01 Oct 2011

Phytoscreening for Chlorinated Solvents using Rapid in Vitro SPME Sampling: Application to Urban Plume in Verl, Germany

Matt A. Limmer

Jean Christophe Balouet

Frank Karg

Don A. Vroblesky

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/civarc_enveng_facwork/2438

Recommended Citation

M. A. Limmer et al., "Phytoscreening for Chlorinated Solvents using Rapid in Vitro SPME Sampling: Application to Urban Plume in Verl, Germany," *Environmental Science and Technology*, vol. 45, no. 19, pp. 8276 - 8282, American Chemical Society, Oct 2011.
The definitive version is available at https://doi.org/10.1021/es201704v

Environmental Science & Technology

ARTICLE

pubs.acs.org/est

Phytoscreening for Chlorinated Solvents Using Rapid in Vitro SPME Sampling: Application to Urban Plume in Verl, Germany

Matt A. Limmer,[†] Jean-Christophe Balouet,[‡] Frank Karg,[§,∥] Don A. Vroblesky,[⊥] and Joel G. Burken*[,†]

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

[‡]Environment International, Paris, France

[§]HPC Envirotec, Rennes, France

[∥]HPC AG Group, Duisburg, Germany

[⊥]United States Geological Survey, Columbia, South Carolina, United States

Supporting Information

ABSTRACT: Rapid detection and delineation of contaminants in urban settings is critically important in protecting human health. Cores from trees growing above a plume of contaminated groundwater in Verl, Germany, were collected in 1 day, with subsequent analysis and plume mapping completed over several days. Solid-phase microextraction (SPME) analysis was applied to detect tetrachloroethene (PCE) and trichloroethene (TCE) to below nanogram/liter levels in the transpiration stream of the trees. The tree core concentrations showed a clear areal correlation to the distribution of PCE and TCE in the groundwater. Concentrations in tree cores were lower than the underlying groundwater, as anticipated; however, the tree core water retained the PCE:TCE signature of the underlying groundwater in the urban, populated area. The PCE:TCE ratio can indicate areas of differing degradation activity. Therefore, the phytoscreening analysis was capable not only of mapping the spatial distribution of groundwater contamination but also of delineating zones of potentially differing contaminant sources and degradation. The simplicity of tree coring and the ability to collect a large number of samples in a day with minimal disruption or property damage in the urban setting demonstrates that phytoscreening can be a powerful tool for gaining reconnaissance-level information on groundwater contaminated by chlorinated solvents. The use of SPME decreases the detection level considerably and increases the sensitivity of phytoscreening as an assessment, monitoring, and phytoforensic tool. With rapid, inexpensive, and noninvasive methods of detecting and delineating contaminants underlying homes, as in this case, human health can be better protected through screening of broader areas and with far faster response times.

INTRODUCTION

Using solar radiation, wind energy, and water potential, tree roots actively withdraw groundwater and constituents from the soil and transport them along the transpiration stream to provide all the water and nutrients to be the dominant terrestrial multicellular biomass on earth. As plants uptake groundwater via transpiration they can also uptake contaminants in the groundwater and soil. Once the transpiration stream is above ground, plants offer a convenient sampling access point to gain information on the underlying groundwater chemistry through the collection of tree cores for contaminant analysis. Thus, the chemical content of tree cores can be useful indicators of subsurface contamination without disrupting the surrounding ecosystem or personal property.[1−7]

Sampling of water from the subsurface is a time-, labor-, and energy-intensive process, with traditional methods of well placement and subsequent groundwater sampling being disruptive to the surroundings and damaging to property. The analysis of plant biochemistry to obtain preliminary mapping of subsurface contaminants has been termed "phytoscreening",[2] which offers a low-impact method of analyzing groundwater to screen for pollutants. Phytoscreening methods have been shown to positively correlate plant and groundwater contaminants for a range of settings,[2−4,8−10] and laboratory studies have elucidated the fundamental mechanisms involved.[2,11−14] In the field, typical methods create a small 0.5-cm hole in the tree, extracting a 2−10-cm core for analysis. Increasing interest in phytoscreening has led to U.S. federal agency developed guidance documents on the methods and discussing potential and limitations of phytoscreening techniques.[3] Advances in analytical methods have allowed detection of groundwater contaminants such as chlorinated volatile organic compounds (CVOCs) at low levels. Among the analytical methods deployed, solid-phase microextraction (SPME) shows promise for rapid contaminant extraction and analysis.

Received: May 18, 2011
Accepted: August 17, 2011
Revised: August 11, 2011
Published: August 17, 2011

SPME is an increasingly applied, solvent-free approach for sample preconcentration, initially developed by Pawliszyn's lab in the early 1990s.[15] The methodology, especially headspace sampling, can be applied to a number of complex matrices and compounds, as SPME fibers can be used as passive samplers, providing a fugacity-based concentration, which allows measurement of the concentration in individual phases (i.e., water).[16−18] While a number of fiber coatings are available, the polydimethylsiloxane (PDMS) fiber is commonly used for nonpolar organics, such as PCE and TCE, due to its high affinity for these compounds and rapid equilibration kinetics. For PDMS, fiber−air partitioning coefficients are positively correlated to octanol−water partitioning coefficients, reaching 2000 for PCE at room temperature.[19,20] In addition to high affinity for these CVOCs, the PDMS fiber also exhibits rapid equilibration. Chai and Pawliszyn showed equilibration of the fiber occurred within five minutes for a number of VOCs.[15,21] In practice, headspace-SPME is well-suited as a screening tool for rapid determination of chemical concentrations in complex matrices. Previous studies have sampled food, beverages, soil, water, and air over a wide range of concentrations. Many studies have measured compounds in or emanating from plant tissues. These lab-scale studies have employed SPME to measure plant-based compounds such as fragrance or flavor molecules or pesticides such as dieldrin.[22−30]

Research presented in this work demonstrates the potential for phytoscreening combined with SPME as an effective tool for mapping and concurrently gaining an understanding of dechlorination potential at an urban groundwater-contaminated site, applied in this case to Verl, Germany. Field-scale application of in vitro SPME analysis has not been previously used to measure contaminants in phytoscreening applications for plant sampling to delineate groundwater plumes.

