Groundwater
Monitoring&Remediation

Comparison of Phytoscreening and Direct-Push-Based Site Investigation at a Rural Megasite Contaminated with Chlorinated Ethenes

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Abstract

The reliable characterization of subsurface contamination of spatially extended contaminated sites is a challenging task, especially with an unknown history of land use. Conventional technologies often fail due to temporal and financial constraints and thus hinder the redevelopment of abandoned areas in particular. Here we compare two site screening techniques that can be applied quickly at relatively low cost, namely Direct Push (DP)-based groundwater sampling and tree core sampling. The effectiveness of both methods is compared for a rural megasite contaminated with chlorinated hydrocarbons. Unexpected pollution hot spots could be identified using both of these methods, while tree coring even enabled the delineation of the contaminant plume flowing into an adjacent wetland inaccessible for DP units. Both methods showed a good agreement in revealing the spatial pattern of the contamination. The correlation between groundwater concentrations and equivalent concentrations in wood was linear and highly significant for trichloroethene. Correlation was less obvious for its metabolite *cis*-dichloroethene, but still significant. As outcome of our study we recommend tree coring and for initial screening in combination with a DP sampling to retrieve quantitative data on groundwater pollutants in order to assess the contamination situation of a non- or only partly investigated site. The subsequent placement of monitoring wells for long-term monitoring of contamination levels is recommended. A combination of methods would achieve more relevant information at comparable or possibly even lower efforts in comparison to a conventional site investigation.

Introduction

In 2006, the European Commission proposed the framework directive for the protection of soil and the preservation of soil functions (European Commission 2006) requesting European Union member states to complete a nation-wide inventory of potentially polluted sites within 25 years, including the determination of concentration levels. This task requires cost-effective site characterization approaches for which megasites are posing a particular challenge (Rein et al. 2011). The current practice in the contaminated site characterization typically consists of an extensive use of drilling, sampling, and laboratory analysis as the main or most often as the only procedure providing information about the degree and spatial extent of subsurface contamination. In fact, the number of sampling points is normally limited and insufficient due to financial constraints (Döberl et al. 2012). Therefore, new approaches that can yield reliable data at comparable or lower costs are needed. One recent suggestion refers to initial screening investigations to deal with uncertainties concerning unknown or unexpected areas of contamination (e.g., Larsen et al. 2008; Rein et al. 2011). To meet these needs, two methods for contaminated sites screening have been (further) developed in recent years, namely phytoscreening and the Direct Push (DP) sampling method.

Phytoscreening of groundwater contamination by tree coring has become a scientifically well-investigated and widely recognized method (Vroblesky 2008; Holm et al. 2011; Trapp et al. 2012). By use of a wood drill, tree cores can be taken from the trunks of trees for chemical analysis. The presence of pollutants in the wood indicates the presence of these pollutants in soil and/or groundwater (Vroblesky et al. 2004; Holm et al. 2011; Burken et al. 2011; Trapp et al. 2012). The principle underlying the method is that contaminants are taken up by roots and translocated upward to the stem (Newman et al. 1997; Doucette et al. 2007; Trapp 2007). Phytoscreening has repeatedly been used to investigate plumes of chlorinated solvents, such as tetrachloroethene (PCE), trichloroethene (TCE), and *cis*-1,2-dichloroethene (cDCE) (Vroblesky et al. 1999; Compton et al. 1998; Ma and Burken 2002; Schumacher et al. 2004; Larsen et al. 2008; Sorek et al. 2008; Holm and Rotard 2011; Algreen et al. 2015), and, recently, for heavy metals (Algreen et al. 2012, 2014).

The DP technology is based on small all-terrain vehicles and achieves subsurface investigations by pushing or hammering small diameter hollow steel rods into the ground to acquire high-resolution depth profiles of different physical and chemical parameters. DP technologies are cost effective and provide minimally invasive access to the subsurface. A

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comprehensive review on DP technologies is given example in Dietrich and Leven (2006) and Leven et al. (2011).

Due to the low costs and the little effort in equipment and planning associated with the tree coring, phytoscreening is well suited for an initial screening of a noninvestigated suspect site. Phytoscreening can provide a spatial overview about plume extension, direction, and hot spots (Vroblesky et al. 1999; Schumacher et al. 2004; Larsen et al. 2008; Sorek et al. 2008; Holm and Rotard 2011; Algreen et al. 2015). Once such information is obtained, a grid for DP subsurface sampling can be better assembled. In addition, DP-based groundwater sampling enables screening investigations in comparison to conventional groundwater drilling in a much more time- and cost-efficient way (Rein et al. 2011). However, such newly applied methods need to be tested and validated properly before being considered resistant to a legal scrutiny (Balouet et al. 2009; Wolff 2012). In a recent study, the DP method for site investigation has been compared to the conventional investigation based on concentration measurements in monitoring wells installed in areas suspected of being polluted (Rein et al. 2011). The DP campaign remarkably reduced the uncertainty concerning the occurrence of groundwater contamination at the site. Taking economical consideration into account, DP-based groundwater screening was recommended to obtain either primary or complementary information on the entire site, and for the selection of locations for long-term monitoring of temporal variability.

Such a step-by-step approach for contaminated sites with an initial screening with tree coring followed by DP site screening and a well-based groundwater monitoring is favorable to minimize the efforts of site investigation and to optimize the information gained from the different investigation methods (Döberl et al. 2012). New integrative approaches for site investigation have also been requested from the U.S. Environmental Protection Agency (US EPA 2006).

The comparison of the noninvasive phytoscreening method and the minimally invasive DP technique presented in this study is based on a screening performed at a rural megasite in the central part of Germany. For the study, 26 wood and 31 groundwater compounds were analyzed in total. Main contaminants were TCE and its metabolite cDCE. Based on the results of our investigation, we give recommendations for a step-wise combination of the screening and monitoring methods.

