Using Tree Core Samples to Monitor Natural Attenuation and Plume Distribution After a PCE Spill

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The potential of using tree core samples to detect and monitor natural attenuation of perchloroethene (PCE) in groundwater was investigated at a PCE-contaminated site. In the area of the known plume with PCE concentrations between 0.004 and >40 mg/L, cores were collected from tree trunks at a height of about 1 m above ground surface. Tree sampling of the site was completed in under six hours. Chlorinated ethenes were analyzed by headspace GC/MS. PCE (0.001 to 7 mg/kg) and natural attenuation products, TCE (<0.001 to 0.4 mg/kg) and c-DCE (<0.001 to 0.46 mg/kg), were detected in tree cores. 1,1-dichloroethene and vinyl chloride were not detected, corresponding to very low concentrations in the groundwater. The contaminant plume was mapped from the concentrations measured in trees, which delineated a probable hot spot area that had been undetected in decades of traditional groundwater monitoring. Natural attenuation products in tree cores increased with distance from the known source area. Concentrations of PCE and reductive dechlorination products in tree cores were correlated with the corresponding groundwater concentrations. Within a range of limitations, tree-core sampling provides a rapid, reliable and inexpensive method to investigate the extent of shallow contamination by chlorinated ethenes in soil and groundwater.

Introduction

Chlorinated ethenes (CE) are chemically stable, inexpensive, and can dissolve grease and oil. Subsequently, chlorinated ethenes are among the most intensively used solvents, e.g., as dry cleaning agents and metal degreasing agents (*1*). Spills, leaks, or intended disposal have made the solvents a major environmental concern worldwide. Perchloroethene (PCE, perchloroethylene, tetrachloroethene) and trichloroethene (TCE, trichloroethylene) are neurotoxic and potentially carcinogenic (*2*), and are the most prevalent groundwater contaminants. Remediation of PCE and TCE polluted sites has high priority (*3*). The chlorinated ethenes PCE, TCE, and c-DCE are volatile compounds with densities higher than water and low solubility (Supporting Information, Table SI 1), leading to slow contaminant dispersal in a plume.

Degradation of PCE and TCE in the subsurface is limited. Aerobic degradation has been observed (*4, 5*) but anaerobic reductive dechlorination is the most common degradation pathway (*6*). In this process, PCE is dechlorinated to TCE, which is dechlorinated to cis-dichloroethene (c-DCE), vinyl chloride (VC), and finally to ethene. Each dechlorination step occurs under a certain range of redox conditions, and generally, more reduced conditions are needed for each successive step (*7*). Overall, this process is termed reductive dechlorination and is the most vital component of natural attenuation.

Preliminary investigations of sites contaminated with chlorinated solvents typically include collection of soil and groundwater samples from boreholes. Not only is drilling of the holes expensive, but it is also time-consuming, and vehicle access to the site is required, which can be quite difficult, invasive, and ecologically damaging. Recent investigations have shown that PCE and its degradation products, TCE and c-DCE, can be taken up and transported from subsurface to above surface by trees (*8–13*). The chlorinated ethenes (CE) can enter the trees by several mechanisms: advective uptake into the roots via the transpiration water, diffusive uptake into the roots from groundwater or soil vapor phase, or diffusive uptake into the leaves and stem from the air. Following the uptake from soil or groundwater (GW), CE may undergo a variety of processes: sorption to wood (*14*), degradation, transport to leaves, or diffusion to atmosphere from stem and leaves (*15, 16*). Ma and Burken (*17*) found in hydroponics that accumulation in poplar cuttings accounted for less than 1% of the total uptake of TCE from solution. Newman et al. (*10*) found that TCE was taken up and metabolized by poplar trees, while uptake and volatilization was shown to be the major fate by Burken and Schnoor (*18, 19*) and Orchard et al. (*11*).

This study compares tree core sampling with the conventional method of borehole drilling for monitoring of subsurface CE contamination and naturally occurring degradation. Limitations and precision of the method were also investigated.