MATERIALS AND METHODS

Site Description. Verl is a relatively small city in Germany, extending 73 km^2, with a population of roughly 25 000. Groundwater contamination by chlorinated aliphatic hydrocarbons is present in an elongated plume in a populated area of Verl. The dominant constituents are tetrachloroethene (PCE), trichloroethene (TCE), and *cis*-1,2-dichloroehene (*c*DCE). TCE and *c*DCE are likely present as dechlorination products of the PCE. Much of the contamination is thought to have originated from a mechanical plant in Verl, where PCE was used at the site in dipping baths from 1948 to 1969 (Figure 1). Groundwater contamination by PCE was discovered in 1972. Dendrochemical investigation, analysis of the chemical composition of tree rings, conducted on that site suggests five asynchronous releases at the site.[31] Historical research conducted after the dendrochemical investigation further uncovered that, in 1948, a hangar with PCE storage was destroyed by a fire. Also, on April 22, 1949, a fire and explosion destroyed another onsite building using PCE for painting. It has also been recently demonstrated that CVOC-contaminated materials were used as fill in the area, causing some additional, secondary sources.

Site Hydrogeology. Generally, the soil surface is uniformly sloping over the approximately 1 km distance of the sampled area: 92 m MSL on the south part of plume and lowering to 89 m in the northern part of plume at the edge of the Olbach River (Figure 1). The groundwater table in the area of contamination is shallow at an average depth of 2 m below land surface (90−86 m relative to MSL) over the SSE to NNW transect. Groundwater

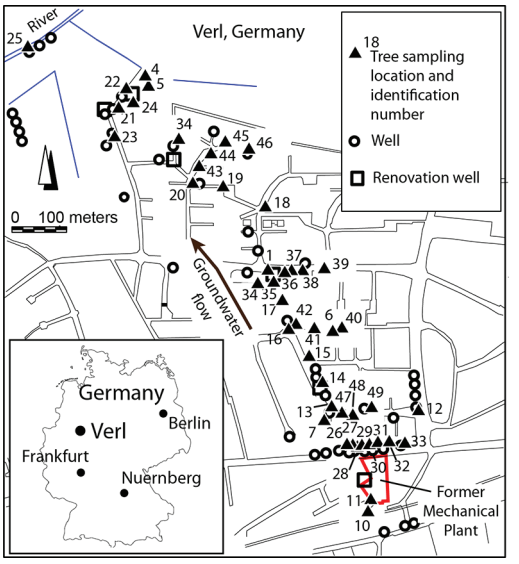

Figure 1. Location of study area with locations of sampling wells and trees that were analyzed in this study.

velocity is estimated to be 30−34 m/year in the area of the plume and is not known to vary considerably. A clay confining layer, or marne, is found an average depth of 23 m, between 75 and 80 m (MSL). Surface horizons are made of top soils, with some backfill material locally present in the build areas. The geology of the contaminated aquifer is generally alluvial/glacial, with sandy materials and some silt and clays. The plume extends beneath a wooded urban area with trees in both public and privately owned areas. The abundance of trees allowed the opportunity to sample tree cores as an alternative plume mapping approach to the more expensive and more time-consuming method of placing and sampling large number of monitoring wells.

Sampling Methods. Groundwater samples were collected in 2010 by tradition techniques of sampling monitoring wells. Contamination depth and concentration relationships are uncertain, as several of the tested wells have unknown screened intervals, with many thought to be over 4 m. Details on the sampling well construction and screened interval are not available with reliable detail. Because of the potential for mixing of the contamination plume with water from uncontaminated zones within the long screened intervals, the groundwater chlorinated-solvent concentrations likely underestimate concentrations for those locations.

Cores for this investigation were collected from 46 trees (Figure 1). The trees represented 21 species from 15 genera (Table 2 in Supporting Information) present in the urban setting, with the majority on public property. Multiple cores were collected for analysis from five trees (samples 1, 5, 6, 7, and 12; Figure 1) to evaluate reproducibility from a single tree. Most of the sampled trees represented locations expected to be near the groundwater contamination. Two trees (samples 10 and 25) were in areas considered to be uncontaminated. Tree cores were collected on May 20, 2010, by using a 5-mm diameter increment hammer (Haglöf, Sweden). The increment hammer collects a core approximately 1 cm deep, with a mass of less than 1 g. Within seconds of collection, the cores were placed into 20-mL PTFE-sealed headspace vials. Samples were shipped the next day.

Samples arrived June 2, 2010, and were weighed and analyzed at the Missouri University of Science & Technology, Rolla, MO.

