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Phytoscreening: A Comparison of In Planta Portable GC–MS and In Vitro Analyses

by Matt A. Limmer, Gregory D. Martin, Christopher J. Watson, Camilo Martinez, and Joel G. Burken

Abstract

Phytoscreening has been proven to rapidly delineate subsurface contaminant plumes for semiquantitative site assessment, with minimal impact to property or ecology through the collection and analysis of tree cores. Here, three phytoscreening methods were applied concurrently to identify multiple chlorinated volatile organic compounds (cVOCs) in a phytoremediation treatment system at a contaminated industrial facility. Tree coring, in planta gas chromatography-mass spectrometry (GC-MS), and in planta passive sampling showed general agreement, with the in planta GC-MS providing the quickest but least quantitative results. The portable GC-MS sampling and analysis method identified six cVOCs in the xylem of hybrid poplars (*Populus* sp.) in the phytoremediation plot. These real-time data can permit onsite identification and delineation of the contaminants, allowing for adaptive sampling during a single mobilization to a site. The in vitro methods provided quantitative data across two sampling campaigns, as relative cVOC concentrations remained similar between the two trips, despite a decrease in absolute cVOC concentrations from August to October. Overall, this research demonstrates the advantages and limitations of three phytoscreening techniques.

Background

Chlorinated volatile organic compounds (cVOCs) have been used in numerous industrial and dry-cleaning operations over the last century (Doherty 2000). Biochemical and physical recalcitrance of many cVOCs and historical handling and disposal practices have resulted in frequent soil and groundwater contamination. These compounds, many carcinogenic, are difficult to delineate and remediate owing to their dense, nonaqueous phase liquid (DNAPL) nature and modest solubility. As a result, one of the most difficult, important, and time-consuming phases of site remediation is accurately determining the extent and concentration of the contaminant plume and development of a site conceptual model (SCM). Improvements in the SCM can improve efficiency and efficacy of the remedial strategy (Carlon et al. 2001). However, improvements in the SCM usually incur the temporal and monetary cost of installing additional subsurface sampling points, an iterative process that requires multiple mobilizations of personnel, equipment, and resources.

Trees are a sustainable source of subsurface contaminant information, particularly at sites with contaminants in the shallow soil profile (Burken et al. 2011). The field of plant sampling for environmental assessment, termed phytoforensics (Burken et al. 2011), has been widely applied in the form of phytoscreening for subsurface cVOC plume delineation (Vroblesky et al. 1999; Vroblesky et al. 2004; Struckhoff et al. 2005; Sorek et al. 2008; Holm and Rotard 2011; Limmer et al. 2011; Wahyudi et al. 2012). The underlying mechanism is a tree's ability to act as a solar-powered groundwater pump and translocate environmental contaminants (Burken and Schnoor 1998; Dettenmaier et al. 2009). While contaminant translocation occurs at attenuated levels due to multiple degradation and transport barriers, improved methods for analyzing compounds in wood both in vitro and in vivo have recently been described for various analytes (Legind et al. 2007; Limmer et al. 2011; Sheehan et al. 2012).

Phytoscreening relies on a correlation between tree and groundwater contaminant concentrations, which is generally considered to be semiquantitative (Sorek et al. 2008), although such relationships are site-specific, depending on hydrogeology and plant species. In a study, tree-core cVOC concentrations were significantly correlated with nearby monitoring well cVOC concentrations when using the spearman rank correlation (Larsen et al. 2008). Log-transformed tree branch cVOC concentrations have also been well correlated with both soil and groundwater cVOC concentrations, with R^2 values exceeding 0.89 in all reported cases (Gopalakrishnan et al. 2007). At another site, log-transformed tree-core tetrachloroethene (PCE) concentrations were significantly correlated with soil and groundwater PCE concentrations (Struckhoff et al. 2005). Total cVOCs in tree cores were well correlated with total cVOCs in groundwater (R^2 = 0.97) when multiple measurements were averaged over a year (Wittlingerova et al. 2013). Standardized ranks have also been used to transform tree-core chloroethene concentrations to map groundwater chloroethene concentrations (Wahyudi et al. 2012). Uncertainty in phytoscreening data has been attributed to a variety of

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environmental variables (Vroblesky 2008; Burken et al. 2011), which will not be further examined here. Much of the variability caused by these factors, such as rooting depth and tree type, has been minimized at this phytoremediation site.

