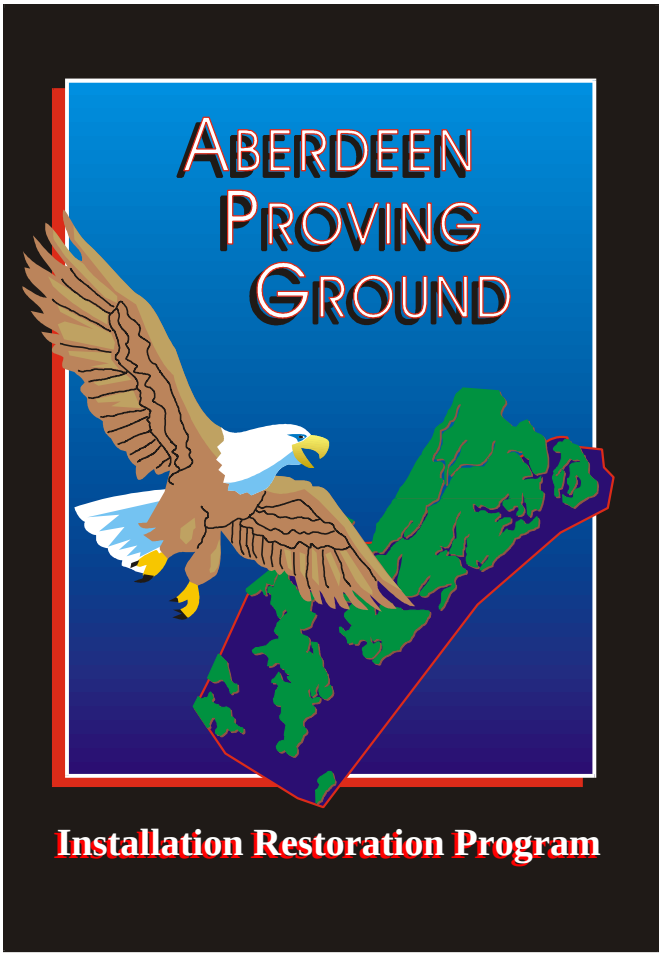

Dialysis Sampler Evaluation of Rhizosphere Phytoremediation Processes in the Poplar Grove at J-Field, Aberdeen Proving Ground, Maryland

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July 2001

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Final Report Aberdeen Proving Ground

Dialysis Sampler Evaluation of Rhizosphere Phytoremediation Processes in the Poplar Grove at J-Field, Aberdeen Proving Ground, Maryland

by J.H. Pardue and W.A. Jackson

CFR Biotechnologies, Inc., Baton Rouge, Louisiana

and

L.E. Martino

Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

July 2001

Work prepared for U.S. Army Aberdeen Proving Ground, Directorate of Safety, Health, and Environment, Maryland

Argonne National Laboratory is operated by The University of Chicago under Contract W-31-109-Eng-38, for the U.S. Department of Energy

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NOTATION

The following is a list of the acronyms, initialisms, and abbreviations (including units of measure) used in this report.

1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
1,1,1-TCA	1,1,1-trichloroethane
1,1,2-TCA	1,1,2-trichloroethane
1,1,1,2-TeCa	1,1,1,2-tetrachloroethane
1,1,2,2-TeCA	1,1,2,2-tetrachloroethane
1,2-DCA	1,2-dichloroethane
AOC	Area of Concern
APG	Aberdeen Proving Ground
BGS	below ground surface
CA	chloroethane
cis-1,2-DCE	*cis*-1,2-dichloroethene
Cl^-	chloride
cm	centimeter(s)
FID	flame ionization detector
ft	foot (feet)
GC	gas chromatograph
HPLC	high-performance liquid chromatography
L	liter(s)
m	meter(s)
Md.	Maryland
mg	milligram(s)
mL	milliliter(s)
mV	millivolt(s)
µg	microgram(s)
µm	micrometer(s)
µmhos	microohm(s)
µmol	micromole(s)
PCE	tetrachloroethene
s	second(s)
SOP	standard operating procedure
TBP	Toxic Burning Pits
TCE	trichloroethene
trans-1,2-DCE	*trans*-1,2-dichloroethene
VC	vinyl chloride
VOC	volatile organic compound

EXECUTIVE SUMMARY

This study reports on the first high-resolution dialysis sampling data collected from the root zone of poplar trees used for phytoremediation at J-Field, Aberdeen Proving Ground, Maryland. The approach was developed as an improved method of monitoring performance of phytoremediation technologies. Two dialysis samplers were designed and constructed for the J-Field application. One sampler was installed in the rhizosphere of one of the existing phytoremediation trees (tree #55), and the other was installed in a control location outside of the phytoremediation grove. The design of the samplers was based on the dialysis sampling approach. In these samplers, depressions, or cells, are drilled in a solid Plexiglas rod. Deionized water is placed in the cells, and the cells are then covered with a membrane filter sheet (0.2 μm). The samplers were designed to allow insertion into the subsurface using direct push technology. After insertion, constituents in the groundwater diffuse across the membrane into the dialysis sampler well. After a period of equilibration, the samplers are retrieved, and the water in the sampler well is sampled and analyzed. Because the sampler can be constructed to any specification, the resolution or spacing of the samples can be specified in the design.