Materials and Methods

Site Description. The North Bohemia Carcass Disposal Plant is located in the northern part of the Czech Republic near Liberec (Figure 1). The company extracts lipids and proteins from animal carcasses, with a total estimated PCE consumption of 4250 t between 1963 and 1988. Frequent operational spills caused a large contamination plume, and the total amount of leaked PCE was estimated at 150–250 t (*20*). The site is located in the Bohemian Cretaceous Basin, the most important source of high quality groundwater in the Czech Republic.

In 1988, PCE was detected at a waterworks 400 m downstream from the source. On-site remediation at the plant was put in place and has been in operation since 1997, employing pump and treat combined with venting and air sparging. Before on-site remediation, the highest GW concentrations were measured at 230, 14, and 72 mg/L of PCE, TCE, and c-DCE, respectively. The remediation efforts and natural attenuation decreased the estimated size of the plume with total CE > 1 mg/L from 8 ha in 1997 to 1 ha in 2005.

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FIGURE 1. Orthophoto of the contaminated site. The dotted line shows the property boundary. The photo is north-oriented to match the maps in Figures 2–4.

TABLE 1. Quantification, detection, and linearity limits for the analytical method and concentrations of compounds in the standards

	concentration (μg/kg wood)					
	c-DCE	t-DCE	TCE	PCE	1,1-DCE	VC
limits						
detection	3.5	2.8	3.4	4.6	1.5	3.5
quantification	7.0	5.7	7.4	10.4	2.1	6.1
linearity	6814	6637	6492	5811	6437	
standards						
1	85.6	83.8	97.3	108	80.9	221
2	428	419	487	541	404	551
3	856	838	973	1082	809	1102
4	2140	2095	2433	2705	2022	2205
5	4280	4190	4867	5410	4043	4409

The groundwater table in the factory area averages 2–3 m below surface and in some areas southwest of the river it intercepts the surface, causing marsh conditions. The geology is formed by quaternary river sediments (sands, gravels) and anthropogenic deposits (ash, soil with bricks and concrete) in the upper layers (2–4 m). The endangered aquifer consists of middle to fine grained Middle Turonian sandstone with a thickness of 67−75 m and is unconfined.

Chemicals and Standard Solutions. All chemicals used were reagent grade and were obtained from Sigma-Aldrich, Brøndby, Denmark. A stock solution was prepared by mixing trans-dichloroethene (t-DCE), 1,1-dichloroethene (1,1-DCE), PCE, TCE, and c-DCE (100 μL of each) and methanol (1000 μL) in a GC vial with Teflon-lined screw lid. Standard solutions were prepared by dissolving the stock solution in distilled water. An internal standard was prepared by dissolving 10 μL of chloroform in 1 L of distilled water.

Sampling and Handling. In early September 2005, tree cores where sampled from the stems of the selected trees at a height of ~1 m above ground surface using a 5 mm increment borer (Suunto, Finland). The tree core sampling points were all placed in the southwestern area of the plume because no trees were found on the factory area (Figure 1). Trees in the center, on the border and from outside of the expected plume area were sampled. Immediately after the sample was taken, it was broken into pieces of 0.5–1 cm and enclosed in a 20 mL crimp-top GC/MS vial capped with a

TABLE 2. Concentrations of Chlorinated Ethenes in Tree Cores (μg/kg Wet Weight) Sampled at a PCE Contaminated Site near Liberec, Czech Republic