Phytoscreening is often employed as a preliminary screening tool at undelineated sites. Thus, the extent of the contamination is generally unknown, requiring large numbers of samples. While the low sampling cost and speed of sampling mitigate this issue, phytoscreening can be further optimized by on-site sample analysis, allowing sampling campaigns to be modified as data are gathered. In this paper, we describe the use of an in planta portable gas chromatography-mass spectrometry (GC-MS) method to identify and qualify contaminants on-site. On-site analysis may aid not only in optimization of the sampling plan, but also in laboratory analysis as the analytes of interest and their relative concentrations can be assessed during sample collection. We also compare this method of phytoscreening with tree coring and passive sampling methods to determine the advantages and disadvantages of employing these phytoscreening tools.

Experimental Methodology

Tree cores, in planta portable GC-MS, and in planta passive samplers were used to identify and quantify contaminants in the trees at an active phytoremediation site. Figure 1 shows the field sampling procedure, which is described in detail in the below sections.

Field Site

The selected field site is the Dow Chemical Canada ULC's former operating site in Sarnia, Ontario, hereafter referred to as the Sarnia site. A number of chlorinated solvents were known to be present in the soil and groundwater underlying the site, including *cis*-1,2-dichloroethene (cDCE), trichloroethene (TCE), PCE, chloroform (CF), carbon tetrachloride (CT), 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), and 1,1,2-trichloroethane (1,1,2-TCA). Previous data have been gathered using a number of groundwater and soil sampling techniques, leading to the creation of a detailed plume map for total cVOCs and an accurate site conceptual model. The plume map shown in Figure 2 shows

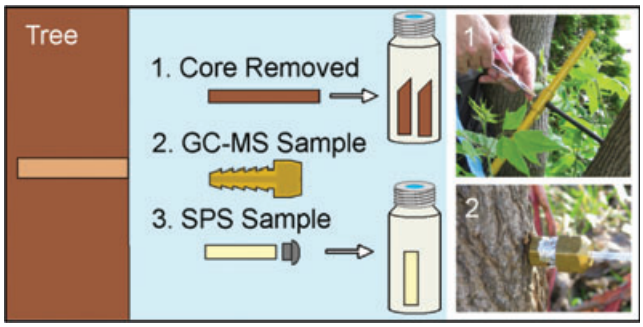

Figure 1. Field sampling procedures for three concurrent phytoforensic technologies.

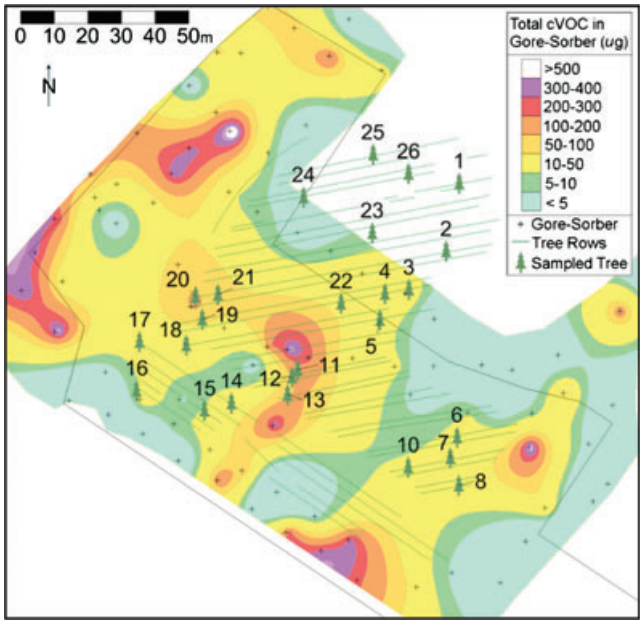

Figure 2. Field site map showing historical total cVOCs determined from Gore-Sorbers and locations of sampled trees.

contamination in the soil gas assessed using Gore-Sorbers (W.L. Gore & Associates, Elkton, Maryland). Eighty-one modules were installed to a depth of 3 feet in September 2008. The main contaminants of concern, 1,2-DCA, CT, and PCE, were summed to create the "total cVOCs" as shown in Figure 2. Current remediation strategies at the site include a permeable reactive barrier, source zone removal, and phytoremediation. Of interest to this study were the rows of a single hybrid poplar clone (*Populus* sp.) planted for phytoremediation purposes on the site in 2008, containing approximately 415 trees in an area of 1 ha. The trees were approximately 3 to 5 m tall and 8 to 10 cm in diameter (breast height) at the time of sampling 2 years later. This diameter is considered to be near the minimum diameter acceptable for tree coring without significantly damaging the tree (Vroblesky 2008).