The initial data collected revealed the following results of note:

1. The volatile organic compound (VOC) depth profile from the control location was relatively constant, with variability on the order of 10%. Both the relative composition of the chlorinated VOC profile and the absolute concentration were relatively constant throughout the sampler depth.

2. The control samples showed strong evidence of reductive dechlorination. The evidence included high concentrations of ethane, ethene, and methane, a high ratio of progeny products (*cis*- and *trans*-1,2-dichloroethene) to parent compounds (1,1,2,2-tetrachloroethane and trichloroethene). Results were consistent with previous monitored natural attenuation sampling in this location of the surficial aquifer.

3. In the tree 55 dialysis sampler, the VOC depth profile was highly variable in both absolute concentration and the relative concentration of parent and progeny products. This highly variable profile is indicative of highly spatially variable biodegradation and uptake near the active roots. The scale of this variability appears to be centimeters, emphasizing the importance of these high-resolution samplers. Several cells in the dialysis sampler were dry, presumably because of the strong suction of nearby roots or a preferential “wicking” effect caused by the geological heterogeneity in the rhizosphere.

4. In the tree 55 dialysis sampler, dissolved gas analyses indicated a less favorable environment for reductive dechlorination than in the control location. Progeny product ethane and ethane concentrations were substantially

lower, and methane concentrations were also low. These conditions are strong indicators that the environment of the poplar rhizosphere is less reducing than the surficial aquifer outside the grove, perhaps encouraging the oxidation of progeny products.

5. Measurements of potential root exudates (organic acids and carbohydrates) in both dialysis samplers and upgradient and downgradient wells did not indicate that a large input of carbon is occurring as water is passing through the grove.

6. Concentrations of monochloro-, dichloro- and trichloroacetic acids, which have been identified as degradation products of chloroethenes in poplars, were below detection in the control location. In the dialysis samplers, measurements were inconclusive. Measurements were below the lowest point on the calibration curve, but a measurable peak was observed with the same retention time and identifying ions as dichloroacetic acid. More water was needed to decrease the detection limit for this compound. This procedure should be conducted in future analyses.

In summary, these results suggest that the impact of the rhizosphere on the chlorinated VOCs is spatially variable and needs to be studied on the measurement scale employed in this investigation. The initial measurements using this sampling technique suggest that the rhizosphere of tree 55 is a less reducing environment. The results represent only one tree with possibly an underdeveloped root system relative to other trees in the grove. Further studies should utilize this measurement technique to assess spatial changes in chlorinated VOCs as groundwater moves through the entire grove.

DIALYSIS SAMPLER EVALUATION OF RHIZOSPHERE PHYTOREMEDIATION PROCESSES IN THE POPLAR GROVE AT J-FIELD, ABERDEEN PROVING GROUND, MARYLAND

by
J.H. Pardue, W.A. Jackson, and L.E. Martino

1 DIALYSIS SAMPLER STUDY OBJECTIVES

Phytoremediation and natural attenuation can play prominent roles in the reduction of chlorinated aliphatics in contaminated subsurface systems. An extensive phytoremediation grove of poplar trees has been planted at the former Toxic Burning Pits Area at J-Field, Aberdeen Proving Ground (APG), Maryland. In addition, monitored natural attenuation studies have been conducted in the upland and wetlands at the Toxic Burning Pits (TBP) Area of Concern (AOC) (Figure 1). Evaluation of the contribution of the poplar grove to the overall natural attenuation of the plumes of chlorinated contaminants in groundwater at J-Field is currently difficult because of the inability to sample discrete depths and the lack of resolution available using routine macro aquifer sampling techniques, such as sampling from wells.