		concentration (μg/kg$_{wet}$)			
no.	species	c-DCE	TCE	PCE	total CE
A1	pine	13	45	203	262
A2	pine	933	536	12 058[a]	13 538
A3	birch	<Q.L.	12	1475	1487
A4	black alder	<Q.L.	<Q.L.	1852	1852
A5	poplar	67	<Q.L.	176	243
A6	black alder	<D.L.	<D.L.	<D.L.	
A7	black alder	<D.L.	<D.L.	<D.L.	
A8	black alder	7	<D.L.	22	30
A9	black alder	40	<D.L.	77	117
A10	black alder	60	<Q.L.	687	747
A11	black alder	<D.L.	<D.L.	2277	2277
A12	oak	14	12	2644	2669
A13	birch	220	86	5136	5442
A14	willow	38	74	944	1056
A15	willow	238	87	8118[a]	8444
A16	willow	<D.L.	9	1559	1568
A17	willow	10	12	1850	1872
A18	Willow	344	379	6344[a]	7068
A19	black alder	<D.L.	<D.L.	258	258
A20	willow	42	86	2467	2594
A21	willow	16	36	1230	1282
A22	willow	29	37	1922	1988
A23	willow	18	10	759	786
A24	willow	9	18	1064	1091
A25	willow	15	16	1572	1603
A26	willow	<Q.L.	<Q.L.	185	185
A27	willow	741	429	14 944[a]	16 130
A28	pine	<D.L.	<D.L.	12	12
A29	beech	<D.L.	<D.L.	<Q.L.	
A30	oak	<D.L.	<D.L.	<D.L.	
A31	oak	<D.L.	<D.L.	<D.L.	
A32	black alder	<D.L.	<D.L.	<D.L.	
A33	oak	<D.L.	<D.L.	<D.L.	

[a] linearity range; D.L. detection limit; Q.L. quantification limit.

Teflon rubber septum. To each vial, 1 mL of 0.01 M HNO_3 had been added for preservation. Capping of the vials was done within 1 min after tree core removal. The capped vials were stored in an insulated bag on site and afterward at −18 °C until analysis. Subsequently, the dry weight of the samples was determined by drying overnight at 105 °C.

Chemical Analysis. Chlorinated ethenes were analyzed by gas chromatography (GC) using an Agilent 6890N gas chromatograph equipped with an Agilent 5973 mass selective detector (MS) and a 25 m × 320 μm × 1 μm (nominal) capillary column (J & W GSQ) with helium as carrier gas. Chloroform as internal standard was added to both samples and standards 24 h before analysis and the vials were shaken and left at room temperature (22 °C) to equilibrate. Initial experiments with TCE and oak wood showed that the concentration measured in the headspace was stable after this time period (see the Supporting Information). Due to eventual variations in the instrument response, the ratio of the signal of the analyzed compound to the internal standard signal was used to determine the concentration of the chlorinated ethenes. The vials were heated to 80 °C for 1 h before equilibrium headspace gas analysis. The heating time was experimentally predetermined by measuring the concentration of the different compounds as a function of time, and it was found that concentrations had stabilized after 1 h (data not shown).

A standard curve for concentrations in wood was prepared by placing 1 g of oak wood (wet weight, newly harvested and comminuted) in a GC-MS vial, adding 1 mL 0.01 M HNO_3, 1 mL of the prepared standards and 1 mL internal standard.

TABLE 3. Concentrations of Chlorinated Ethenes Measured in Groundwater Wells (µg/L) and in Cores Taken from Adjacent Trees (µg/kg); Correlation Coefficient of the Bivariate Linear Pearson Product-Moment Correlation and the Spearman Rank Correlation between Groundwater (GW) and Adjacent Tree Concentrations

		c-DCE			TCE			PCE			total CE	
well	adjacent tree	GW	tree	ratio	GW	tree	ratio	GW	tree	ratio	GW	tree
HJ-105	A1	19.0	12.9	0.68	5.9	45.5	7.7	80.5	203	2.5	105	264
HJ-131	A31	3.1	0.9	0.29	0.3	0.6	2.0	4.1	1.4	0.34	7.4	3.9
HJ-600	A27	140	66.9	0.48	96.2	4.8	0.05	5813	176	0.03	6049	16130
HJ-620	A8	187	19.2	0.10	99.0	1.4	0.01	7146	40.1	0.01	7437	31.0
HJ-621	A4/A10[c]	63.8	41.2	0.65	36.4	5.8	0.16	3860	1076	0.28	3961	13176
HJ-622	A2/A13[c]	583	457	0.78	330	236	0.72	40 571	7443	0.18	41 484	9491
HJ-515	A33	40.3	0.5	0.01	2.6	0.3	0.12	11.2	6.3	0.56	54.2	1.3
HJ-516	A29	12.0	<D.L.		0.9	<D.L.		8.2	2.9	0.35	21.1	2.9
	Pearson correlation	0.961[b]			0.898[b]			0.975[b]			0.374	
	Spearman rank correlation	0.714[a]			0.690[a]			0.786[a]			0.643*	