Tree Coring

Tree cores were obtained from 25 trees using a 0.5-cm increment borer (Forestry Services Inc., Pawleys Island, South Carolina) during two trips (August 26, 2010 and October 25, 2010) (see Figure 2). During each trip, tree coring was completed in fewer than 5 h with one sampling team (three people). Equipment use was limited to a small number of hand tools, which were carried in a small field bag (45 × 20 × 20 cm). The cores were 6 to 8 cm in length and were taken at 1 m height or less. Typically, cores are taken at breast-height (1.3 to 1.5 m), but were taken at a lower height owing to the small diameter of the tree. To avoid negative impacts of repeat coring on these small diameter trees, cores were generally taken from a neighboring tree (<3 m away) for the second sampling event. While sampling such trees introduced an additional source of error, and this error is considered minimal given that adjacent trees were similar in age and size. Duplicate cores and field blanks were taken approximately every 10 samples. Upon removal from the

tree, the core was transferred immediately to a 20-mL vial with a screw-top cap and polytetrafluoroethylene (PTFE)/silicone septa (Supelco, Bellefonte, Pennsylvania) for laboratory analysis, which is described below.

Portable GC-MS

Two Inficon Hapsite Smart portable GC-MS units with Tenax concentrators analyzed cVOCs in the trees at the site during the October trip only. Thirty-two samples were completed using two portable GC-MS units over a 2-d period (eight samples per unit per day). To perform GC-MS sampling in planta, the air-sampling probe from the GC-MS was inserted into a sampling port installed in the tree (see Figure 1). The port was constructed of a 1/4-inch brass coupler (hose barb x threaded) attached to a 1/4-inch cap, designed to occupy the space vacated by the tree-coring procedure. The cap had a 1/8-inch hole (0.32 cm) to receive the probe. An aluminum septum was wrapped onto the threaded end of the hose barb and the cap was screwed on sufficiently tight to allow sealing but prevent tearing of the foil. The barbed end of the port was then inserted into the xylem volume vacated by the coring procedure. At the commencement of sample collection, the GC-MS sample probe pierced the aluminum septum and sampled the air within the xylem void volume. The time between port installation and sampling (i.e., equilibration time) was varied between 0 min and 25 h to determine if equilibration had been reached. The GC-MS instruments were not specifically calibrated for the mixture of target contaminants, but peak areas were normalized against the internal standard. The internal standard (bromopentafluorobenzene) is integrated into the operation of the instrument and is used as part of the automatic tuning and calibration process.

A 15-min air sampling standard method on the instrument was used. This included a 1-min line purge with VOC-free nitrogen, followed by a 1-min concentrator fill at a rate of 100 mL per minute. The concentrator temperature was held at 60 °C for 7 min, ramped at 10° per minute for 3 min, and then held at 160 °C for 30 s. Prior to sampling on each day, a background air sample was analyzed to ensure that no background levels of target contaminants would interfere with the sample. Following each sample analysis, a high temperature concentrator bakeout was run for 3 min at 150 °C. The system was considered clean if the peak total ion count (TIC) was below 500,000. If this threshold was exceeded, further cleanout runs were conducted until the threshold was met. Compounds were identified using the Automated Mass-spectral Deconvolution and Identification System (AMDIS) library with a weighted value of greater than 90 set as the minimum for a positive identification. Optimized portable GC-MS methods (not used here) have been developed for various contaminants of interest (for cVOCs, e.g., Gorder and Dettenmaier 2011). Such methods may be necessary at less contaminated sites.

Solid Polymer Samplers

Passive sampling devices, termed solid polymer samplers (SPSs) (Shetty et al. 2013), were constructed from 0.5 g ± 2% of Tygon tubing (Formulation R-3603, ID: 1.6 mm, OD: 4.8 mm). Stainless steel wire was looped through the tubing to aid insertion and removal of the SPS from the tree. In preparation for use, SPSs were cleaned in methanol for 2 d and then dried in a 100 °C oven for 3 d. SPSs were then wrapped in aluminum foil until used at the site. SPS blanks were vialed on-site at the beginning and end of each day of sampling. No detectable amounts of cVOCs were observed in these blanks.

After removing the tree core and taking the core space air sample with the portable GC-MS, SPSs were placed into the vacated core-space in the tree to allow comparison of the three methods. A #10 - 32 × ½˝ machine screw was used to seal the SPS in the tree. Following 3 to 4 weeks of equilibration, the SPSs were removed and placed into 20-mL vials with a screw-top cap and PTFE/silicone septa. These vials were refrigerated until analyzed using the method described below.