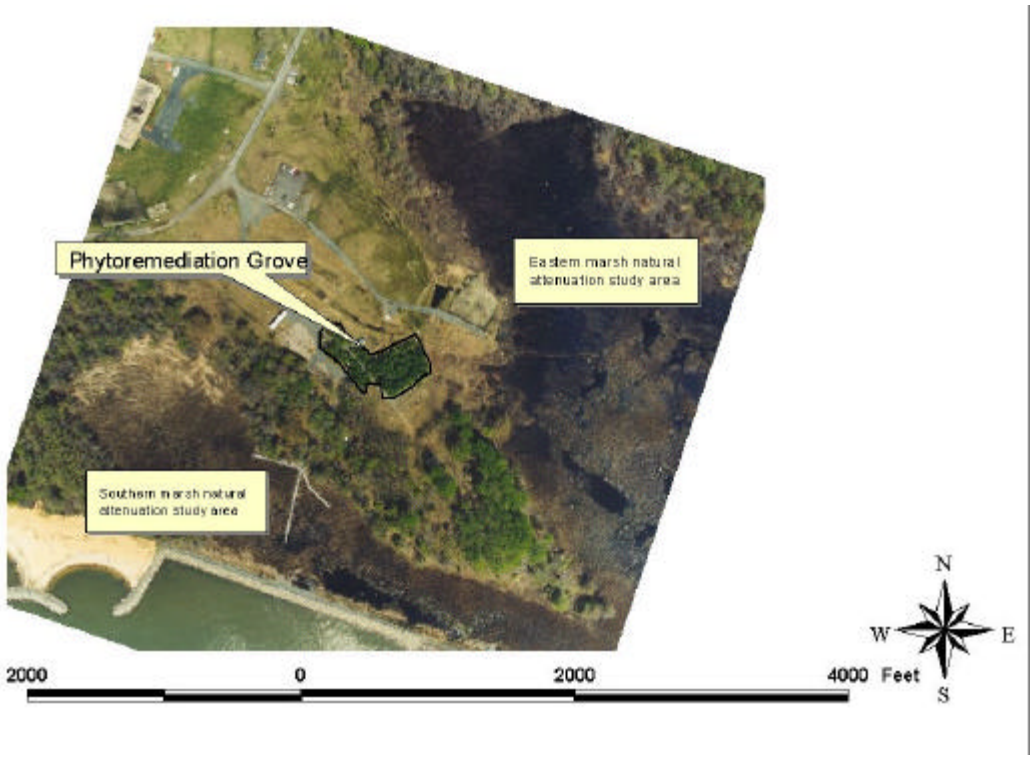

FIGURE 1 Aerial Photograph Showing the Poplar Tree Phytoremediation Grove in the Toxic Burning Pits Area of J-Field, Aberdeen Proving Ground

Currently, a number of wells, lysimeters, and piezometers are located within and outside of the grove, and sampling of these sources gives valuable information regarding the overall fate and transport of contaminants in this area of J-Field. However, these sampling points cannot provide the vertical or spatial resolution needed to differentiate between gross microbial reactions within the aquifer and more discrete plant-microbe interactions within the rhizosphere of the poplar trees.

The objectives of this study were to use dialysis samplers to examine the effects of the rhizosphere on natural attenuation processes, volatile organic compound (VOC) concentrations and distribution, and geochemistry. The dialysis samplers used were specially designed to sample at the depths and resolution necessary for this study. In conjunction with use of the dialysis samplers, a number of wells were sampled to study the gross changes in VOCs and root exudates along a flow line through the poplar grove. The results of this study will help determine the contribution of the poplar grove to the reduction and final fate of VOCs in the J-Field area.

2 EXPERIMENTAL DESIGN

2.1 OVERVIEW

A plume of chlorinated solvents is present in the surficial aquifer adjacent to the Toxic Burning Pits Area of J-Field at APG. The groundwater has been contaminated by sources from past operations at the Toxic Burn Pits and migrates into receiving waters referred to here as the Eastern Marsh and the Southern Marsh. The potential for the remediation of contaminated groundwater through natural attenuation in upland and wetland areas at the Toxic Burning Pits Area was investigated between 1997 and 2000 (Yuen et al. 2001).

In a phytoremediation project to address this groundwater contamination, 183 hybrid poplar (HP-150) trees (*Populus deltoides x trichocarpa*) were planted in 1996 as a method of intercepting the plume. Each tree in the grove has been numbered to aid in monitoring tree health. (For more information on the phytoremediation grove, see Roy F. Weston, Inc. 1999)

The objective of this study was to evaluate the effects of the poplar grove remediation project on the overall natural attenuation of VOCs in groundwater at J-Field. Specifically, this study included two tasks. Task 1 was to determine the concentration of chlorinated solvents, progeny (or degradation) products, and organic acids along a flow line within the J-Field poplar grove by sampling 13 wells located within the grove and two wells slightly outside the grove. Task 2 used two dialysis samplers to determine the vertical distribution of parent chlorinated solvents, progeny products, dissolved gases (methane [CH_4] ethene, ethane), chloride (Cl^-), root metabolites of solvents, and root exudates in the rhizosphere of a particular poplar tree (tree #55) located within the phytoremediation grove and at one location outside the grove at a similar depth (control location).