[a] Significant (P < 0.05). [b] Highly significant (P < 0.01); D.L., detection limit. [c] Average of two adjacent trees.
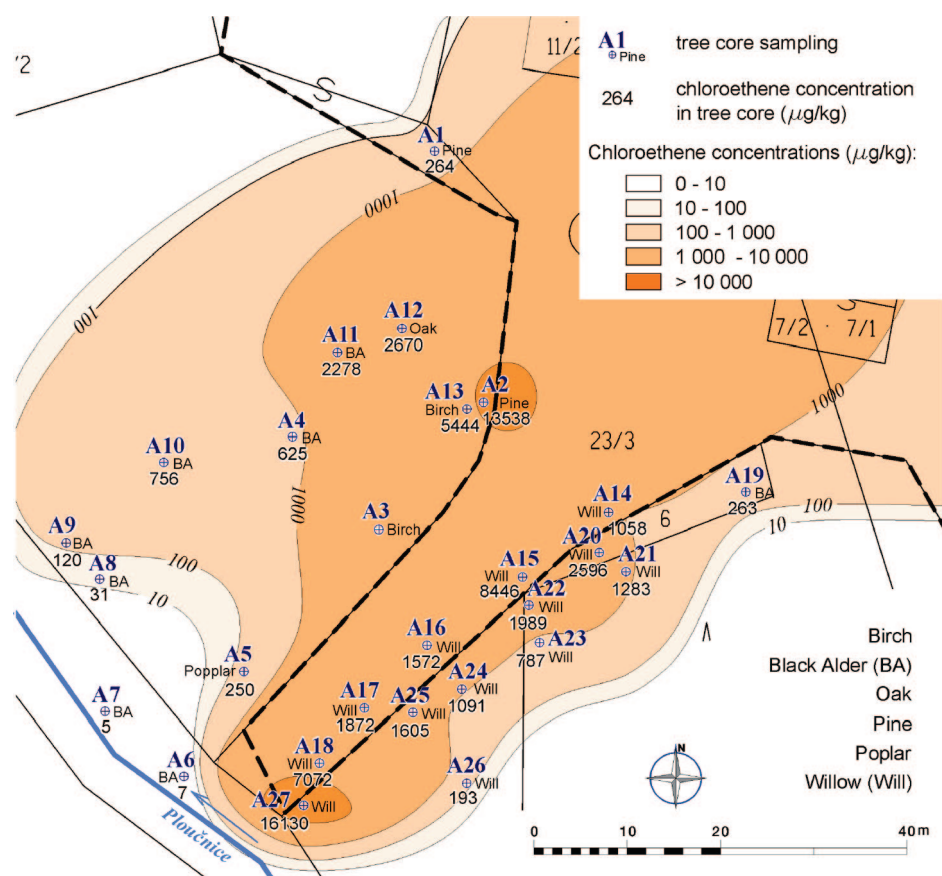
FIGURE 2. Estimated distribution of the contaminant plume in the groundwater, based on concentrations of total chlorinated ethenes measured in trees in early September 2005. The dotted line shows the property boundary. Sampled trees are numbered from A1 to A27. See legend for concentration ranges and tree species.

The vial was shaken and left to equilibrate for 24 h before analysis as described above. Concentrations of the standards and detection and quantification limits (calculated as blank plus 3 or 10 times the standard deviation of 10 replicates, respectively) can be seen in Table 1.

Method Evaluation. For the measurement of all field samples, the standard curves were prepared with oak wood. To investigate whether the use of oak wood in all standard curves comprises an uncertainty factor, standards of oak tree were compared to standards made with other tree species such as willow, pine and spruce. To clarify the influence of the mass of wood, standard samples with varying amount of oak wood were compared. All measured concentrations in the trees are given as µg/kg fresh weight.

Membrane Interface Probing. In 2006, Membrane Interface Probing (MIP) was applied to determine the vertical contaminant distribution at the field site. MIP permits a semiquantitative determination of contamination in a continuous depth profile. The maximum detector response was used to construct a map of the horizontal contamination. A detailed description of the method is found in the Supporting Information.