Materials and Methods

Site Description

Investigations were carried out at the former military base Potsdam-Krampnitz, which is located at west of Berlin, Germany. The site covers an area of about 120 ha and is subject to subsurface contamination of partly unknown spatial extent. Contaminants were released during a variety of activities while used as a military site between 1937 and 1992, including the operation of a dry cleaning facility, gasoline stations, garages and repair facilities, leaky chemical storage tanks and sewer systems, and on-site waste dumping (Holm and Rotard 2011; Rein et al. 2011). Main groundwater pollutants are halogenated volatile organic carbons (HVOC), and BTEX (benzene, toluene, ethylbenzene, and xylenes), in which latter are present in low concentrations. Predominant HVOC constituents are TCE and the metabolic product cDCE. *Trans*-1,2-dichloroethene, vinyl chloride, and 1,1-dichloroethene were detected in lower concentrations (Rein et al. 2011). The main groundwater contamination is located in northwestern parts of the site, consisting of HVOCs originating from the operation of a former dry cleaning facility. Main groundwater flow in this area is to the north, resulting in a contaminant plume flowing into the adjacent wetlands, which are part of a natural protection area. At the time of tree core sampling, HVOC concentrations up to 176 mg/L were measured in groundwater in this area. Repeated groundwater sampling from conventional wells was performed between 1996 and 2001 in the suspected areas. However, due to a partly unknown history of site use large uncertainties existed concerning the presence of polluted areas and their spatial extension. Indeed, the DP-sampling campaign performed by Rein et al. (2011) revealed unexpected contaminated areas at different parts of the site.

These observations, and the present work, relate to groundwater from an aquifer which is predominantly built up by sands of fine to medium grain size, intermixed with silt layers. These periglacial deposits were formed during the Pleistocene epoch and resulted in complex structures varying locally at a small scale. In northern parts of the site and adjacent wetlands, moor deposits were identified at lower depths. The western part of the site is morphologically elevated and is roughly delineated with the highest hydraulic head (Figure 1) from where groundwater flows to the north and northeast (toward receiving wetlands and drains) as well as to the southwest and southeast (toward receiving lakes). Groundwater levels are between 1.30 and 7.00 m below the surface in most areas, as shallow conditions prevail in the west (Figure 1). However, at some DP-sampling points in central and eastern parts of the site, no water was found above a depth of 9 m or deeper, which might suggest connections to deeper aquifers (Figure 1, for more details see Rein et al. 2011). This also leaves an open question concerning the hydrological situation directly south of the site. Hydrogeological conditions are thus rather complex, including evidence of perched groundwater (small-scale shallow aquifers) at some parts within the site, similar to the situation in the wetlands to the north of the site.

Sampling Campaigns

Sampling of both groundwater (DP-campaign, Rein et al. 2011) and tree cores was performed following a regular grid of measurement points (approximately 100 × 100 m) covering the entire site. DP and tree core sampling points were placed as close as possible to each other, in most cases the distances were less than 10 m. Additional tree core sampling was performed in the wetlands to the north and in an area to the southwest. DP-based groundwater sampling was carried out from August 6 to August 22, 2007 (Rein et al. 2011), and the tree core sampling between August 6 and September 20, 2007. If available at foreseen sampling locations along the grid, tree species that had been used in pre-studies on phytoscreening were preferred (birches, willows, poplars, and other species). In total, 220 deciduous trees were sampled including birches (58), willows (*Salix* sp., 46) and poplars

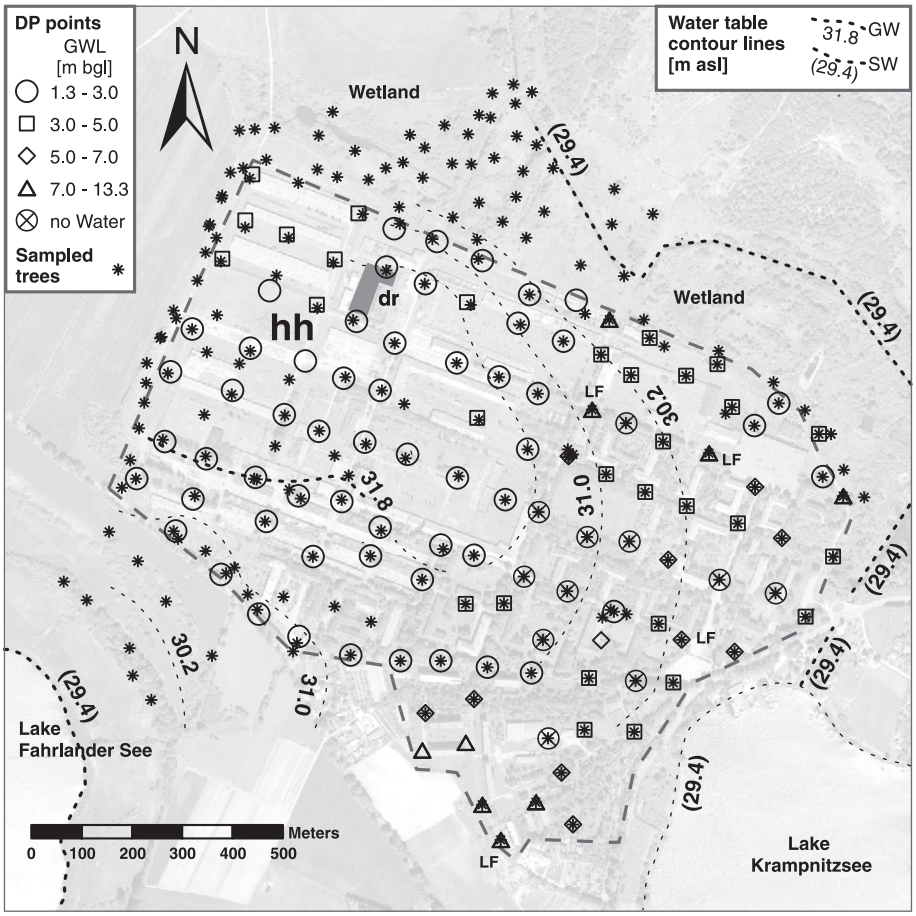

Figure 1. Location of sampled trees and DP measurement points at the Krampnitz site, including groundwater level (GWL) ranges observed at the DP points. Dotted curves: water table contour lines determined from observations at permanent groundwater wells. m bgl, meter below ground level; m asl, meter above sea level; GW, groundwater; SW, surface water; LF, DP-points with low groundwater flow; dr, location of dry cleaning facility and above-ground TCE storage tanks; hh, hydraulic height.

(*Populus* sp., 29) as well as locust (24), maple (14) and linden trees (13), oaks (*Quercus* sp., 7), hackberry (*Prunus padus*) trees (6), ashes (*Fraxinus excelsior*) (4), beeches (*Fagus sylvatica*) (2), sycamore (*Platanus* sp.) trees (2), one chestnut tree (*Castanea sativa*), 1 apple tree (*Malus domestica*), and 13 undetermined tree species. Tree core samples were taken at a height of 0.5 m above ground using an increment borer (Suunto, Finland, length 15 cm, internal diameter 0.5 cm). Three tree cores were taken close to each other (distance: 2 cm or smaller) from each tree. The bark and the phloem (the part separated by the cambium during secondary ring growth) were discarded to avoid atmospheric influence, so that the remaining wood tree core (mostly sapwood) had a length of 5 cm. It was broken into half and put into an empty headspace vial which was sealed immediately.