2.2 SAMPLING

2.2.1 Monitoring Wells

The grove of poplar trees was planted downgradient from areas at the TBPs known to be groundwater contamination sources. Numerous wells, piezometers, and lysimeters have been installed to monitor groundwater quality in the area. The locations of wells sampled for the study and the position of tree 55 are shown in Figure 2. The wells used for sampling were selected so as to achieve a large spatial distribution and a variety of depths. However, numerous wells were dry or had extremely low flow rates, in which case a deeper piezometer was sampled. Two wells were sampled outside the grove. One of these, well JFP4, was sampled on the extreme southeastern edge of the grove, and the other, well P4, was sampled near the northwestern side of the grove. These wells were sampled to find a location within the solvent plume but outside the

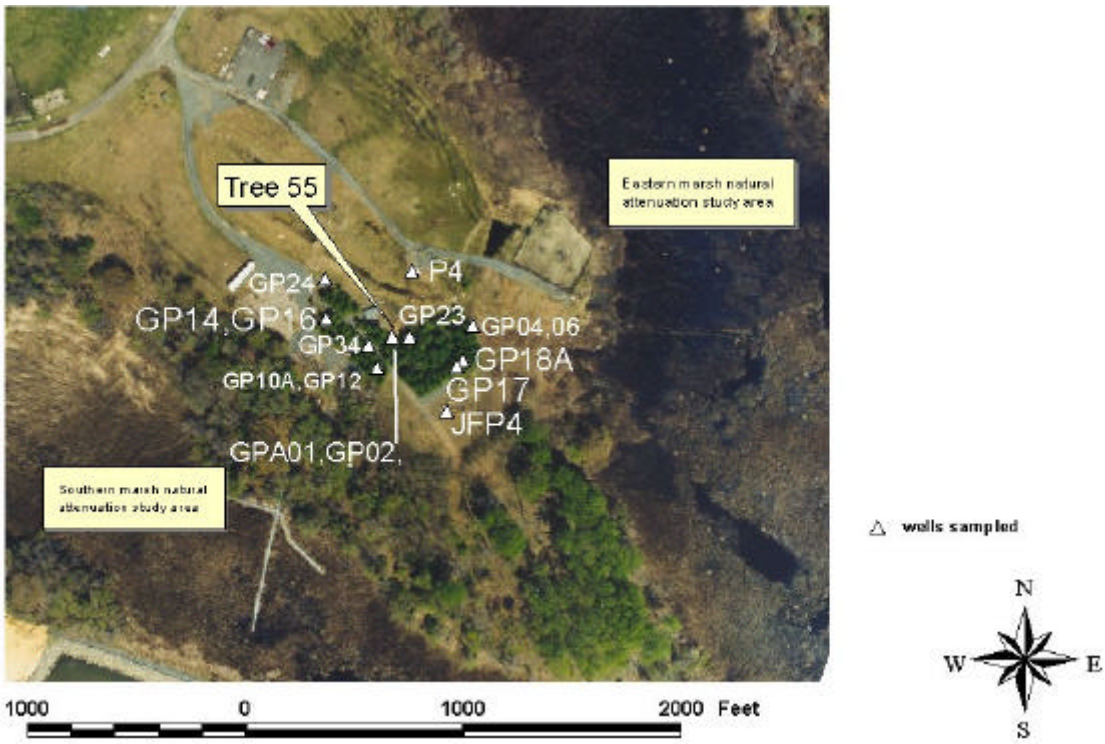

FIGURE 2 Aerial View Showing Study Sampling Locations

influence of the grove for use as a control site for the dialysis sampler study. Wells were sampled on June 21, 2000, with standard techniques described below. Wells were purged and formation water was collected for analysis. If wells were used to obtain samples, Standard Operating Procedure O13 – Collection of Groundwater Samples (U.S. Army Corps of Engineers 1999 as amended) was performed before sampling. Results of this sampling produced 15 data points.