Data Treatment. If not mentioned otherwise, the bivariate Pearson product-moment correlation was used to determine linear correlations between variables. The significance of the correlations was judged using tabulated threshold values (21). If the preconditions of the Pearson correlation (21) were violated, the Spearman rank correlation was used instead,
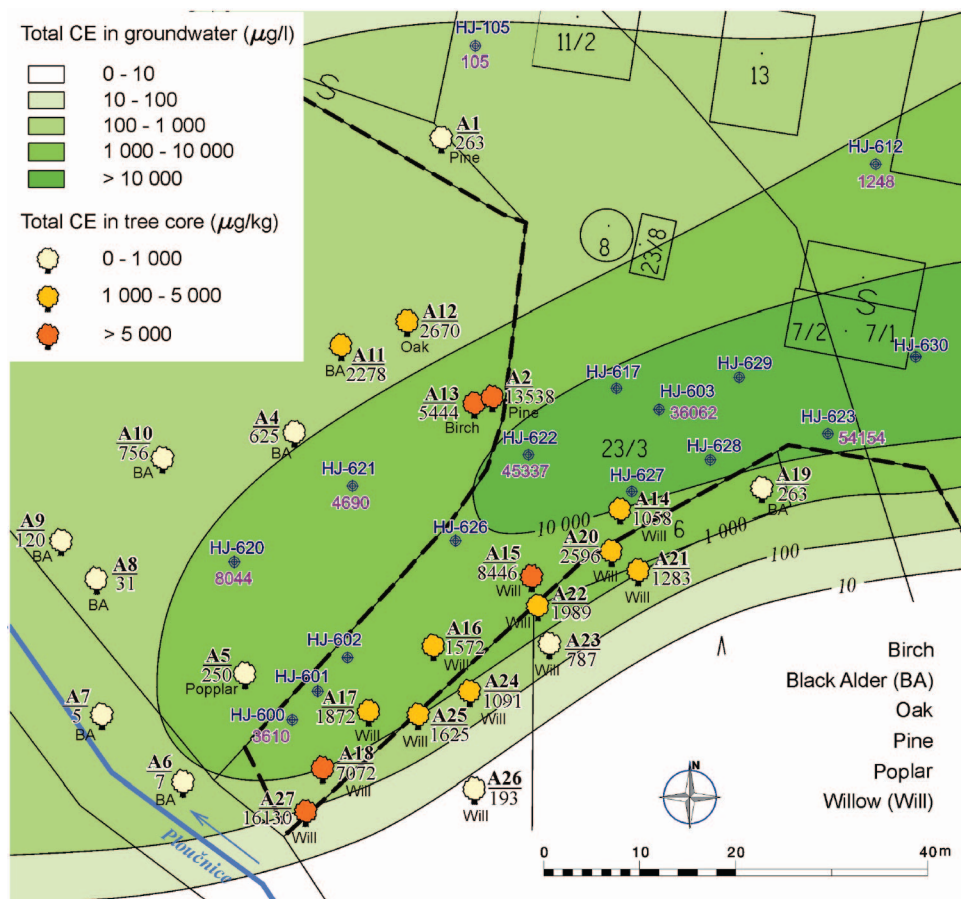
FIGURE 3. Estimated distribution of the contaminant plume in the groundwater, based on concentrations of total chlorinated ethenes (CE) measured in groundwater samples taken from May to October 2005. The dotted line shows the property boundary. The small dots labeled HJ show the location of the monitoring wells. The larger, tree-shaped symbols show the location of the trees (A1–A27) sampled in early September 2005. See legend for concentration ranges.

to avoid invalid correlation results. Maps of the plume distribution were created using the software Surfer 6 with Kriging as interpolation method between the sampling points.