Wet and dry masses were determined after analysis and subsequent oven-drying at 100 °C for 24 h. The wet mass of the core was used to correct for sample depletion as contaminants partition to the headspace. This mass-balance approach is shown in Ma and Burken,[12] using wood−air partitioning values from the literature.[11,12,14] The samples were analyzed using solid-phase microextraction (SPME) of the vial headspace (HS). The SPME fibers were desorbed into an Agilent 7890 gas chromatograph (GC) equipped with a micro-electron-capture detector (μ-ECD) fitted with a CombiPAL SPME auto sampler (CTC Analytics, Zwingen, Switzerland).

The cores were analyzed using a 100-μm PDMS fiber (Supelco, Bellefonte, PA), with an extraction time of 5 min, followed by a desorption time of 3 min. The injector was set at 230 °C, with purge flow occurring after 0.75 min. Average column velocity was 33 cm/s using nitrogen as the carrier gas in constant flow mode. The column was a VOCOL column with dimensions of 10 m x 200 μm × 1.2 μm (Supelco, Bellefonte, PA). The temperature was held at 40 °C for 0.75 min and then ramped at 20 °C/min until 160 °C was reached, which was the termination of the run. The μECD detector was set at 250 °C.

Calibration was obtained using 10 mL of water in a 20-mL vial spiked with PCE, TCE, and *c*DCE. The headspaces of five different standards were sampled, and a linear calibration plot was obtained from three standard sets. The concentrations and peak areas were log-transformed to ensure equal variances for least-squares regressions. Check-standards were placed every 10−15 samples to ensure that the calibration remained valid (±10%). Method detection limits (MDLs) were estimated using EPA methods. Because the tree core matrix is inherently variable and difficult to mimic in the laboratory setting, water standards must be used to determine the MDL (see Supporting Information). Using headspace(gas):aqueous:tissue partitioning coefficients for the different contaminants, mass corrections were carried out to calculate the in planta concentrations of the target analytes. Mass correction protocols (see Supporting Information) also incorporate the mass of the tissue and the mass of water in the samples. Mass correction protocols also show the importance and relationship of the sample mass and contaminant properties in the application of phytoscreening.

Headspace and SPME Comparison. To compare HS and SPME across a concentration range in a controlled, laboratory experiment, tree cores were spiked with TCE and PCE using an air bridge at 20 °C (5 mg/m^3 TCE and 10 mg/m^3 PCE; 160 mg/m^3 TCE and 40 mg/m^3 PCE). Four different genera of trees were tested at two concentrations, resulting in 24 total cores. Each core was analyzed by HS and then by SPME using identical chromatography methods. Further experimental details can be found in the Supporting Information.

A doubly multivariate repeated measures model was created in SAS (SAS Institute Inc., Cary, NC) to statistically test the effect of sampling method and any additional interactions between variables (proc GLM). Concentrations were log transformed to improve homogeneity of variances. The linear model was used to test if the methods were equivalent in determining core concentrations and to test for significant interaction between the chemical and method.

RESULTS AND DISCUSSION

HS and SPME Comparison. The SPME analysis demonstrated superior performance over a traditional splitless headspace (HS) method. Method detection limits using SPME were an order of magnitude lower than HS, Table 1. The table also displays the number of tree core samples from the Verl site that would be considered nondetectable at the corresponding MDLs. The lower MDLs for SPME allowed quantifiable analysis of more trees over a greater sampled area and delineation of the fringes of the plume with more accuracy than the traditional HS sampling. A full description of methods for determining the MDLs can be found in the Supporting Information.

Table 1. Method Detection Limits (MDLs) for HS and SPME and the Percent of Samples Considered Nondetectable for Each Methods

	MDL (ng/L)		Percent of samples below MDL	
Method	TCE	PCE	TCE	PCE
HS	195	6.7	39	31
SPME	8	0.5	12	0

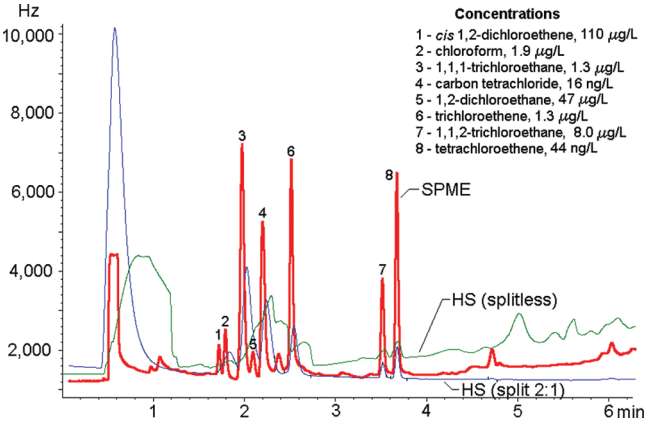

Figure 2. HS and SPME chromatographs for a variety chlorinated solvents of interest.

The SPME method also yielded improved chromatographic separation of eight tested chlorinated solvents observed in trees. Figure 2 shows the chromatographs overlaid for a sample spiked with eight common chlorinated solvents. While the separation of the headspace method can be improved by operating the inlet in split mode, the sensitivity is lower than that of SPME (Figure 2). Low detection limits are critical in phytoforensic applications, as the water concentrations in trees are inherently lower than groundwater concentrations.