2.2.2 Dialysis Sampler Methodology

Sampling in the rhizosphere was accomplished with Plexiglas dialysis samplers inserted in the rhizosphere by use of a Geoprobe™. The specially designed samplers, called "phyto-dialysis samplers" are 4-ft (1.2-m) long Plexiglas tubes approximately 2 in. (5 cm) in diameter. The tube has multiple depressions or cells cut into the Plexiglas (Figure 3) spaced approximately 3 in. (8 cm) on center. Each cell holds approximately 19 mL of water. The dialysis samplers were assembled in a bath of deionized water so that the initial composition of the water in the cells was uncontaminated. One side of the cells was then covered with two membranes that would allow dissolved constituents in both solid and gaseous states to equilibrate between porewater in the cells. One membrane was a 0.2-µm pore size Teflon membrane, and this was overlaid with a more durable 8-µm pore size membrane. The membranes were held in place with a thin Plexiglas cover attached by stainless steel screws and containing windows exposing the membrane-covered cells (Figure 3). The design is a modification of the original dialysis sampler design by Hesslein (1976).

The dialysis samplers were inserted into the ground with a modified Geoprobe™ driving rod. The dialysis samplers were inserted into a standard 2.25-in. (5.7-cm) driving rod, which had a drive point on the insertion end and a nylon screw to hold the sampler in position within the drive rod (Figure 4). The rod had been modified to expose the windows and membranes in the dialysis sampler cells by cutting 0.5-in. (1.25-cm) slots to correspond with the windows on the sampler (Figure 3). Before insertion, a Geoprobe™ sampling core was removed and used to make a pilot hole. This procedure eased the insertion of the sampler, preventing the possible shattering of the Plexiglass, and also allowed a core to be removed for examination.

Two dialysis samplers were inserted into the surficial aquifer at J-field on September 8, 2000, and were allowed to equilibrate for 2 weeks. One dialysis sampler was placed in the rhizosphere of tree 55, and one was placed in a control location (no trees) at the same depth. Specifically, one sampler was inserted approximately 1 ft (0.3 m) downgradient of tree 55 (Figure 5), while the control dialysis sampler, was placed 3 ft (0.9 m) upgradient of well P4 (Figure 6). Soil cores were removed before sampler insertion and examined for soil type and roots, as well as water saturation. Tree 55 was chosen as the insertion point since numerous other studies were ongoing on this particular tree, and its location is within a portion of the groundwater plume with high concentrations of contaminants. In addition, wells are located both upgradient and downgradient of the tree. The control site was chosen to be outside of the grove's possible influence, at the same approximate groundwater gradient, and located near a groundwater sampling point that was known to contain chlorinated solvents.

The dialysis sampler at tree 55 was inserted to a depth of 7.4 to 11.3 ft (2.25 to 3.45 m) below ground surface (BGS). The control dialysis sampler was inserted to a depth of 5.9 to 9.8 ft (1.80 to 3.00 m) BGS. Depths were chosen on the basis of examination of the soil core removed before insertion and water levels in nearby wells. The insertion point was chosen to be as close as possible to the upward saturated sediments while ensuring that the sampler would remain below the capillary fringe and would thus be saturated for the duration of the 2-week equilibration time. During this time, the de-ionized water equilibrated with the groundwater in the surficial aquifer in these two locations. Groundwater surface elevations for a time period approximately midway between when the well points were sampled and when the dialysis samplers were inserted into the ground are depicted in Figure 7.

FIGURE 3 Photo of Dialysis Sampler (partially inserted into a modified Geoprobe™ driving rod)

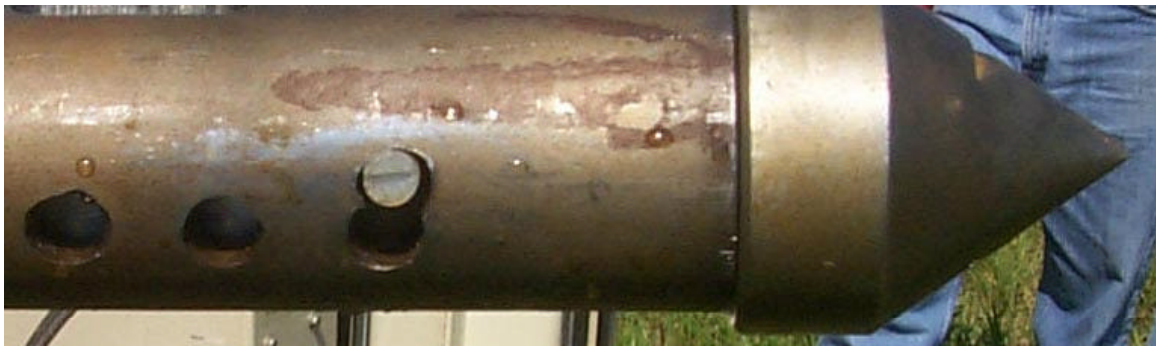

FIGURE 4 Photograph of Nylon Screw Used to Hold Dialysis Sampler in Position and Assembled Drive Point