SPSs are made from a characterized material and do not require additional coring of the tree, thereby allowing repeated sampling of individual trees while providing uniform sampling media between different trees. Tree coring and SPSs are known to give similar concentration values (Shetty et al. 2013), assuming partitioning coefficients are large enough to provide negligible depletion during equilibration in the vial (Mayer et al. 2003), the SPS is adequately sealed in the tree, tree contaminant concentrations remain consistent over the equilibration period, and the SPS reaches equilibrium in the tree.

Laboratory Analysis

Tree cores and SPSs were analyzed using headspace solid-phase microextraction gas chromatography (HS-SPME-GC), following the procedure described previously (Limmer et al. 2011). A polydimethylsiloxane (PDMS) SPME fiber was allowed to equilibrate with the vial headspace prior to desorption into the GC inlet. Analytes were separated on a VOCOL column and detected using electron capture detection (ECD). This method has good sensitivity for chlorinated solvents, with detection limits in the low ng/L range for TCE and PCE, and provides a fugacity-based measurement, yielding a water concentration (ng/L), rather than a mass concentration in the xylem tissue (ng/kg). Other analytes measureable by this method include chlorinated methanes and chlorinated ethanes.

Results and Discussion

Plume Delineation

Phytoscreening is generally employed to quickly delineate plumes and locate hot spots. Concentrations were mapped in Surfer 9 (Golden Software Inc., Golden, Colorado) overlain on the historical vapor plume map developed from Gore-Sorber data. The plume data given were in total cVOCs (only PCE, 1,2-DCA, and CT), so total cVOCs were calculated for each tree to enable comparison between contaminant plume and phytoscreening data. Compounds considered in the phytoscreening contaminant total included 1,1,1-TCA, 1,1,2-TCA, CF, CT, cDCE, TCE, and PCE. Trees with multiple samples were averaged. To

stabilize data variance, the $\log_{10}$ of the average concentration was taken. Figures 3 and 4 show the tree-core cVOC data for the August and October trips, respectively.

For comparison, phytoscreening maps in Figures 3 and 4 share the same legend. In both cases, trees 11 to 14 revealed high contaminant levels and appear to be nearest to a hot spot. In addition, overall tree cVOC concentrations from the October trip are lower than the August trip, likely because of seasonal decrease in plant contaminant concentration as plant transpiration decreases during autumn senescence. These seasonal losses were greatest for the highly volatile CT, which averaged 0.92 log µg/L loss.

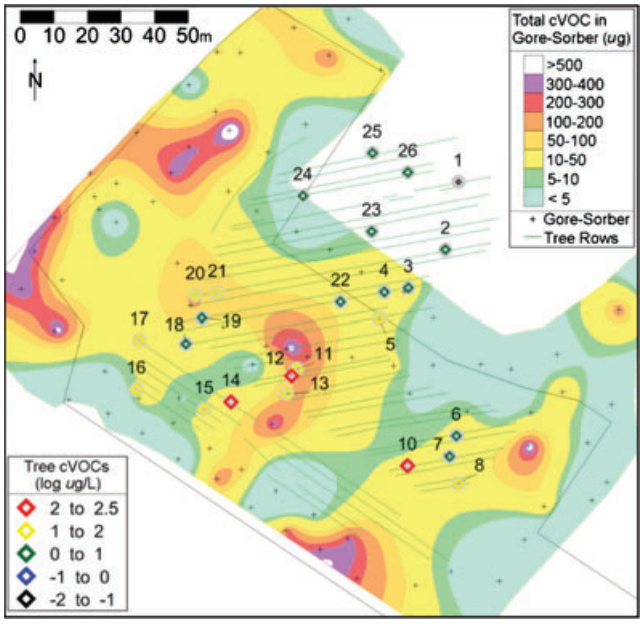

Figure 3. Total cVOCs detected in tree-core xylem water via in vitro HS-SPME-GC from August 2010 samples (log µg/L) compared to contaminant mass measured in Gore-Sorber.

