural changes in the lenticel during the growing season to allow vapor transport of respiratory compounds such as CO<sub>2</sub>, O<sub>2</sub>, and water vapor.<sup>47</sup> This seasonal fluctuation in trunk permeability may explain the sharp drop of cVOCs in the trunk as ET<sub>0</sub> decreases in the fall as well as the subsequent nearly constant concentration of cVOCs during the winter months, when trunk permeability is comparatively low. Alternatively, phytodegradation could be responsible, which would be expected to occur at a faster rate during the growing season, causing the steep decline in cVOC concentrations in autumn. Deconvolution of these loss mechanisms is difficult given the available data.

**Dilution by Rainfall.** Rainfall events have been reported to decrease tree cVOC concentrations resulting from the uptake of less-contaminated rainwater. This phenomenon was best demonstrated by Vroblesky et al. through an artificial irrigation experiment.<sup>11</sup> After a simulated 50 mm rain, TCE concentrations in a 75 cm diameter eastern cottonwood (*Populus deltoides*) tree dropped by 20–30% when measured 1–3 days post-irrigation. The effect of recent rainfall at this field site was assessed using two different predictor variables: total rainfall between SPME measurements and total rainfall during the day prior to sampling. The log<sub>10</sub> of the total rainfall data was taken to stabilize the variance for regression analysis. Neither approach was significantly associated with changes in cVOC *in planta* concentration between sampling events (all regression *p*-values >0.25; see Supporting Information for regression plots).

The lack of a significant concentration change due to recent rainfall, while not supportive of the findings of Vroblesky et al.,<sup>48</sup> is explainable by the large amount of chemical mass partitioned to the wood tissue. Assuming a typical xylem unit contains 1 g of dry wood, 1 mL of water, and 1 mL of air, approximately 97% of the PCE and TCE is partitioned into the woody tissue (see Supporting Information for calculation details). Assuming the incoming transpiration stream is void of cVOCs after a rainfall and a local equilibrium exists between the transpiration stream and solid tissues, numerous pore-volumes of transpired water are required to reduce the total contaminant mass in the xylem. For TCE, the 20–30% reduction in total contaminant mass observed by Vroblesky et al. would require 9–14 pore volumes of clean water (see Supporting Information for calculation details).

**Application of Phytomonitoring.** As the effects of environmental variables on tree cVOC concentrations are better understood, phytomonitoring is likely to gain in practical application at many sites. From this work, sapwood cVOC concentrations appear well correlated to transpiration, suggesting phytomonitoring of sapwood should occur during periods of similar transpiration rates each year. Concentrations in the heartwood appear more buffered, suggesting this tissue may be more appropriate for LTM. However, more work is needed to assess the response time of a tree during site remediation. At this site, recent rainfall appeared to have minimal impact on tree cVOC concentration, particularly when compared to seasonal variation. As additional phytomonitoring data are gathered with greater frequency, seasonal variations may be predictable from widely available meteorological data, further increasing the efficacy of phytomonitoring.

Phytomonitoring has the potential to reduce the environmental impacts, monetary costs, and temporal requirements for

long-term monitoring of chlorinated solvent plumes, although seasonal fluctuations in cVOC concentration need to be predictable for effective implementation and widespread acceptance. The expense of installing and sampling monitoring wells could be reduced by installing fewer wells and using phytomonitoring to sample at greater spatial and temporal resolution. Such a monitoring technique will be particularly beneficial for phytoremediation sites where long-term monitoring requirements may be longer and direct evidence of contaminant removal is beneficial.

## ■ ASSOCIATED CONTENT

### Supporting Information

Details of the evapo-transpiration calculations and rainfall dilution calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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