FIGURE 5 Photograph of Dialysis Sampler Being Inserted at Tree 55

FIGURE 6 Photograph of Control Dialysis Sampler Being Prepared for Insertion near Well P4

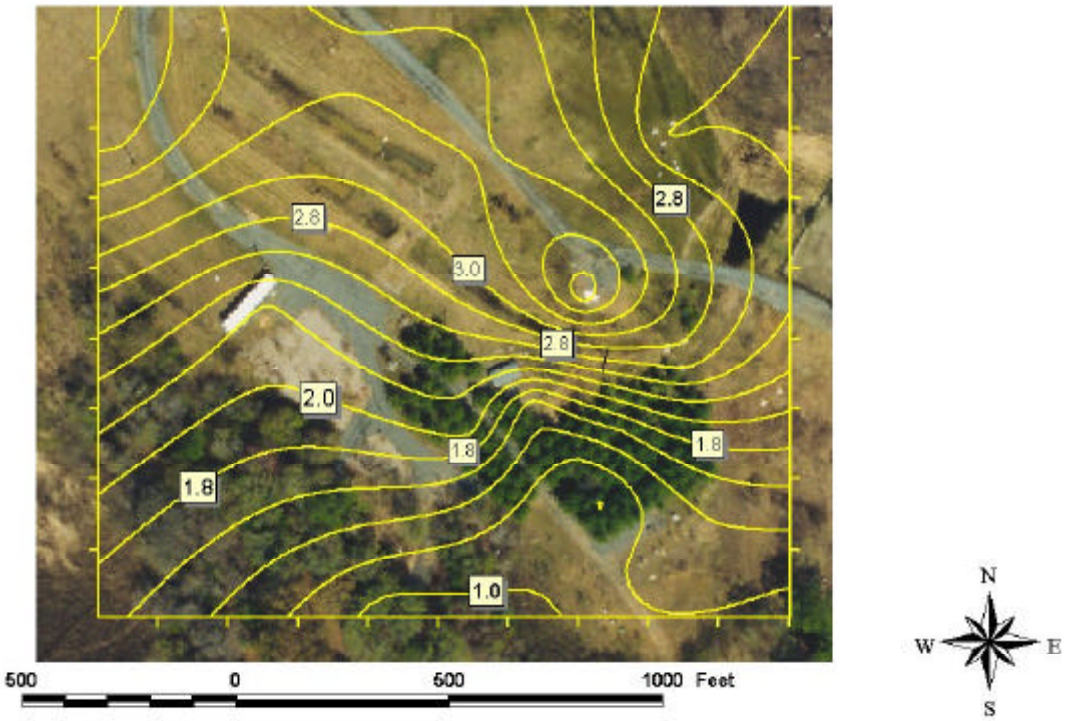

FIGURE 7 Groundwater Surface Elevations in July 2000 (ft msl)

After the 2-week equilibration period, the dialysis samplers were retrieved with a Geoprobe™. The equilibrated water was then removed from the cells by inserting a sterile needle into each well through the membranes and withdrawing the water into a glass syringe (Figure 8). Samples were then transferred to standard sample vials (10 mL, 5 mL, and 1.8 mL). Syringes were rinsed twice with distilled water and needles were replaced between cells. Samples were placed on ice upon collection and were transported to the laboratory.

Logistics had a significant impact on the equilibration time that was used. A combination of equipment problems and scheduling difficulties precluded deployment of the experimental devices until the second week of September 2000. After deployment, of primary concern was the fact that tree 55 was to be excavated in late September as part of another experiment. The tree 55 dialysis sampler had to be removed prior to the excavation to ensure that the sampler would not be damaged. A longer equilibration time might, or might not, have affected the concentrations of natural attenuation parameters detected in the dialysis samplers. Nonetheless, both the control dialysis sampler and the tree 55 sampler were subject to the same equilibration time. Thus, for the purposes of this study, comparisons between the two dialysis samplers are appropriate

The optimum equilibration time in the tree rhizosphere is unknown because of the potential for both advection and diffusion to control the equilibrium in the dialysis sampler. Two to three weeks was chosen as an incubation time because it represents the most common deployment time of dialysis samplers in the field (Gaillard et al. 1986; Tessier et al. 1989; Hare et al. 1994; Lorah et al. 1999). Several theoretical approaches are available to predict

FIGURE 8 Photograph of Water Samples Being Extracted from Dialysis Sampler

equilibration times (Harper et al. 1997; Webster et al. 1998). (Note that the “peeper” referred to in the Webster et al. reference relies on the same advection and diffusion principles as the dialysis sampler used for this tree rhizosphere study.)