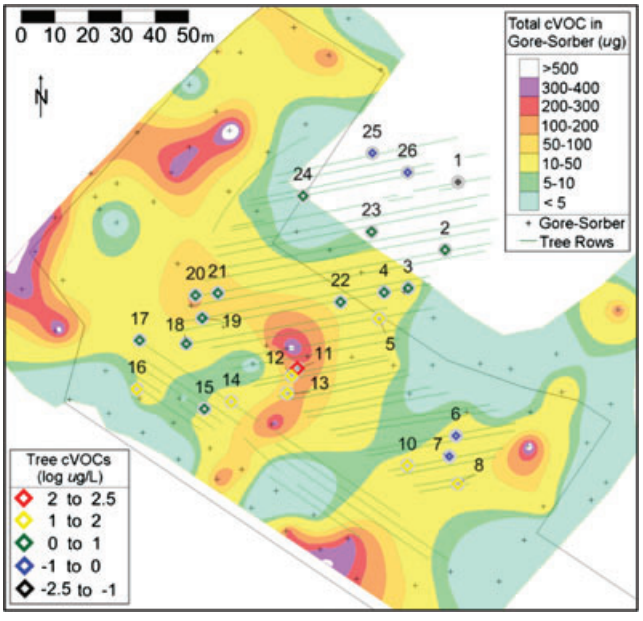

Figure 4. Total cVOCs detected in tree-core xylem water via in vitro HS-SPME-GC from October 2010 samples (log µg/L) compared to contaminant mass measured in Gore-Sorber.

For sites with trees of similar age and type, relative hot spots can also be identified by comparing the relative contribution of each tree to the total contaminant found in all the trees. For example, the below equation shows the percent contribution (%PCE_i) of tree *i* to the total PCE concentration found in all sampled trees (*n*).

$$\%PCE_i = \frac{[PCE]_i}{\sum_{i=1}^{n}[PCE]_i} \times 100\%$$

A plot of the percent contribution for both trips is shown in Figure 5. For clarity, only trees that contained greater than 5% of any analyte from the August trip are shown. No additional trees exceeded the 5% criterion for the October trip. The figure shows that trees 10, 11, and 12 contained a high percentage of the target analytes. Trends between various chemical classes can be elucidated as well. For example, tree 8 is high in both tri-chlorinated ethanes, while having minimal concentrations of other cVOCs, likely indicating an area more contaminated with trichloroethanes. Trees 16 and 20 appear to have mainly chlorinated ethenes, while tree 10 is mostly contaminated with chlorinated methanes. These observations likely indicate nearby contaminant-specific source areas (or former source areas).

Percent contributions should be more stable over time compared to absolute concentrations, as aforementioned seasonality affects tree contaminant concentrations (Nietch et al. 1999). The trends between trips are similar, with trees 8, 10, 11, 12, 13, and 14 representing a majority of the contaminant load. The most notable exception is tree 13, which was relatively more contaminated in the October trip, while trees such as 20, 21, and 23 fell below 5% contribution to the total contaminant load in October. Tree 16 also showed a substantial decrease in contaminant load from September to October, perhaps owing to its proximity to a steep plume gradient combined with the practice of sampling different trees during the October trip.

Portable GC-MS

Thirty-two in planta GC-MS samples were taken over a 2-d period from 19 ports in 14 unique trees during the October sampling trip. Some of these samples were replicates taken in the same port, but with different equilibration times to determine optimum equilibration times for sampling. The instruments were able to detect 1,1-DCA (not identified in tree-coring analysis) in addition to the cVOC compounds identified in the cores (cDCE, TCE, PCE, CF, CT, 1,2-DCA, 1,1,1-TCA, and 1,1,2-TCA). The GC-MS analysis was more sensitive for less-chlorinated compounds, such as 1,1-DCA, as compared to the ECD used in laboratory analysis. In vitro ECD of highly chlorinated compounds such as PCE and CT showed improved sensitivity. Figure 6 shows the comparison between the tree-core concentration and the GC-MS corrected peak area, with statistics shown in Table 1. Note that these averaged samples often include data from both GC-MS instruments and varying port equilibration times.