The doubly multivariate repeated measures model used to analyze the HS and SPME analysis of the laboratory-dosed cores was found to be significant ($p < 0.0001$) as was the interaction between chemical and method ($p < 0.0001$). This indicates that the two sampling techniques are statistically different for the spiked cores. The significant interaction term may be interpreted as significant competitive sorption occurring using SPME. However, for use as a screening tool, it is important to consider the magnitude of these effects relative to other variables, such as tree type. Figure 3 shows the least-squares means calculated for each method and compound across each tree genus. Pairwise comparisons between trees indicated that most tree genera were significantly different, regardless of sampling method (see Supporting Information for more details). Note that the difference between tree genera was larger than the difference

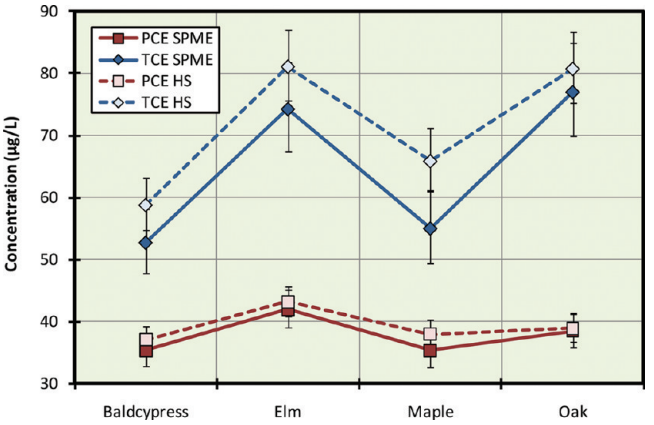

Figure 3. Least-squares means for the trees analyzed by HS and SPME including 95% confidence intervals for genera.

between methods for a given genera, with minimal interaction observed. While for exacting analytical procedures SPME may result in quantitative difficulties, it is ideal for rapid screening of numerous samples with improved detection limits and resolution of multiple analytes.

Site Investigation Results for Verl. Traditional groundwater analysis revealed PCE concentrations ranging from 10 to >1000 μg/L in the vicinity of the former mechanical plant and 10 and 100 μg/L in areas up to 190 m downgradient (Figure 4). The plume extends northwestward from the mechanical plant in a series of apparently discontinuous plume sections. Visual observation of the PCE concentrations in groundwater and in tree cores from Verl reveals a clear relationship. The areal discontinuity differs from the plume configuration in 2000, when the plume was largely interpreted as a continuous body, with concentrations of total chlorinated solvents exceeding 5000 μg/L over much of its length. The difference in groundwater plume concentration and continuity likely is due to a combination of multiple releases, differential degradation, or differences between groundwater monitoring well configurations. The plume was not likely influenced by remediation wells (i.e., removal, pump, and treat) as the plume already appeared to be noncontinuous before they were installed and because the wells had only been used only for a few days prior to the phytoscreening sampling without a period to establish effective treatment.

Comparison of chlorinated solvent concentrations from multiple samples collected from the same trees showed a close correlation for some trees and not for others. PCE in the two samples from tree 1 had a relative percent difference (RPD) of only 2.5% (78 and 80 ng/L), but 31% for TCE (825 and 1127 ng/L). The two cores from tree 7 showed a RDP of 6.1% for PCE (84 and 79 ng/L) and 7.4% for TCE (1225 and 1138 ng/L). The close reproducibility demonstrates that variations in the concentrations shown spatially are not likely due to the sampling or analytical methods. Other trees contained substantially different concentrations among the multiple cores. Trees 5 and 12 showed RPDs greater than 100% between the two cores from each tree (e.g., tree 5, PCE 58 and 13 ng/L). Tree 6 was midrange, with RPDs of 35.3% for PCE (7 and 10 ng/L) and 17.2% for TCE (1549 and 1304 ng/L). Large variations in concentration from differing parts of tree trunks are not unusual in groundwater-contamination scenarios.[3,9,10,13,32] A variety of factors potentially can contribute to such directional variations,