Weather conditions during sampling did not vary considerably. Dry and rainy phases were alternating regularly (2–4 days duration). Rain rates were rarely above 10 mm/d (3 days around 20 mm/d), and there were no long dry periods. Daily maximum air temperatures were around 25 °C in August (partly varying about 5 °C; slightly lower toward the end of the month), and between 15 and 20 °C in September.

DP-based sampling was done at 118 measurement points, taking one groundwater sample per sampling point for chemical analysis and recording the groundwater level. Sampling depth varied from point to point, depending on the presence and amount of water flow (between 2.2 and 14.5 m below ground level, see Table S2 (Supporting Information) for each point; some locations showed low or even absent water flow). Further details on this campaign as well as a comparison to monitoring at permanent (conventional) groundwater wells and details on observed hydraulic conditions are reported by Rein et al. (2011).

The extent of the root zone depends on a variety of factors including tree species and size, soil and climate conditions, as well as the density of planting (Canadell et al. 1996). Lateral root extension extends well beyond the crown of a tree (Dobson and Moffat 1995). The average maximum rooting depth of coniferous and deciduous trees in temperate zones is 3.9 and 2.9 m, respectively (Canadell et al. 1996). However, the range of phytoscreening may go beyond the root zone. Chlorinated solvents from groundwater at depths of 12.5–19 m below the surface could be detected in tree cores (Sorek et al. 2008).

Sample Preparation and Analytical Methods

Tree core samples first received 8 h of ultrasonic treatment. The samples were heated to 35 °C for 30 min, and volatile organic compounds were extracted using solid-phase microextraction (SPME). Chemicals were desorbed

from the SPME fibers for 1 min at 250 °C in a split/splitless injector onto a DB624 column of a gas chromatograph (GC) HP 6890 (Hewlett-Packard Inc., Palo Alto, California) and detected by an Agilent mass spectrometer 5973 Network MSD (Agilent Technologies, Santa Clara, California) in Selected Ion Monitoring (SIM)-mode. The SPME fibers were conditioned at 300 °C before each sample series (for 90 min) and each analysis (for 15 min). The loss of sensitivity of the carboxen/polydimethylsiloxane fibers was considered by alternating standard and sample analysis (Holm and Rotard 2011), and the drift was corrected. The mass spectrometry program was calibrated with EPA-standard 624 calibration Mix A (Supelco) plus cDCE. Calibration curves were established from aqueous samples, and the resulting peak areas were ranked by a semi-quantitative scale (1: no detection to 10: very high levels). The semi-quantitative scale, related peak areas and equivalent concentrations in aqueous solution (aqueous samples from calibration) are given in Table 1. All samples were analyzed in duplicate, with a third parallel sample stored as reserve. Peak areas below 500 were rejected as uncertain, as were results with only one replicate above the threshold. This relates to 1 and 2 of the semi-quantitative scale, which we define in the following as "not determined" or being below the quantification limit. More details on analytical procedures (GC conditions, data processing etc.) are found in Holm and Rotard (2011).

Groundwater sample preparation and analysis (applying headspace gas chromatography with flame-ionization detection and mass-selective detection) is described in Rein et al. (2011). Detection limits were at 0.2 µg/L and quantification limits at 20 µg/L for all analyzed compounds except for ethene (detection limit 0.8 µg/L) and vinyl chloride (detection limit 5 µg/L).

Data Treatment and Analysis

Contaminant levels measured in groundwater and trees were compared, and a range of other data were documented, such as boring depth, DP-well screening, groundwater levels (variations and final levels), tree species, stem circumference, direction of sampling, sampling date and time, weather conditions, and temperature. The location of groundwater sampling points and sampled trees was measured with a hand-held GPS (accuracy of 5–8 m), and ArcGIS (ESRI Inc., Redlands, California) was used for data visualization. Most data in both data sets (wood and groundwater) were below quantification limit (not detected or uncertain), and rather few data pairs showed both results above quantification limit. Statistics was done with and without data pairs below quantification limit. Additionally, the sampling direction of the tree core (radial direction) was compared to the DP results to see any directional influence.

Results

Direct Push

Chemicals analyzed in groundwater are listed in Table S1. Of these 31 compounds, only cDCE, TCE, and 1,2-dichloroethane (DCA) were detected at concentrations above 1 mg/L. TCE was in 27 of 111 samples above detection limit, cDCE in 24 and DCA in 15, tetrachlorethene in 4 and vinyl chloride in 3 samples. BTEX were below detection limit in all but a few samples, with maximum concentrations never exceeding 6 µg/L. Summarized, TCE and cDCE were the main groundwater pollutants detected by DP sampling, and partly DCA in elevated concentrations, whereas all other investigated compounds were absent or present in very low concentrations. The spatial distribution of TCE and cDCE in the GW samples are shown in Figures 2 and 3, respectively. Maximum contamination was found in wells adjacent to or in the area of the suspected source of the former tanks of the dry cleaning facility (TCE and cDCE up to 174 and 11.3 mg/L, respectively). Three additional and unexpected areas of contamination were identified, including (1) the eastern vicinity of the dry cleaning facility (at point PK1 and vicinity, with up to 0.3 and 0.01 mg/L of TCE and cDCE, respectively), (2) an area in the northeastern part (PK 18 and around, with TCE up to 0.2 mg/L), (3) a point in the center (PK23, with 0.05 and 1.2 mg/L of TCE and cDCE, respectively). Some positive results were also obtained at other sampling points, but usually at low levels.

Table 1
Semi-Quantitative Scale for the Content of Chemicals in Tree Core Samples, Related Peak Areas and Equivalent Concentration in Aqueous Solution (Calibration Samples) C_{aq} for TCE and cDCE

Scale	Peak area	C_{aq} of TCE [ng/L]	C_{aq} of cDCE [ng/L]
1	nd		
2	Uncertain		
3	500–10,000	1–23	1–28
4	10,000–25,000	23–56	28–70
5	25,000–50,000	56–112	70–139
6	50,000–100,000	112–225	139–278
7	100,000–1,000,000	225–2,250	278–2,780
8	1,000,000–10,000,000	2,250–22,500	2,780–27,800
9	10,000,000–100,000,000	22,500–225,000	27,800–278,000
10	>100,000,000	>225,000	>278,000

nd, not detected.