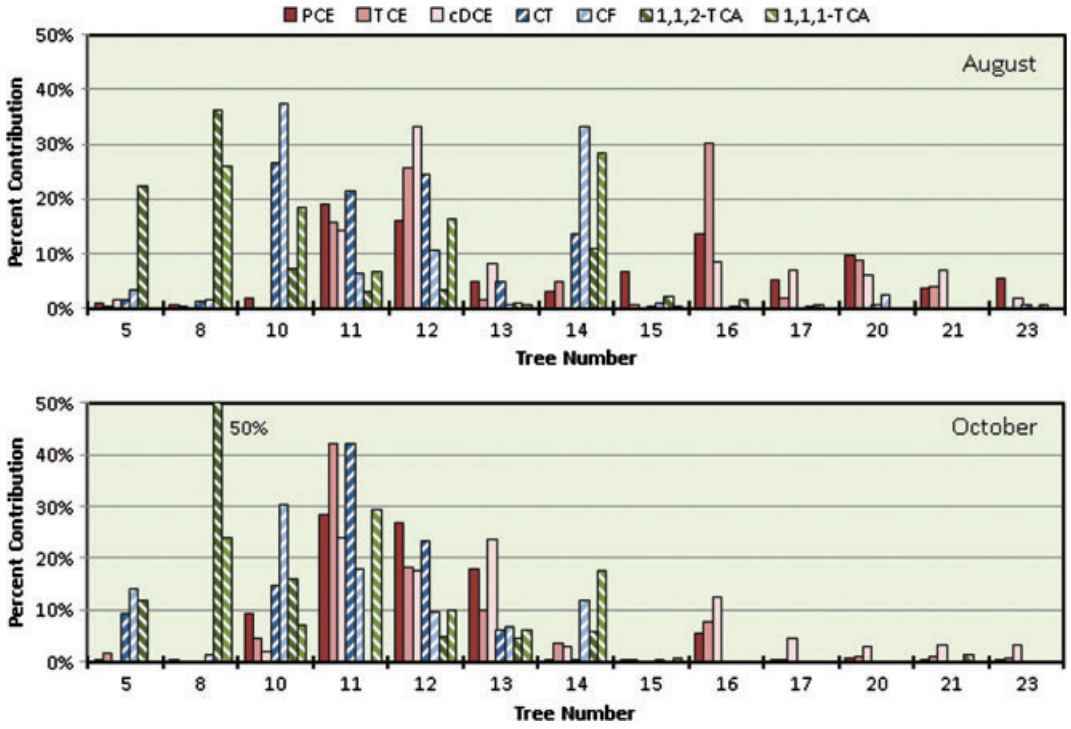

Figure 5. Percent contribution graph for August (top) and October (bottom) sampling campaigns. Graphs show trees 8, 10, 11, 12, 13, and 14 represent a majority of the contaminant load for both sampling events, indicating these trees are located near hot spots.

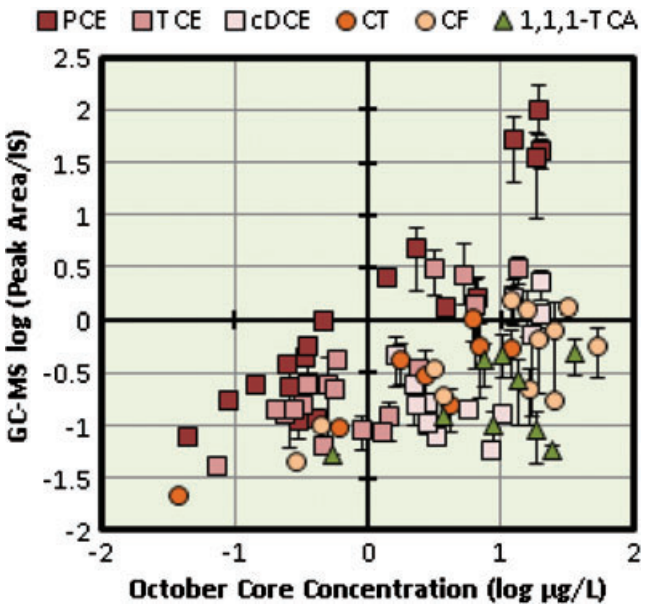

Figure 6. Comparison of in planta GC-MS data to core concentrations determined in vitro via HS-SPME-GC. Error bars indicate the range for repeat samples.

Of all the compounds, the most linear relationship was for the PCE data, with an R^2 of 0.84 and a slope of 1.17. Other compounds show decreased linearity, with R^2 values as low as 0.04 for 1,1,1-TCA. In general, GC-MS response (i.e., peak area) does not appear to increase at the rate comparable to core concentrations determined in vitro, limiting quantitative use of portable GC-MS method developed and applied herein. This may be explained by compound leakage out of the ports for these compounds or an inability to consistently capture contaminant mass volatilizing from the wood during the active sampling period.

Port equilibration time (i.e., the time between port installation and GC-MS sampling) was investigated to determine if sufficient time had elapsed to allow the cVOCs in the trunk to equilibrate with the port internal air volume. Replicate samples were taken from the same tree, allowing the port to equilibrate for different periods prior to sampling. Note that the port was resealed after each sample. The amount of analyte measured was not highly dependent on port equilibration time over the timescale investigated (data not shown).