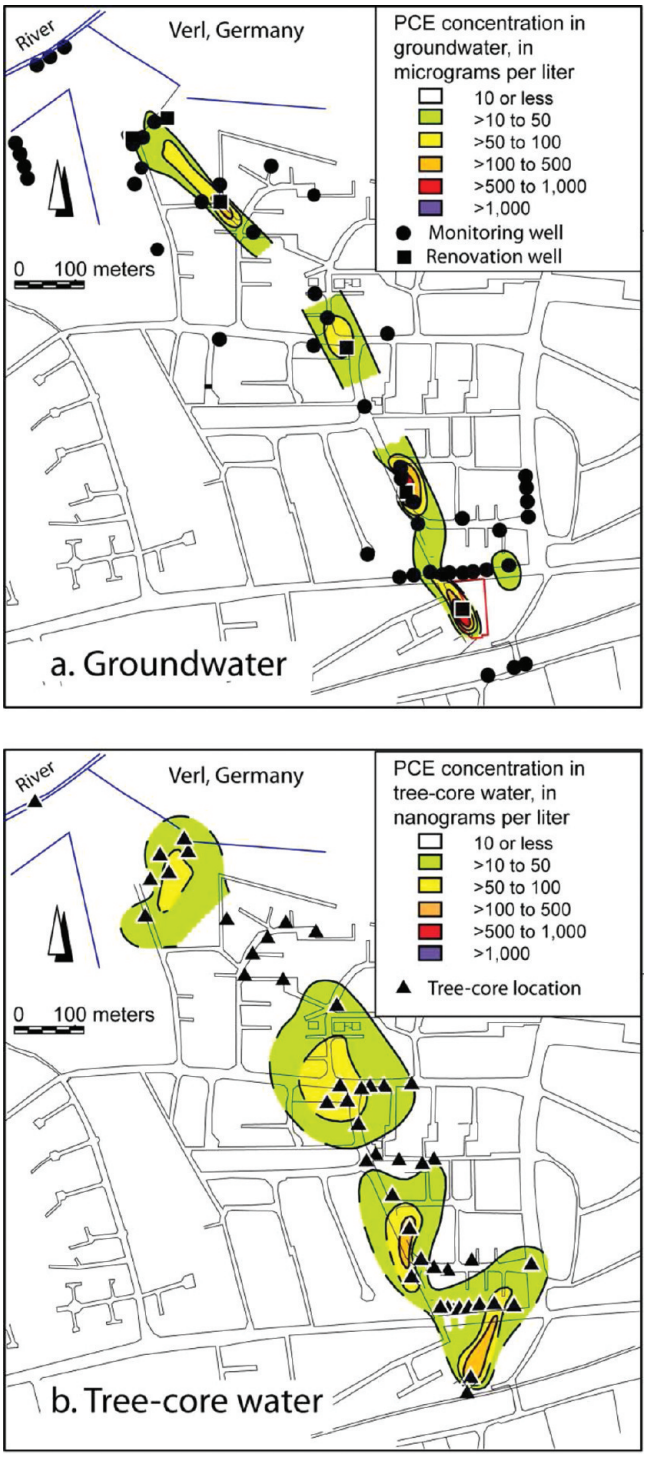

Figure 4. Tetrachloroethene (PCE) concentration in groundwater (a) in micrograms/liter and in tree-core water (b) in nanograms/liter, in 2010.

including injuries, disease and insect damage, gas embolisms within the xylem flow, spiral transport up the trunk, and variations in subsurface VOC concentrations taken up by root systems on differing sides of the tree.[3] Such tree-specific variations can often be noted in field observations and should be noted in phytoscreening analyses and all phytoforensics methods.

The groundwater PCE concentrations depict at least four major areas of PCE contamination. Likewise, the PCE concentrations in tree-core water show PCE detections in approximately the same separated areas. The tree-core PCE concentrations are substantially lower (measured in ng/L) than in the groundwater (measured in μg/L). Lower concentrations in trees are due to exclusion at the water-root boundary, degradation either prior to uptake or after uptake by endophytic bacteria or directly by the plants, sorption to plant matter, volatilization from the plant tissues, and dilution as water uptake for the trees may also come from rainfall or irrigation capture, substantially diluting the contribution from the contaminated groundwater.[2,3,10,12,33−35] The ratio of contaminant concentrations in groundwater to plant transpiration-stream varies from site to site, but relationships have been shown to exist for sites with relatively uniform hydrogeologic properties.[36] In other cases across large areas, a defendable relationship was not observed at all tested locations.[2] Given all the variables noted above, considerable variability should be expected across a site with a variety of species and different aged trees.

The small differences in areal extent can be attributed to a variety of factors. The capture zone of a tree-root system is large compared to the capture zone of a well, as one review found lateral root spread averaged near 8 m and 50% of trees had root spreads between 4 and 14 m.[37] Extensive root systems may allow trees to sample contaminated groundwater that may be beyond the sampling radius of an adjacent well. In some areas, the sampled trees are more laterally distributed from the plume center than the existing monitoring wells, allowing better lateral resolution than the installed well network. Conversely, some wells may show contamination not found in the adjacent tree. In this case, the groundwater contamination may be overlain by a veneer of uncontaminated recharge water or by an impervious layer that makes it impractical for the tree roots to extend to the contaminated zone.[10] Regardless of the small differences, subsurface PCE distribution determined from the tree core analysis shows a strong areal correspondence to the groundwater PCE distribution (Figure 4).

The lateral extent of PCE and TCE plumes appears larger in trees, as compared to groundwater. Although the phytoscreening data is in nanograms/liter and the groundwater data in micrograms/liter, the overall distribution of CVOCs as documented by phytoscreening suggest a high probability of additional PCE and TCE contamination, especially in the soil-gas of the unsaturated zone due to backfilling contaminated materials (Figures 4b and 5b). Further investigations regarding site history[31] suggest that contamination due to placement of contaminated fill material is a potential source of contamination, as initially indicated by the phytoscreening data shown here.

The areal distribution of TCE depicted from tree cores also shows a strong likeness to the distribution of groundwater TCE concentrations (Figure 5). TCE often appears as a daughter product from PCE dechlorination. Again, both the tree-core TCE distribution and the groundwater TCE distribution show a plume extending toward the northwest in a similarly discontinuous manner. Differences in TCE concentration between the tree-core water (measured in nanograms/liter) and the groundwater (measured in micrograms/liter), and minor differences in the areal distribution are presumably due to the same reasons cited for PCE above.