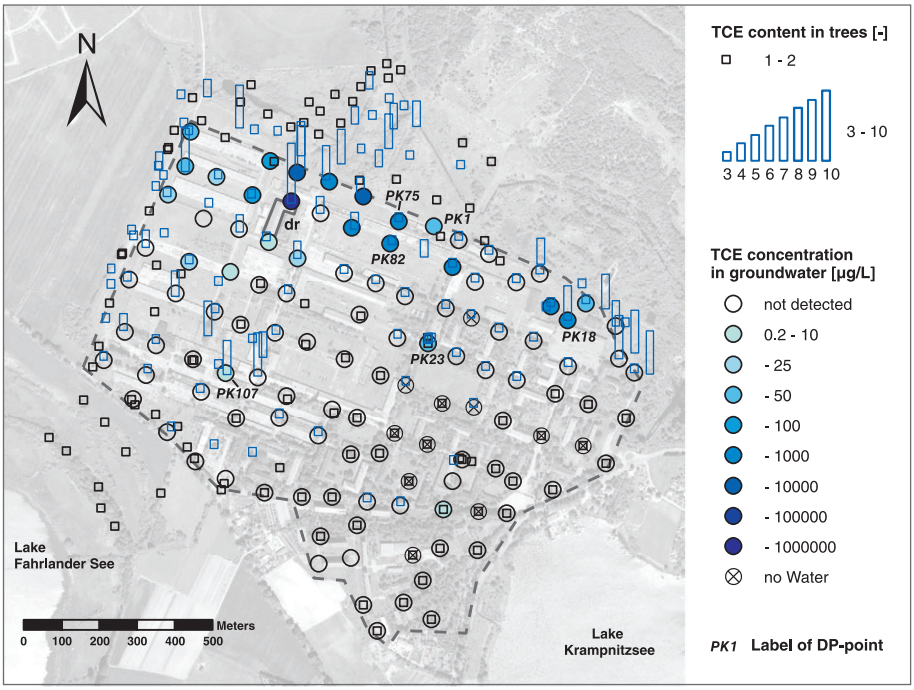

Figure 2. Trichloroethene (TCE) concentration in groundwater (DP campaign) versus TCE content in trees.

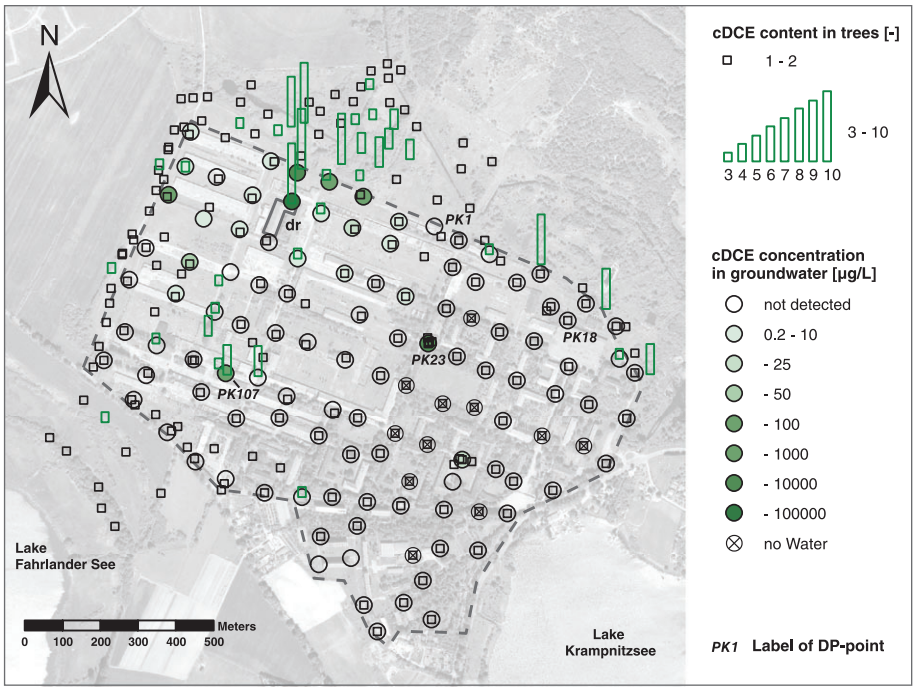

Figure 3. *Cis*-dichloroethene (cDCE) concentration in groundwater (DP campaign) versus cDCE content in trees.

Phytoscreening

In total, 26 different volatile organic compounds were analyzed in tree core samples (Table S1). Most of these were not detected in any tree sample, or erratically in very low concentrations. Among these were bromomethanes, chlorobenzenes, and chloropropenes. As none of these compounds were found in the DP samples, it may be concluded that they were absent or present at very low concentrations only. False positives in trees (detections in trees always accompanied by nondetects in groundwater) were also obtained for chloromethanes, PCE, BTEX, and 1,2-dichloropropane, which may have resulted from the applied analysis method (based on SIM) but was not evaluated further due to the low relevance of these compounds at the site. DCA was not analyzed in wood samples because DCA and TCE have very similar retention times in the applied method. As TCE has a higher relevance as site contaminant, the determination of DCA was omitted in favor of TCE quantification. However,

other chlorinated alkanes (1,1,2-trichloroethane and 1,2-dichloropropane) were detected in tree samples. In the wetlands north of the contaminated site, 1,1-dichloroethane was found in traces. Overall, the concentrations of chlorinated ethanes and propanes were too low to draw reliable conclusions about contamination levels.

The concentrations in tree cores of TCE and its metabolite cDCE, which are the most relevant groundwater pollutants, in contrast show an interesting pattern. Figure 2 shows the semi-quantitatively measured concentrations of TCE in tree cores compared to those found in groundwater. The maximum response for TCE was of level 9 on the semi-quantitative scale, translating to a peak area of up to 100,000,000, which corresponds to a TCE concentration in aqueous solution of up to 225 µg/L (Table 1). Several detects reached 7 on the semi-quantitative scale. These high responses correspond well with the maximum peaks detected in the groundwater samples. However, previously unknown areas of contamination were also detected, (1) in the northeast of the site, including the neighboring wetland (contamination extending east of PK18) and (2) in the southwest (PK107 and vicinity). TCE in small amounts was found in many areas within the site, except for in the south.

cDCE was found in lower concentrations: the maximum response was 8 on the scale, corresponding to a peak area of maximum 10,000,000, or to a concentration between 2.78 and 27.8 µg/L in aqueous solution. As with TCE, high cDCE levels were also found in the area of the former dry cleaning tanks, corresponding to the findings of the groundwater sampling. Tree core sampling showed that the main plume reaches into the wetland north of the source of contamination and ends at the stillwater zone of the former drainage ditch.