Results and Discussion

Method Evaluation. Using standard samples with wood from four different tree species, the largest peak areas for all compounds were measured for the vials with oak (Supporting Information Figure SI 1). This indicates that with the headspace procedure applied, the sorption to oak wood was lower than the sorption to wood from the other tested tree species. Only data for standard four are shown, but the pattern was similar for the other standards. The three chemicals TCE, c-DCE, and t-DCE showed the same trend in peak area for willow, pine, and spruce, while areas for oak were higher. For PCE, the peak areas for oak and pine were almost similar. Generally, the sorption increased (the peak area decreased) with increasing log K_{OW}, except for spruce.

During field sampling it was not possible to weigh the tree cores on site because quick closure of the vials was necessitated by the volatility of the investigated compounds. While targeting 1 g samples, slight variation in the sampled mass of the cores occurred. The amount of wood in the standards was always 1.0 g. An increase of the amount of wood gave a higher sorption of PCE and TCE and a lower sorption of c-DCE, compared to the sorption of the internal standard, chloroform (see Supporting Information Figure SI 2). The distribution of chemicals in the sample vials was calculated assuming chemical equilibrium (see the Supporting Information). Accordingly, even at the headspace temperature of 80 °C, a relevant fraction of the test

compounds remained sorbed to wood, for PCE about 1/3 of the total mass in the vial.

The method evaluation showed that the analytical results vary with type of wood and the mass of wood in the sample vial (details found in the Supporting Information). Generally, the analytical method can be used to give a qualitative measurement of the concentration of CE in any tree core. For quantitative determination, standard curves would have to be prepared separately for each tree species that is sampled, and the weight of wood placed into the vials needs to equal 1 g or another well-defined mass.

Concentrations of Chlorinated Ethenes in Tree Cores from the Field Site. Concentrations of chlorinated ethenes (c-DCE, TCE, and PCE) measured in tree cores from the field site are shown in Table 2. Concentrations of chlorinated ethenes were above the quantification limit in 28 out of 35 samples. PCE showed the highest concentrations in all samples. PCE concentrations varied from below detection limit (4.6 μg/kg) to above linearity range (5800 μg/kg). Concentrations of TCE and c-DCE were factor 10 to >100 lower than PCE. In 10 out of 21 quantifiable samples, c-DCE concentrations were above those of TCE. Chloroethenes could be detected in all types of tree species at the site. The trees A2 (pine) and A13 (birch) were neighbored (distance <1 m) and of similar size. CE concentrations in the pine, especially TCE, were much higher than in the birch.

Chemical analysis also encompassed t-DCE, 1,1-DCE, and vinyl chloride (VC). 1,1-DCE and VC in analysis were not detected or were below detection limit in all samples. Low concentrations of t-DCE were detected in A2 (10.5 μg/kg),
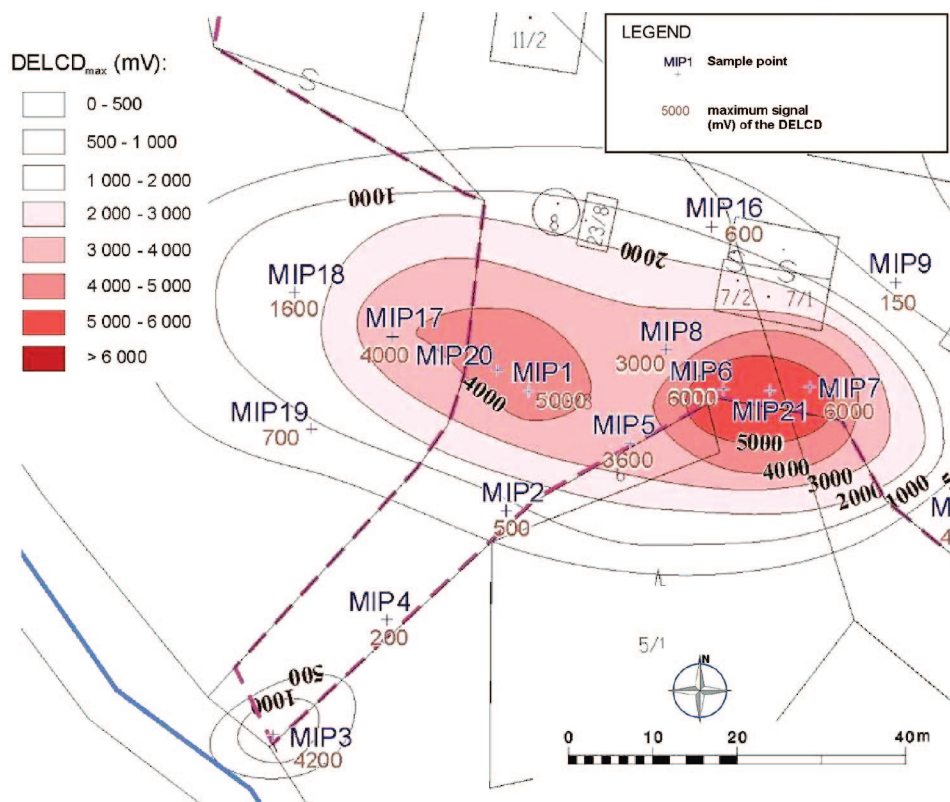
FIGURE 4. Estimated distribution of the contaminant plume in the groundwater, based on the maximum response of the DELCD detector of the membrane interface probing (MIP). The dotted line shows the property boundary. See legend for ranges of detector response.