The data clearly show that tree coring can be a simple and effective sampling approach to provide preliminary mapping of

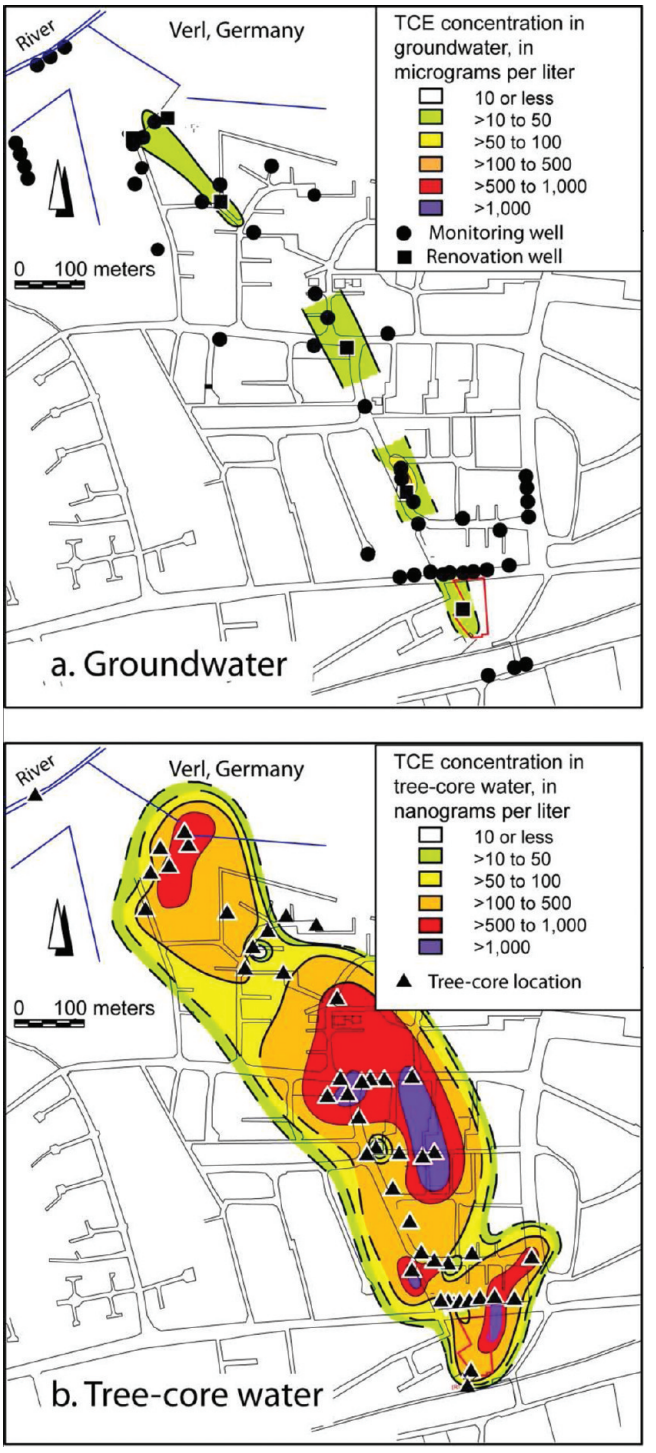

Figure 5. Trichloroethene (TCE) concentration in groundwater (a) in micrograms/liter and in tree-core water (b) in nanograms/liter, in 2010.

chlorinated solvent contamination in shallow groundwater. All of the tree core samples were collected in 1 day, demonstrating the rapid nature of phytoscreening methods. Although differences in source water concentration can cause substantial differences in the absolute concentrations in tree cores and groundwater, the chlorinated solvent concentrations in the tree cores are, for the most part, a diluted version of the groundwater chlorinated solvent plume. The relative proportions of PCE and TCE in

tree-core water are also a reflection of the relative proportions of PCE and TCE in groundwater. In the Verl tree cores, the PCE:TCE ratio show a striking similarity to the groundwater PCE:TCE ratio (Figure 6). Higher PCE:TCE ratios indicate a larger proportion of parent (PCE) relative to its dechlorination breakdown product (TCE). Microbial dechlorination of PCE can decrease the PCE:TCE ratio by producing TCE through chemical reduction of PCE.[4,24] Zones of relatively high PCE:TCE ratio can indicate areas where a small percentage of PCE has undergone microbial degradation. Lower PCE:TCE ratios can indicate areas where increased amounts of microbial degradation of the PCE have taken place. Phytoscreening PCE:TCE ratios likely delineate zones of differing biodegradation activity in the aquifer in this urban setting.

The tree cores were collected with little damage or impact to individual private properties in this urban setting in just a few hours. The plume was delineated with a level of accuracy acceptable for preliminary site characterization using concentrations in the vascular tissue detected to 0.5 ng/L with SPME sampling methods. The range of tree species and age of the trees tested in the urban environment also shows the robust nature of phytoscreening. This investigation demonstrates that phytoscreening has broad application potential as a reconnaissance-level plume mapping tool for chlorinated solvents in an urban, developed setting and has the ability to delineate areas of potential differing biodegradation activity.