Comparison of Results from Phytoscreening to DP Findings

As it is obvious from a qualitative comparison of the findings shown in Figures 2 and 3, the results from DP and phytoscreening exhibit a strong agreement for areas with high groundwater contamination, whereas only little agreement is found for the zones of low contamination. In all parts where TCE was detected in the DP campaign, phytoscreening also gave positive findings, albeit showing low levels at some locations. However, phytoscreening also detected TCE at several other locations (Figure 2). The comparison of DP and tree coring for cDCE is somewhat problematic due to the few data points where both methods gave positive results. In the center of the contamination source and to the west and the east of it, cDCE was detected in groundwater, though at moderate concentrations (Figure 3). cDCE in tree cores from these areas were elevated, but not particularly high. There was also one isolated point in the center of the site (point PK23) where DP yielded quite high concentrations of cDCE in GW (1.2 mg/L), but no elevated levels of cDCE in the tree cores were detected around this point despite three additional samplings (discussed below). On the other hand, cDCE was found in several tree cores at sites where DP was negative. Excluding these differences, both methods yielded similar results for most of the area. An advantage of the phytoscreening method was that it also allowed sampling in the wetland area where the extension of the plume is expected and DP could not be applied.

Figure 4 shows the equivalent concentrations of TCE and cDCE in wood expressed as aqueous concentration compared to the concentrations measured in groundwater. Only data with a response above the quantification limit (peak area >500 or semi-quantitative scale >2) were used for this comparison. The data resemble a log-normal distribution, and thus the graph is in log-log scale. For TCE, the Pearson linear log-log correlation is considered to be highly significant (n = 18, r = 0.75, R^2 = 0.56, P < 0.001). The slope of the regression line is 1.06 and thus is surprisingly close to 1 (Figure 4a). A Spearman's rank correlation

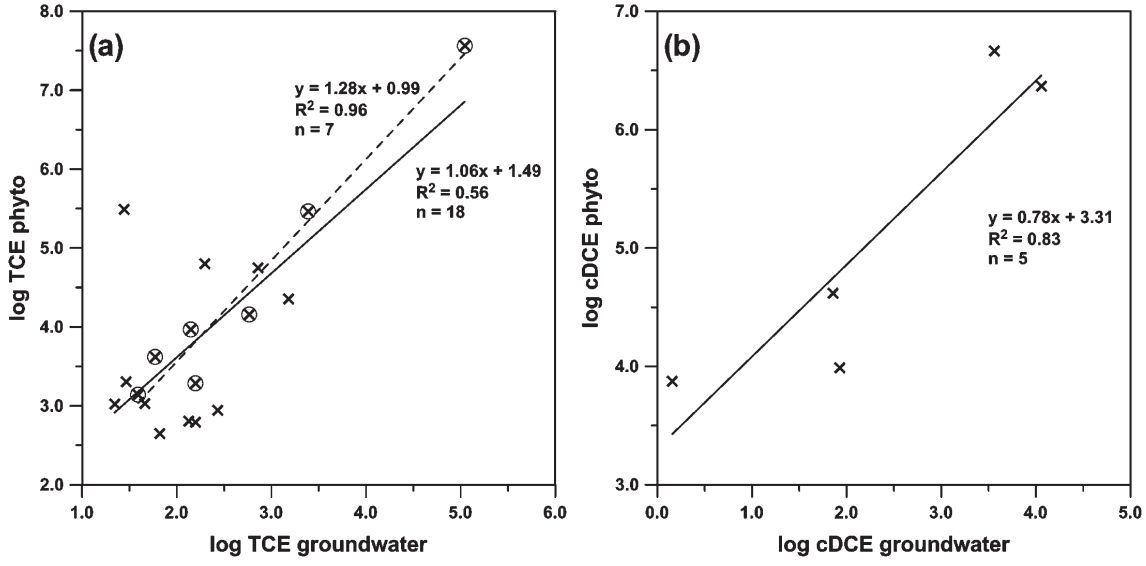

Figure 4. Log-log relation of TCE (a) and cDCE (b) in tree cores (denoted by phyto; i.e., equivalent concentration in aqueous solution in units of ng/L, cf. Table 1) versus groundwater (DP measurements; concentration in units of µg/L). Crosses indicate responses above quantification limit, circles indicate tree cores taken in direction toward the adjacent DP sampling point. *n*, number of values; R^2, coefficient of determination (linear fit on the plotted data points).

performed on the data (distribution free) is significant at the 10% level (r = 0.42). When only tree cores taken in direction toward the adjacent DP sampling point are considered (circles in Figure 4a), the correlation is even higher (Pearson r = 0.98, Spearman rank r = 0.89). However, the significance level for these points remains the same due to the smaller number of data points (n = 7). If uncertain and zero-detection data points are included in the statistical analysis, a data set of n = 97 data pairs results for TCE. Bearing in mind that the following results are disputable (many zero values included), the Pearson log-log correlation yields a r of 0.50 (R^2 = 0.25, highly significant with P < 0.001) and the Spearman's rank correlation gives r = 0.45, which is, due to the higher number of degrees of freedom, significant at 1%.

cDCE was mainly found in the wetland, where the application of DP was not possible. Thus, the number of common data points with quantifiable result is very low. Of 105 samples with available data pairs (DP vs. tree cores), only 23 GW concentrations and 13 tree-core concentrations are above quantification limit for cDCE. Only five data pairs have at the same location a quantifiable cDCE concentration. A Pearson log-log regression with these five data points gives a significant r of 0.91 (n = 5, P < 0.05, R^2 = 0.83). The corresponding Spearman's rank correlation gives r = 0.90 (significant at 5%) and R^2 equals 0.81. While it is statistically questionable to do a correlation with data mostly equal to zero, we also correlated the complete cDCE data set using the DP and phytoscreening results with a log-log-correlation. The correlation coefficient r is 0.34 and the Spearman rank correlation returns a correlation coefficient of 0.36 (n = 105, highly significant with P < 0.01).

Discussion

Concentrations in Wood vs. GW

For TCE, which is the main groundwater contaminant at the investigated site, obtained results from phytoscreening and DP were, in general, in good agreement, supporting the feasibility of phytoscreening for this compound once more. At some locations, concentrations were elevated in groundwater, but rather low in trees (e.g., PK75 and PK82, Figure 2). As a possible explanation for such observations, tree roots might have missed the main portion of groundwater contamination at higher depths, sampled by DP (see well screen depths in Table S2).