Each theoretical approach makes different assumptions, and, at present, there is no agreement on which method yields useful results. Using the approach described by Webster, we predicted that 70-90% equilibration would be reached for the contaminants of concern in the rhizosphere after the 2-week period. In making this estimate, we used the most conservative assumption that diffusion alone was acting in the rhizosphere. If water was advecting, as it would near tree roots, the equilibration time would be significantly reduced. The approach by Harper et al. (1997) suggests a faster equilibration time than 2 weeks because desorption of contaminants such as TCE and 1,1,2,2-TeCA from the soil near the dialysis sampler would be occurring and would buffer the porewater concentration. On the basis of these studies, we feel that the 2-week equilibration time was reasonable for this study.

2.3 CHEMICAL ANALYSES

Chlorinated VOCs were measured using EPA Method 8260B, with typical detection limits of 40 µg/L and lower detection limits of 5 µg/L when needed. Dissolved light gases (methane, ethane, ethylene) were measured with a gas chromatograph (GC) with a flame ionization detector (FID). Standard operating procedures (SOPs) of the analytical laboratory (CFR Biotechnologies, Inc.) were used with the following modification. Since volumes recovered from the dialysis sampler were so small, a 5-mL water volume was utilized instead of a 40-mL vial for volatile organics. The concentrations of electron donors were measured by high-performance liquid chromatography (HPLC) according to CFR Biotechnologies, Inc.'s SOP. Chloride was measured by ion chromatography. The analytical suite is summarized in Table 1. Copies of analytical methods for gases and electron donors are attached as Appendix A.

TABLE 1 Analytes for Dialysis Sampler Study

Volatile Organic Compounds	Organic Acids	Phytodegradation Products	Gases
1,1,1,2-Tetrachloroethane	Lactate	Monochloroacetic acid	Methane
1,1,2,2-Tetrachloroethane	Butyrate	Dichloroacetic acid	Ethane
1,1,2-Trichloroethane	Benzoate	Trichloroacetic acid	Ethylene
1,1-Dichloroethane	Acetate		Carbon dioxide
Chloroethane	Proprionate		
Tetrachloroethene	Formate		
Trichloroethene	Salicylate		
cis-1,2-Dichloroethene			
trans-1,2-Dichloroethene			
Vinyl chloride			

3 RESULTS

3.1 PRELIMINARY PIEZOMETER SAMPLING

3.1.1 Groundwater Sampling Data

Table 2 presents information on the wells sampled and groundwater parameters measured. The "GP" microwells were installed in 1998 with direct push technology. For additional information on microwell installation, see U.S. Environmental Protection Agency (2000). Water depths were used to determine which wells were most likely screened in the groundwater/phreatic zone in which the dialysis samplers were to be installed.

TABLE 2 Groundwater Data for Wells Sampled

Piezometer	pH	Conductivity (µmhos/cm)	Total Dissolved Solids (mg/L)	Temp (°C)	Oxidation-Reduction Potential (mV)	Depth Below Ground Surface (ft)	Water Depth Below Ground Surface (ft)
GP18A	6.99	916	711	24.1	23	9.39	4.84
GP17	6.98	1056	825	21.2	16	6.76	1.9
GP04	7.05	1278	1012	19.3	-37	6.57	2.36
GP-06	6.85	2458	2054	21.2	-43	9.38	5.35
GP-23	7.2	771	595	19.7	22	14.99	9.46
GP-A01	6.9	826	640	20.8	5	13.77	6.81
GP-02	7.15	801	620	18.1	9	9.79	2.62
GP-34	6.83	475	360	20.8	2	13.69	5.33
GP16	6.7	276	204	19.7	5	14.41	7.34
GP14	6.45	475	360	19.9	-39	9.92	2.59
GP-10A	7.38	320.2	239	20.6	13	14.15	5.73
GP-12	6.9	738	571	18.6	28	11.35	2.99
GP-24	6.6	0.28	NA	15	-5	19.58	12.16
Well-P4	5	3.3	NA	18	-10	20.0	
Well-JFP4	6.6	270	NA	18	-5	13.5	