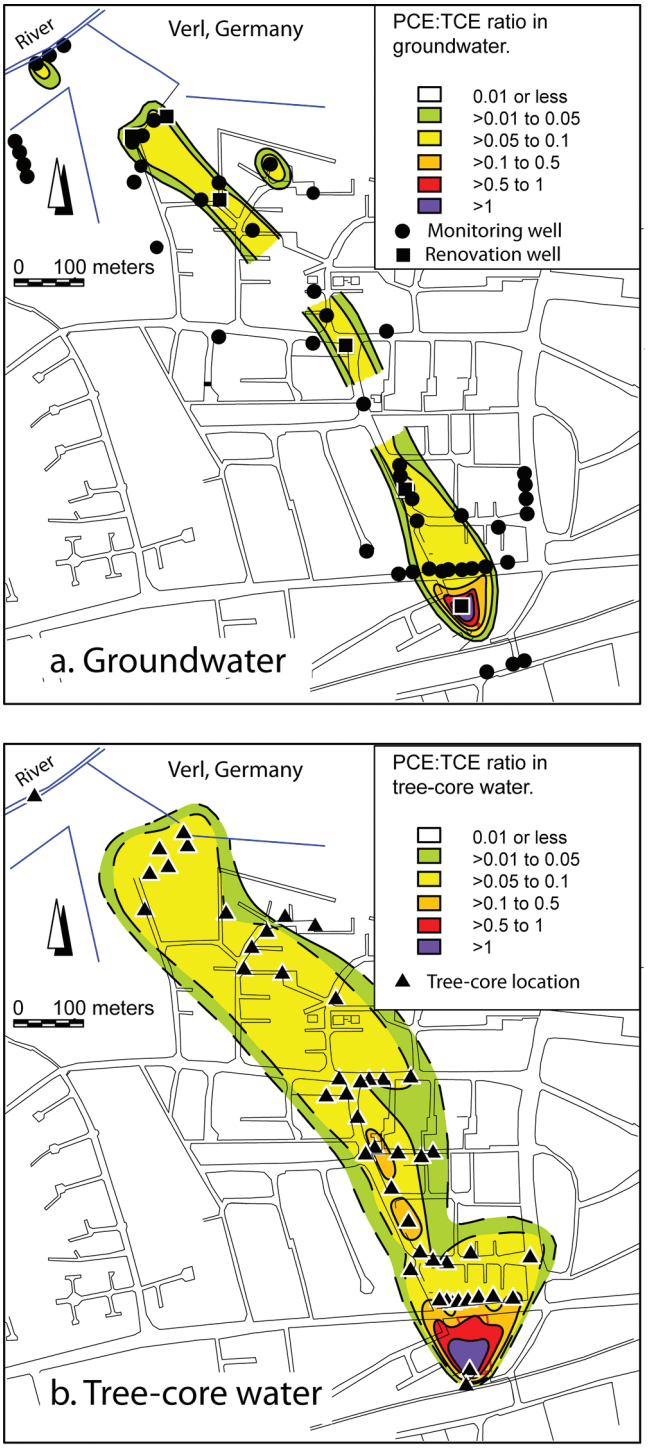

Figure 6. Tetrachloroethene:trichloroethene ratio (PCE:TCE) in groundwater (a) and in tree-core water (b) in nanograms/liter, in 2010.

■ ASSOCIATED CONTENT

Supporting Information. Description of the methods detection limits protocol and additional information on the direct comparison experiments for the traditional, accepted headspace analytical methods for phytoscreening and the SPME methods developed for this particular research; information on the mass-correction methods applied in this work and guidance for applying the mass corrections for a variety of other compounds or applications in phytoscreening; and site-specific information, including listing of the tree-specific data for trees sampled in this study. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: burken@mst.edu; phone: 573-341-6547; fax: 573-341-4729.

■ ACKNOWLEDGMENT

The present research has been funded by HPC AG, R&D Division, and is part of PIT (Pollution Investigation by Trees), an international research program led by Ademe (Agence de l'Environnement et de la Maîtrise de l'Energie, France). The authors are very thankful to Dr. Honlgan Shi and Mikhil Shetty and other members of the Environmental Research Center at Missouri S&T for support and analytical assistance, and we also offer our thanks to Mr. Gary Bigham, Exponent, and Dr. Kevin T. Smith, USDA Forest Service, for their review and assistance in the manuscript preparation. The authors are also indebted to Dr. Ralf Suttka and Dr. Ulrike Hintzen, of HPC AG, for their support in the field, historical research, early maps, review of initial report and manuscript, as well as establishing the needed authorizations for field sampling.

■ REFERENCES

(1) 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.

(2) 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.

(3) Vroblesky, D. A. *User's Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds*; U.S. Geological Survey USGS 2008-5088, 2008; p 59.

(4) Vroblesky, D. A.; Nietch, C. T.; Morris, J. T. Chlorinated ethenes from groundwater in tree trunks. *Environ. Sci. Technol.* **1999**, *33* (3), 510–515.

(5) Vroblesky, D. A.; Yanosky, T. M.; Siegel, F. R. Increased concentrations of potassium in heartwood of trees in response to groundwater contamination. *Environ. Geol. Water Sci.* **1992**, *19* (2), 71–74.

(6) Vroblesky, D. A.; Yanosky, T. M. Use of tree-ring chemistry to document historical groundwater contamination events. *Ground Water* **1990**, *28* (5), 677–684.

(7) 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.

(8) 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. *Environ. Sci. Technol.* **2008**, *42* (5), 1711–1717.

(9) 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.

(10) Vroblesky, D. A.; Clinton, B. D.; Vose, J. M.; Casey, C. C.; Harvey, G. J.; Bradley, P. M. Groundwater chlorinated ethenes in tree trunks: Case studies, influence of recharge, and potential degradation mechanism. *Ground Water Monit. Rem.* **2004**, *24* (3), 124–139.

(11) 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.

(12) Ma, X.; Burken, J. G. Modeling of TCE diffusion to the atmosphere and distribution in plant stems. *Environ. Sci. Technol.* **2004**, *38* (17), 4580–4586.

(13) Clinton, B. D.; Vose, J. M.; Vroblesky, D. A.; Harvey, G. J. Determination of the relative uptake of ground vs. surface water by *Populus deltoides* during phytoremediation. *Int. J. Phytorem.* **2004**, *6* (3), 239–252.

(14) Gopalakrishnan, G.; Burken, J. G.; Werth, C. J. Lignin and lipid impact on sorption and diffusion of trichloroethylene in tree branches for determining contaminant fate during plant sampling and phytoremediation. *Environ. Sci. Technol.* **2009**, *43* (15), 5732–5738.