Occasionally, TCE was found at low levels in wood without being detected in groundwater. A potential reason for this finding is that the analytical method employed for wood samples (including an additional SPME extraction step) was more sensitive than the method for groundwater (headspace extraction). An alternative explanation is that tree roots integrate over a much larger subsurface volume than DP, and may also extract TCE from fine pores, which are not connected to the convective groundwater stream. TCE may have been present in the volume available to the roots, but not in the samples taken by the DP sampling. Moreover, DP sampling relies on the concentration of contaminant present at the time of sampling, while trees integrate over weeks or even months (Trapp 2007; Wittlingerova et al. 2013). The length of the tree cores was 5 cm, which is in agreement with recent suggestions (Holm et al. 2011). The shorter the tree core, the more the concentrations in wood should be related to the actual concentration in sap stream (and thus subsurface water), because xylem flow occurs only in the outer rings in most trees (Huber 1956). The thickness of the sapwood differs with tree species. Also, the adsorption of organic compounds underlies some variations, depending mainly on the lignin content and the density of the various wood types (Davis et al. 1998; Trapp et al. 2001). However, no relation between wood species and TCE content could be found in the previous study.

Another more speculative explanation is an influence of soil gas transport: on one hand, volatile organic compounds may travel at a considerable velocity through the unsaturated zone (Christophersen et al. 2005). On the other hand, these compounds are taken up also from the vadose zone gas phase into the roots (Trapp 1995; Burken et al. 2005; Struckhoff et al. 2005; Baduru 2008). However, uptake from ambient air can be excluded, for at least two reasons: first, the outer layer of bark and phloem was rejected from the sample. Second, concentrations in air do not change on short distances. Thus, all trees would have been affected by uptake from ambient air, not simply some individuals.

As shown in Figure 4, the relationship between concentrations in groundwater and equivalent concentrations in wood is highly significant. It can be concluded that phytoscreening is a good predictor for GW contamination with TCE at this site and for this sampling campaign. However, various earlier studies found only qualitative but monotonic relationships between GW contamination and phytoscreening results (Gopalakrishnan et al. 2007; Larsen et al. 2008; Sorek et al. 2008; Vroblesky 2008; Holm et al. 2011).

Many of the tree core samples in which cDCE was detected were outside the former military facilities in the wetland area that was inaccessible for DP. In fact, some of the highest concentrations in wood were found in samples from these areas (Figure 3). An advantage of phytoscreening is that it does not rely on heavy equipment and can thus also be used in swampy areas (Larsen et al. 2008; Holm et al. 2011). This is confirmed by our study. The comparison to the DP results is impeded by the equipment, and the correlation between the results from the two methods was less obvious for cDCE. Still the relation between concentrations in wood and GW was significant both with the Pearson log-log and with the Spearman's rank correlation. There were very few disagreements, for example the point in the center of the study area (point PK23), where a level of cDCE in GW of 1.2 mg/L was not accompanied by high levels measured in tree cores taken from four trees of different size and species (maple, sycamore, locust, and birch). During the DP campaign, hydrological "anomalies" were observed for central and eastern parts of site, with areas of low water flow or even an absence of water (for probing depths between 9 and 14 m). Point PK23 is just within this region where no water was found at the adjacent points to the south (Figure 1). The groundwater sampled at point PK23 is perhaps not the same water that the trees can access. Vice versa, cDCE could be detected in several tree core samples at moderate levels where no cDCE was detected in groundwater (Figure 3).

This might be a hint on contamination that has not yet reached the saturated zone.

Compound concentrations in trees are reported to show seasonal variations and may also give indication on long-term developments of subsurface contamination. Wittlingerova et al. (2013) monitored levels of chlorinated ethenes (mainly PCE and TCE) over a one-year period and found lowest levels in summer and highest levels in autumn and early winter. This behavior correlated well with groundwater level fluctuations (higher levels in winter), but other studies also point toward possible volatilization loss in summer due to high temperatures (e.g., Vroblesky 2008; Holm and Rotard 2011). The high monthly variations of concentrations in tree cores observed by Wittlingerova et al. (2013) do not indicate long-term storage of chlorinated ethenes in wood. Model simulations (Trapp 2007) yield half-lives for loss by volatilization from stems between three weeks (TCE, summer conditions) and about 3 months (PCE, winter) which means each tree core sample (typically between 5 and 10 cm in length) integrates the GW concentration of several weeks but most likely not over longer periods.

Concentration profiles over 70 annual tree rings reported by Wittlingerova et al. (2013) show highest amounts of chlorinated ethenes in the middle of the wood core, with the fraction of degradation products declining toward the center. The observed concentration profiles can be explained by (1) historical groundwater contamination and (2) biological and physicochemical processes (leading to lateral movement across tree rings), but there seems to be more evidence for the latter explanation. A historical (dendrochronological) evaluation is however feasible by monitoring the mineralization products (chloride) in tree rings (Balouet and Oudijk 2006; Burken et al. 2011), keeping in mind uncertainty due to possible additional chloride sources (Balouet et al. 2009). Annual growth of tree rings can be reduced when levels of chlorinated ethenes in groundwater are higher (as observed by Algreen et al. 2011), which can give another hint on the historical development of the plume.

Comparison to Other Findings

In a separate study at the Krampnitz site with tree core and birch sap sampling around the tree trunks, Holm and Rotard (2011) showed that the direction of sampling impacted the concentration of *cis*-DCE and TCE in the samples. However, at the Krampnitz site this did not allow conclusions on the gradient of the contaminants in the subsurface and had thus little or no impact on the outcome and interpretation of the phytoscreening.

Wahyudi et al. (2012) have raised the issue of true statistical relation between groundwater measurements and tree core samples using detailed data on chloroethenes from a site at the Czech Republic (Larsen et al. 2008). Bivariate analyses of rank-transformed data based on cross-covariance functions failed to indicate a clear spatial correlation between groundwater and tree core measurements. A reason given for this is the dynamic nature of concentrations in time, and also nonstandardized conditions of tree core sampling, which can lead to a certain variance in the resulting data. Despite the deviations between concentrations obtained in GW and in wood, the spatial trend of contaminant distribution on the map based on tree cores was found to be in close agreement with the map obtained from groundwater sampling and membrane interface probe (MIP) measurements. They concluded that the placement of groundwater sampling locations could have been optimized, if knowledge about hot spot and plume areas would have been available beforehand. In this regard, phytoscreening would have been suitable as a semi-quantitative method for contaminated plume detection.