As port equilibration time could not be determined to be significant, all data were used to approximate the contaminant concentrations in the trees. Therefore, where multiple samples were taken, peak areas were averaged to determine an overall peak area for each tree. The average contaminant peak areas were added together to calculate a total cVOC peak area for each tree. Note that PCE was the dominant contaminant in most samples, so total cVOCs were strongly influenced by PCE peak area. Without a quantitative method developed to standardize instrumental response, comparison of relative peak areas between contaminants at each location may not be valid. Nevertheless, this approach was the best comparison technique given the lack of calibration data. These average cVOC concentrations were plotted against the known soil-gas plume in Figure 7, resulting in a map comparable to those produced from tree coring and SPSs.

In general, portable GC-MS analysis appears to be efficient and sensitive for identifying a range of cVOCs and determining relative levels of tree contaminants; however,

Table 1

Comparison of In Planta GC-MS Data to Core Concentrations Determined In Vitro via HS-SPME-GC: Regression Coefficients, Statistics, and Chemical Properties for Data in Figure 6

Compound	Slope	Pearson's R^2	p-value	Log K_{ow}[1]	Henry's Constant[2]	Boiling Point (°C)[1]
PCE	1.17	0.84	<0.0001	2.88	0.58	121.1
TCE	0.85	0.61	<0.0001	2.42	0.34	87.0
cDCE	0.86	0.37	0.0015	1.86	0.14	60.0
CT	0.62	0.51	0.0012	2.77	1.0	76.7
CF	0.45	0.27	0.0113	1.95	0.12	61.4
1,1,1-TCA	0.20	0.04	0.426	2.49	0.57	73.9

[1]Data from Schwarzenbach et al. 2003.
[2]20 °C (data from EPA).

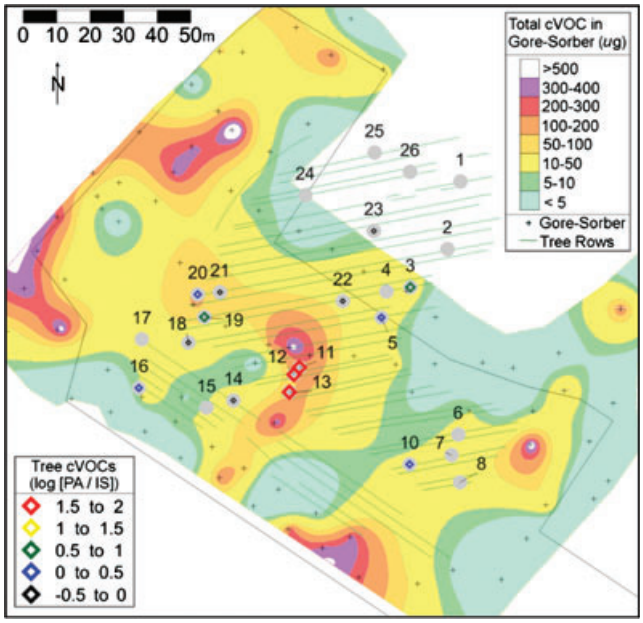

Figure 7. GC-MS mapping of tree concentrations (log PA:IS) compared to contaminant mass measured in Gore-Sorber.

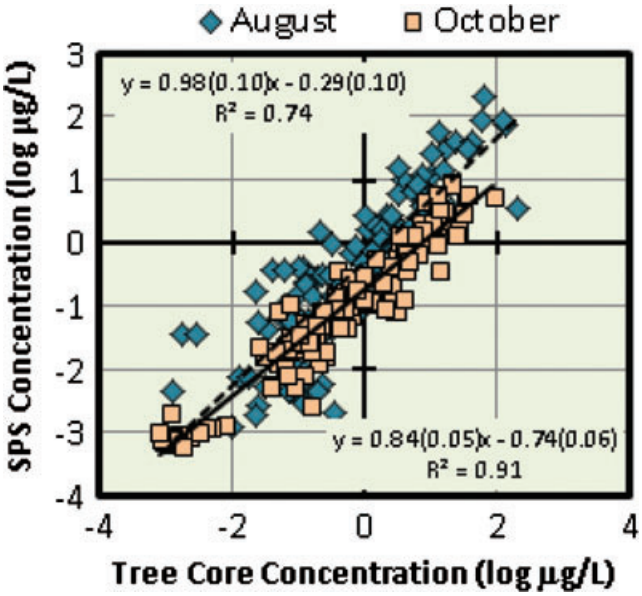

Figure 8. Comparative graph of SPS and tree-core data for both campaigns. Each data point represents an individual cVOC tree-core SPS comparison. Values in parentheses are 95% confidence intervals.

the linearity with core concentration was lacking for analytes other than PCE. Ongoing steps in refining the accuracy of this approach include: optimization of the port design, particularly allowing for a greater sampling volume; development of a specific analytical method for the target compounds; and additional sampling to establish a minimum equilibrium time.