and A27 (17 μg/kg), while all other samples were below detection or quantification limit.

Correlation between Ce Concentration in Groundwater and Trees. The concentration of chlorinated ethenes in the groundwater has been monitored since 1996 through groundwater sampling in observation wells. Some wells were monitored monthly while other wells were monitored three to four times per year. Average CE groundwater concentrations measured during the relevant growth season, May–October 2005, compared to concentrations in adjacent trees are shown in Table 3. Concentration ratios between tree core and GW varied widely, from 0.01 to 0.78 for c-DCE, 0.01 to 7.7 for TCE, and 0.01 to 2.5 for PCE, with average values of 0.37, 1.35, and 0.54 for c-DCE, TCE, and PCE, respectively. A few high points strongly influence the Pearson correlation, therefore the Spearman rank correlation should be used instead. The rank correlation obtained was highly significant ($P < 0.01$) for c-DCE and significant ($P < 0.05$) for PCE, TCE, and the sum of CE (Table 3).

Out of 90 GW samples taken at the area during the growth season 2005 (May–October), 1,1-DCE was measured in only 28 samples at levels above detection limit (0.5 μg/L). The average of these 28 concentrations was 3 μg/L; the maximum was 15 μg/L. Similarly, t-DCE was above detection limit (1 μg/L) in only 24 out of the 90 GW samples, with an average of 3.4 μg/L and a maximum of 8 μg/L. The concentration of vinyl chloride was above detection limit (4 μg/L) in 10 out of 45 GW samples, the average (10 samples) being 21 μg/L and the maximum 71 μg/L.

The lack of VC in tree core samples indicates that the concentration ratio, tree core to GW, of VC is lower than for the other CE compounds (Table 3). This could be due to the low log K_{OW} and high K_{AW} of VC, which may lead to lower accumulation in wood (14), or due to aerobic degradation of VC. As the roots are obligate aerobic organisms, oxygen in present and VC is the most rapidly degraded of all CEs (5).

However, no conclusion should be drawn about the feasibility to track subsurface VC with tree cores, due to the low GW concentrations at this site. Further investigations at sites with high VC content in groundwater or soil are necessary for an evaluation of the capacity of tree core sampling for detection of VC.

For PCE, TCE, and c-DCE, the results indicate that concentrations in GW and trees are related, but the relation is not linear or constant. Similar observations were noted earlier. Vroblesky et al. (12) found TCE and c-DCE in tree trunks from several species. The concentrations varied with location, species, time, and sampling height, but could be used to delineate the pollution plume. In a study carried out at a PCE contaminated former dry cleaning facility (22), significant quantitative relations were found between PCE concentrations in trees and subsurface soils, while the relation between concentrations in trees and underlying groundwater was less apparent. For a phytoremediation site in France (13), a correlation between groundwater concentrations of CE and concentrations in branches of willow and poplar trees could be established. According to the authors, the regressions are site-specific and need to be determined for each site prior to monitoring subsurface contamination from branch samples.