(15) Zhang, Z. Y.; Pawliszyn, J. Headspace solid-phase microextraction. *Anal. Chem.* **1993**, *65* (14), 1843–1852.

(16) 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.

(17) Ouyang, G.; Pawliszyn, J. Recent developments in SPME for on-site analysis and monitoring. *Trac-Trends Anal. Chem.* **2006**, *25* (7), 692–703.

(18) Mayer, P.; Tolls, J.; Hermens, J. L.; Mackay, D. Equilibrium sampling devices. *Environ. Sci. Technol.* **2003**, *37* (9), 184A–191A.

(19) Avila, M. A. S.; Breiter, R. Estimating the PDMS-coated, SPME-fibre/water- and fibre/gas-partition coefficients of chlorinated ethenes by headspace-SPME. *Chromatographia* **2007**, *66* (5−6), 369–376.

(20) DiFilippo, E. L.; Eganhouse, R. P. Assessment of PDMS−water partition coefficients: Implications for passive environmental sampling of hydrophobic organic compounds. *Environ. Sci. Technol.* **2010**, *44* (18), 6917–6925.

(21) Chai, M.; Pawliszyn, J. Analysis of environmental air samples by solid-phase microextraction and gas chromatography/ion trap mass spectrometry. *Environ. Sci. Technol.* **1995**, *29* (3), 693–701.

(22) Supelco SPME Application Guide, 5th ed.; http://www.sigmaaldrich.com/etc/medialib/docs/Supelco/General_Information/1/t199925.Par.0001.File.tmp/t199925.pdf.

(23) Chen, W.; Poon, K. F.; Lam, M. H. W. The application of solid phase microextraction in the analysis of organophosphorus pesticides in a food plant. *Environ. Sci. Technol.* **1998**, *32* (23), 3816–3820.

(24) Lord, H. L.; Möder, M.; Popp, P.; Pawliszyn, J. P. In vivo study of triazine herbicides in plants by SPME. *Analyst* **2004**, *129*, 107–108.

(25) Skaates, S. V.; Ramaswami, A.; Anderson, A. G. Transport and fate of dieldrin in poplar and willow trees analyzed by SPME. *Chemosphere* **2005**, *61* (1), 85–91.

(26) Wajs, A.; Pranovich, A.; Reunanen, M.; Willför, S.; Holmbom, B. Headspace-SPME analysis of the sapwood and heartwood of *Picea abies*, *Pinus sylvestris*, and *Larix decidua*. *J. Essential Oil Res.* **2007**, *125−133*, 19.

(27) Wajs, A.; Pranovich, A.; Reunanen, M.; Willför, S.; Holmbom, B. Characterisation of volatile organic compounds in stemwood using solid-phase microextraction. *Phytochem. Anal.* **2006**, *17* (2), 91–101.

(28) Xiong, G. H.; Goodridge, C.; Wang, L. M.; Chen, Y.; Pawliszyn, J. Microwave-assisted headspace solid-phase microextraction for the analysis of bioemissions from *Eucalyptus citriodora* leaves. *J. Agri. Food Chem.* **2003**, *51* (27), 7841–7847.

(29) Zadra, C.; Borgogni, A.; Marucchini, C. Quantification of jasmonic acid by SPME in tomato plants stressed by ozone. *J. Agri. Food Chem.* **2006**, *54* (25), 9317–9321.

(30) Ouyang, G.; Vuckovic, D.; Pawliszyn, J. Nondestructive sampling of living systems using in vivo solid-phase microextraction. *Chem. Rev.* **2011**, *111* (4), 2784–2814.

(31) Balouet, J. C.; Burken, J. G.; Karg, F.; Vroblesky, D.; Smith, K. T.; Grudd, H.; Rindby, A.; Chalot, M. Dendrochemistry of multiple VOC releases at a former industrial site. Manuscript in preparation.

(32) Gopalakrishnan, G.; Negri, M. C.; Minsker, B. S.; Werth, C. J. Monitoring subsurface contamination using tree branches. *Ground Water Monit. Rem.* **2007**, *27* (1), 65–74.

(33) Larsen, M.; Karlson, U.; Burken, J. G.; Machackova, J.; Trapp, S. Using tree core samples to monitor natural attenuation and plume distribution of a PCE contamination. *Environ. Sci. Technol.* **2008**, *42* (5), 1711–1717.

(34) Struckhoff, G.; Burken, J. G.; Schumacher, J. G. Phytoremediation of vadose zone VOCs. *Environ. Sci. Technol.* **2005**, *39* (6), 1563–1568.

(35) Weyens, N.; van der Lelie, D.; Taghavi, S.; Vangronsveld, J. Phytoremediation: Plant−endophyte partnerships take the challenge. *Curr. Opin. Biotech.* **2009**, *20* (2), 248–254.

(36) Schumacher, J. G.; Struckhoff, G. C.; Burken, J. G. *Assessment of Subsurface Chlorinated Solvent Contamination Using Tree Cores at the Front Street Site and Former Dry Cleaning Facility at the Riverfront Superfund Site, New Haven Missouri, 1999−2003*; Report 2004-5049; US Geological Survey, May 2004; p 35.

(37) Schenk, H. J.; Jackson, R. B. Rooting depths, lateral root spreads and below-ground/above-ground allometries of plants in water-limited ecosystems. *J. Ecol.* **2002**, *90* (3), 480–494.