Wittlingerova et al. (2013) studied the issue of correlation between concentrations in groundwater and tree cores based on monthly data obtained over a full year at the site in the Czech Republic mentioned above. In contrast to our study, they, however, found only weak and often insignificant correlations between concentrations of chloroethenes in GW and tree cores, and for some sampling points only negative correlation were found over time. Moreover, the groundwater level at the site was identified as the most important single factor influencing the concentrations in wood. However, when the correlation was done with long-term average concentrations over the spatial scale (four GW wells at four sampling points with five trees), the correlation was positive, strong, and highly significant. This suggests that tree coring might be used to delineate the plume, but that a monitoring of the development of concentrations in time depends on many local factors. Both studies at the site in the Czech Republic suggest the importance of a standardization of tree core sampling in order to reduce the variance in the data and to allow a better comparison of results. Such an effort was undertaken in the "Guide to Phytoscreening" (Algreen et al. 2011; Holm et al. 2011).

Algreen et al. (2015) illustrated the usefulness of prescreening methods for the characterization of an abandoned military site. For the former Soviet military airbase in Szprotawa, Poland, the outcome of phytoscreening with tree coring, soil gas measurements, DP with MIP and laser-induced fluorescence sensors were compared to sampling from soil and from groundwater monitoring wells. The large-scale application of non- or low-invasive pre-screening led to the detection of previously unknown hot spots and allowed directing and focusing the subsequent, more expensive investigation methods. Moreover, extensive drilling and DP on that site would have been risky due to leftovers from the military usage of the area, while phytoscreening was safe (Algreen et al. 2015).

Cost Assessment

Rein et al. (2011) estimated the expenses of the conventional site investigation vs. the DP-based groundwater screening for the Krampnitz site used in this study. The cost estimation of the conventional site investigation was based on price level of central Europe and included historical survey, installation of 25 monitoring wells, 3 sampling campaigns, and chemical analysis. Resulting costs were estimated to be much larger than €75,000. The efforts of a DP investigation included 120 measurement points, push/drag, sampling (done within 2.5 weeks), and laboratory analysis, and were estimated to be €60,000. Tree coring is still very rarely offered on the market, and prices have not

yet been established. Totally 120 data points (in duplicate) could be sampled within 3 days by two persons. Rein et al. (2011) calculated personal costs to be €2500 per day for two persons, and €20 for laboratory analysis per sample. Using these numbers, tree coring could be done for €7900 for such a site.

Combination of Tree Coring, DP, and Conventional Methods

The state-of-the-art site characterization is generally motivated by two facts: (1) contaminated land management is often, if not always, fraught with legal issues and responsibilities, and therefore only "ground-trusted" information is considered appropriate to face scrutiny in court, and (2) many other approaches, based on less-invasive techniques, at the present stage seem not mature enough to face the same requirement of legal robustness (Balouet et al. 2009; Döberl et al. 2012; Wolff 2012). Based on the data derived from phytoscreening, DP, and conventional monitoring wells, we can show that a combination of all three results would allow gathering of more and more precise information with similar efforts.

Figure 5 shows interpolated maps of groundwater contamination with TCE and cDCE obtained by (a) conventional monitoring of the (suspected) center of pollution at