Many parameters can affect the concentration ratio between wood and subsurface, e.g. groundwater depth, seasonal variations, recent precipitation, and tree size. A model for prediction of chemical concentrations in trees was developed recently (16). This model contains 31 parameters that may influence concentrations in stems. For chloroethenes, such as PCE, TCE, and c-DCE, sensitive parameters include, besides bioavailable concentration in soil or groundwater, root radius and mass; root water, lipid and gas content; transpiration stream; growth rates; water flow velocity in xylem; and others. These parameters vary with species, location, season, and meteorological conditions. Therefore,

it will be practically impossible to precisely predict concentrations in stems from concentrations in groundwater and vice versa. However, tree core sampling can clearly provide valuable semiquantitative information for plume delineation and characterization.

Mapping of the Plume. The spatial distribution of the pollution plume was estimated from the total concentration of CE measured in the tree cores (Figure 2). The plume distribution of the chlorinated ethenes based on the average groundwater concentrations measured during the relevant growth season, May–October 2005, is shown in Figure 3, where the measured concentrations in tree cores are indicated by tree-like symbols in varying colors. Both maps are similar with respect to area, direction, and center of the plume. Generally, the closer to the center of the plume (estimated from groundwater monitoring) the tree was located, the more CE was found in tree trunks, supporting the correlation between CE concentrations in groundwater and trees. A major difference between the two maps can be seen for the southwestern edge of the plume. High concentrations of chloroethenes were found in trees A27 and A18. As no sampling wells were set nearby, the groundwater investigations from 1997 to 2005 did not indicate a high contamination level in this area.

The presence of CE in the trees at this location triggered new investigations using membrane interface probing (MIP) in 2006 (Figure 4). The distribution of contamination based on MIP shows a pattern which is comparable to the tree core sampling results and confirms the presence of a "hot spot" at the southwestern corner of the property.

The discovery of a new hot spot with only six hours of tree core sampling after almost two decades of groundwater sampling at the site demonstrates the benefits of tree coring in plume delineation. The minimal costs of tree coring allow more sampling points during initial investigations, and thus also a more detailed spatial resolution and directed placement of sampling wells to attain necessary groundwater samples.

Monitoring of Natural Attenuation. The parent pollutant (PCE) as well as the products from reductive dechlorination, TCE, and c-DCE were found in the samples taken from groundwater wells and in most of the tree cores. The concentration ratio c-DCE/TCE increased with increasing distance form the source, which also indicates that reductive dechlorination is occurring. These findings demonstrate that tree core sampling can be used to detect and monitor not only plume distribution, but also to qualitatively assess natural attenuation. The potential impacts are substantial. The U.S. Air Force (USAF) alone has an estimated 50 000 CE monitoring wells, and at a cost of $2500 per well per sampling event, the entire monitoring program can run in the tens of millions annually. In 2005, an estimated 32% of the overall USAF remediation budget was spent on long-term monitoring (*23*). The overall expenditures worldwide by the private sector and government agencies certainly run in the hundreds of millions in U.S. dollars. Tree cores may also be sampled at sites which are difficult to access with heavy equipment; for example, private gardens in residential areas or dense forests.

In conclusion, tree core sampling should be used for assessing the presence of pollutants rather than determining exact subsurface concentrations. From tree core measurements alone, precise evaluation of subsurface pollution will not be possible. Furthermore, some compounds, e.g., vinyl chloride, were not detected in trees. Screening an area suspect of CE pollution in the upper aquifer with the tree core method prior to boring observation wells can determine optimal location of these wells rather than blindly placing the initial wells, which reduces the number of wells necessary for the investigation and thus reduces overall costs. Within the range of limitations, tree-core sampling is a reliable and inexpensive alternative method for investigating and monitoring the extent of shallow CE contaminations, and for evaluating the occurrence and extent of natural attenuation of chlorinated ethenes in soil and groundwater.

Supporting Information Available
Detailed description of the membrane interface probing (MIP) system and results from the method evaluation on the impact of sample mass and the distribution of chemicals in the sample vial. This information is available free of charge via the Internet at http://pucs.acs.org.

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