Tree Core—SPS Comparison

The SPS data were plotted against the tree-core data for both trips (Figure 8). In this figure, each data point represents a single tree sample, where the concentration in the xylem water was calculated from both the core and SPS. Note that a single tree core or SPS often contained multiple cVOCs, so one core-SPS pair may be represented by numerous points. All cases where either the SPS or tree core did not detect contaminants were omitted for clarity.

For SPS concentrations to be proportional to tree concentrations, the slope of the fitted line should be near unity with an intercept of zero. This appears to be more true for the August data (slope: 0.98 ± 0.10) than the October data (slope: 0.84 ± 0.05), as the noted 95% confidence interval includes unity. For this investigation, the assumption of constant tree concentration may have been violated, as the October trip SPSs were not collected until after tree transpiration had decreased or potentially ceased due to winter senescence, resulting in decreasing tree contaminant concentrations over the SPS sampling period. Once evapotranspiration ceases the contaminants are not resupplied to the trunk, allowing diffusive losses to dominate (Ma and Burken 2003; Ma and Burken 2004). An alternate explanation is that the SPSs had not yet reached equilibrium because of the colder temperatures. Equilibrium has been shown to occur in 10 d at 20 °C (Shetty et al. 2013), although this has not been tested at colder temperatures.

Comparison of Sampling Methods

All the three methods are appropriate sampling techniques under certain site conditions and offer specific benefits and limitations. Portable GC-MS analysis is effective at providing

Table 2

Comparison of Sampling Methods for Phytoscreening

	Tree Coring	SPSs	Portable GC-MS
Time to obtain sample	~5 min	~5 min + equilibration time	~30 min
Time from Sample Collection to Obtain Concentration Data	~3 d	~3 d + equilibration time	~30 min
Equipment cost	~$300	~$5	~$500/d (rental)
Consumables	Sample vials	Sample vials, SPS, machine screw	Carrier gas, internal standard
Analysis cost per sample	~$50–$100	~$50–$100	N/A
Relative standard deviation (RSD)	35% (n = 22)	4% (n = 7)	56% (n = 43)
Implementation limitations	Repeated sampling requires additional bore holes in tree	Return to field site required for sampler retrieval Sampler kinetics and partitioning must be known	Availability/transport of instrument

real-time, albeit semiquantitative data, and is a promising application in source area investigations and screening for contaminants where identification of contaminants and plume extent are required in a timely manner. Tree coring and SPSs exhibited improved sampling speed and analytical quantitation, although repeatedly sampling a tree via tree coring may substantially damage the tree. SPSs avoid such a problem, but require an additional site visit to retrieve the samplers. Relative standard deviations (RSD) were largest for the portable GC-MS and lowest for the SPSs. SPSs were anticipated to yield the lowest RSD because of the homogeneous, reproducible matrix. Advantages and limitations of the samplers are described further in Table 2.

Conclusions

At the Sarnia site, three phytoforensic tools were employed in coordination to rapidly identify cVOC hot spots and map concentrations in a phytoremediation plot. Two campaigns were completed with approximately 30 trees samples taken each trip. Tree coring time was approximately 5 h for the entire site with minimal equipment mobilization (all coring and passive sampling equipment contained in one checked luggage). Total cVOC concentrations in the trees spanned approximately six orders of magnitude and were found to qualitatively agree with soil-gas plume data collected using Gore-Sorbers.

A seasonal drop in contaminant concentrations (from August to October) was observed, although concentration differences between trees were still clear and quantifiable. Tree coring and SPSs yielded similar data, while real-time portable GC-MS data were less correlated to tree coring and SPSs for compounds other than PCE. Further work is needed to improve the portable GC-MS method's reproducibility for in planta applications; however, the utility of using this instrument as a real-time screening tool for cVOCs in a phytoforensics investigation was demonstrated.

Acknowledgments

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