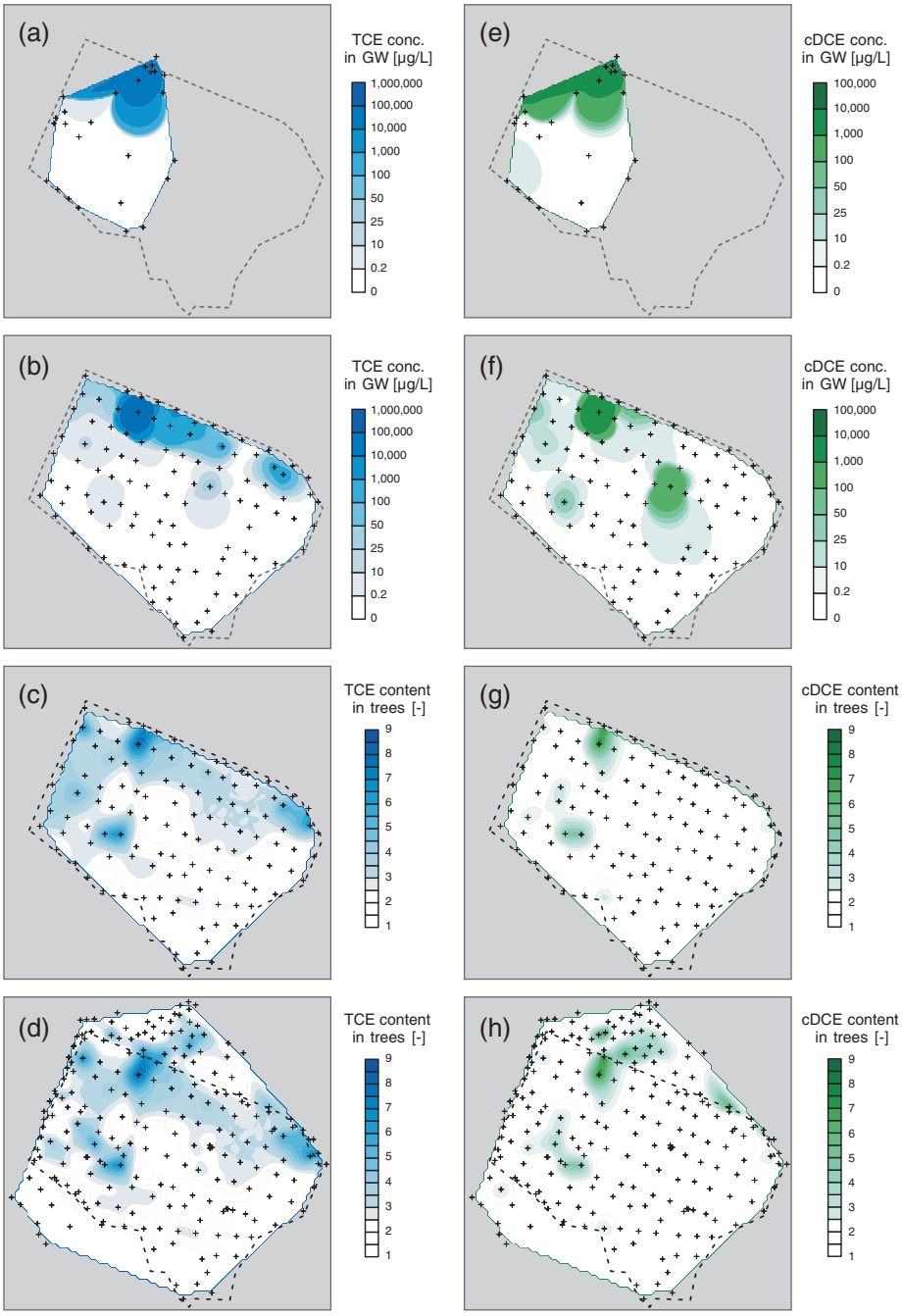

Figure 5. Interpolated maps of TCE (a to d) and cDCE (e to h) in GW and trees using information from monitoring at conventional GW wells (a, e), DP GW sampling at the pre-defined grid (b, f), tree coring at the pre-defined grid (c, g), all sampled trees at and near the site, including the wetlands to the North (d, h). Crosses indicate the location of sampling.

25 monitoring wells (Figure 5a and 5e), (b) screening of the entire site by the DP method (105 samples, Figure 5b and 5f)), (c) screening of the site with the tree core method (116 samples, Figure 5c and 5g), and (d) tree core sampling at and near the site, including the wetlands to the north (220 samples, all tree cores taken; Figure 5d and 5h). Natural neighbor interpolation was used in all cases due to large scattering in the monitoring data from the conventional GW wells, in order to achieve comparable maps. Phytoscreening (Figure 5c and 5d) yields a relatively similar distribution of TCE as DP (Figure 5b). This is not surprising given the high correlation between both methods. The difference between Figure 5c and 5d is that the latter includes data from additionally sampled trees in areas of doubt (differences to results from GW sampling) and in areas adjacent to the site. Indeed some refinement of site investigation could be achieved, such as a more detailed distribution in western parts of the site, and valuable further information about the wetlands (inaccessible for DP).

An advantage of the phytoscreening method is that it also allowed for following the plume into the swampy wetland and detection of the end of the plume at the drainage ditch. Neither of the other two methods could yield data from the wetland. One limitation of phytoscreening was that it did not directly result in quantitative data on concentrations in groundwater. Another limitation was, in this case, false positive results for several compounds (tetrachlorethene, BTEX) which may be caused using SIM. Such false positives would have been quickly detected by the DP method and also have not been reported from other phytoscreening campaigns. Groundwater monitoring with conventional, permanently installed wells is the most common and frequently applied technique. A disadvantage of this method is immediately apparent by inspection of Figure 5a and 5e: even though it was the most expensive of all applied methods, the area sampled with groundwater wells is much smaller than the area screened with the two other methods. Due to the lesser number of sampling points (25 vs. 105 for DP), only the suspected hot spots were evaluated. The extension of the plume both in east and into the wetland remained undetected. Remediation measures based on this information alone would have "overlooked" half of the contaminated area. An advantage, however, is the possibility for carrying out long-term monitoring of contaminant concentrations, as high temporal variations can occur (up to two orders of magnitude or more were observed; see Rein et al. 2011).

Based on this comparison of results, we recommend that an initial pre-screening with tree coring is done whenever applicable. With this, information on the spatial extension of a potential plume and occurrence of contaminants can be gained inexpensively. A DP investigation covering, as a minimum, the area with positive phytoscreening results can then yield quantitative data about the groundwater pollutants on the delineated area. This information then allows for a rational decision about the optimal placement of (expensive) permanent monitoring wells for long-term monitoring of contamination levels and natural attenuation. Repeating the phytoscreening after years will avoid overlooking a plume spreading with time.

Conclusions

In this study, we compared concentrations of volatile organic compounds in groundwater samples taken by DP with those in wood samples from tree coring. From the contaminants suspected at the site, most were not found in groundwater or wood. A few compounds, among them PCE and BTEX, were found at moderate levels in wood samples but not in groundwater. TCE, which is the most relevant groundwater contaminant at the site, could be detected by both methods in high concentrations. The correlation between concentrations of TCE in groundwater and wood was significant, and the spatial pattern of the GW plume became obvious both by DP and by phytoscreening. cDCE is the main metabolite of TCE and was also present in groundwater and wood samples. The agreement between the two investigation methods was less obvious, as phytoscreening allowed detection of cDCE in the neighboring wetland, while DP cannot be applied there.

Several factors have been shown to have an influence on concentrations in wood, among them meteorological conditions (Holm and Rotard 2011), distance to groundwater (Sorek et al. 2008; Wittlingerova et al. 2013), time required for sampling (in particular for highly volatile compounds, Vroblesky 2008), species influence (Larsen et al. 2008; Sorek et al. 2008; Wittlingerova et al. 2013) and season (Sorek et al. 2008; Wittlingerova et al. 2013). Due to the many (uncontrolled) factors that impact the concentration in wood, phytoscreening is generally considered to be a semi-quantitative method (Holm et al. 2011; Trapp et al. 2012), even though strong correlations between groundwater and wood concentrations can be obtained under homogenous conditions (Gopalakrishnan et al. 2007, also the present study). An initial screening can give a rapid (and not very costly) overall picture of size and direction of the plume. Once that is known, DP samples can be taken with more efficiency. Based on the outcome of such investigations, permanent groundwater wells can be installed at locations of concern for the long-term monitoring of GW contamination. The combination of phytoscreening with DP and GW monitoring at selected locations has the potential to become a widely applied standard procedure for the evaluation of a previously noninvestigated contaminated site. These methods have their indispensable and unique role and do not compete with each other, but are complementary.

An advantage of using SPME fibers is the possibility of in-plant application, enabling repeated sampling and analysis in the same sampling port (Burken et al. 2011). For this type of application a tree needs to be cored only once and detection limits are decreased, compared to the headspace technique. In our study, the SPME extraction indeed proved to be a very sensitive method, but this sensitivity was not required to delineate the subsurface plume. Contrary, many low-level signals may act as a kind of "noise," distorting the picture. Moreover, additional analytical procedures always mean more time, more efforts, and more error sources. The conclusion is that unless a lower detection limit is needed, the rapid and efficient head space extraction of wood samples that was employed in earlier studies (e.g., Larsen et al. 2008) will usually be sufficient.

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Supporting Information

The following supporting information is available for this article:

Table S1. List of Compounds Analyzed in Groundwater and Tree Core Samples

Table S2. Well Screen Depths and Groundwater Levels Measured at the Direct Push Points (m bgl, meter below ground level)

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