3.1.2 Chlorinated VOC Distribution

Three of the compounds analyzed — 1,1,1-trichloroethane (1,1,1-TCA), 1,2-dichloroethane (1,2-DCA) and chloroethane (CA) — were not detected in any sample (Table 3). In addition, 1,1-dichloroethene (1,1-DCE), 1,1,2-trichloroethane (1,1,2-TCA), 1,1-dichloroethane (1,1-DCA), and vinyl chloride (VC) were found at concentrations less than 24 μmol/L, or approximately 1% of highest parent compound concentration. The distribution of parent compounds (tetrachloroethene [PCE], trichloroethene [TCE], and 1,1,2,2-tetrachloroethane [1,1,2,2-TeCA]) and progeny products (*cis*-1,2-dichloroethene [*cis*-1,2-DCE] and *trans*-1,2-dichloroethene [trans-1,2-DCE]) suggests that the main degradation pathway is dihaloelimination of 1,1,2,2-TeCA to *cis*- and *trans*-1,2-DCE in addition to reductive dechlorination of PCE to TCE to cis-1,2-DCE (Table 4). The lack of VC suggests that (1) reducing conditions are not sufficiently low to support dechlorination to VC, or (2) any VC produced is being oxidized through iron reduction.

Contour maps showing distribution of chlorinated VOCs in the poplar grove are presented in Figures 9 through 12. Data only from wells with depths of 10 to 14 ft (3 to 4.3 m) BGS were used to construct the contour maps, with the exception of GP-06. GP-06 had a depth of 9.5 ft BGS, but is located at the bottom of the grove and thus should be close to the absolute elevation of the other piezometer screens. Wells P4 and JFP4 are included as references, although they are screened over a larger interval, including some portion of the surficial aquifer below the sampled zone of the other wells. The figures discussed in the following paragraph present a picture of the distribution of chlorinated VOCs in and around the grove. These maps are not meant to be definitive plumes but rather indicate a general trend in the grove, especially near tree 55.

A 1,1,2,2-TeCA plume is centered near GP-23, in the center of the grove, with high concentrations of that compound extending to the southwest and to the northeast to GP-06 (Figure 9). TCE concentrations are highest west and southwest of GP-23 at GP-34 (Figure 10). Major progeny products are centered near tree 55 at GP-23 (Figures 11 and 12). These trends indicate that dechlorination appears to be occurring within the grove, especially near the center of the grove. Of more importance is the comparison of chlorinated VOC concentration and distribution within the wells near tree 55 to concentrations in samples from the dialysis sampler installed in the root zone. This comparison should provide a good indication of whether biotic and abiotic processes in the root zone are of a different magnitude than those found in the bulk groundwater and if similar or dissimilar processes dominate.

TABLE 3 Concentrations of Chlorinated VOCs in Wells

	Concentration in µmol/L								
Piezometer	1,1,2,2-TeCA	1,1,2-TCA	1,1-DCA	PCE	TCE	*cis*-1,2-DCE	*trans*-1,2-DCE	1,1-DCE	VC
GP-18A	3.43	BDL[a]	BDL	0.38	3.4	0.84	0.45	BDL	BDL
GP-04	132	BDL	BDL	BDL	68.08	8.54	BDL	BDL	BDL
GP-06	2090	23.9	8.22	23.8	24.15	BDL	BDL	BDL	BDL
GP-23	1584	5.44	BDL	7.16	451.5	301.0	107.29	BDL	0.58
GP-A01	1082	BDL	8.06	4.15	433.1	112.1	29.79	BDL	BDL
GP-02	48.9	BDL	BDL	BDL	18.62	2.19	BDL	9.58	BDL
GP-34	1134	9.85	BDL	6.59	778.5	72.92	25.0	BDL	BDL
GP-16	64.3	BDL	BDL	2.51	19.31	0.90	BDL	BDL	BDL
GP-14	38.1	BDL	BDL	4.18	0.92	BDL	BDL	BDL	BDL
GP-10A	224.7	BDL	BDL	1.83	45.46	14.58	4.48	BDL	BDL
GP-12	148.4	BDL	BDL	BDL	18.77	22.92	8.35	BDL	BDL
GP-24	0.58	BDL	BDL	0.02	0.36	0.76	0.20	BDL	BDL
GP-17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Well-P4	61.2	BDL	BDL	BDL	9.97	106.5	42.29	BDL	BDL
Well-JFP4	2.51	BDL	BDL	BDL	0.45	2.19	0.85	BDL	BDL

TABLE 3 (Cont.)

	Concentration in mg/L								
Piezometer	1,1,2,2-TeCA	1,1,2-TCA	1,1-DCA	PCE	TCE	*cis*-1,2-DCE	*trans*-1,2-DCE	1,1-DCE	VC
GP-18A	0.57	BDL	BDL	0.06	0.44	0.08	0.04	BDL	BDL
GP-04	21.9	BDL	BDL	BDL	8.85	0.82	BDL	BDL	BDL
GP-06	347	3.16	0.81	3.9	3.14	BDL	BDL	BDL	BDL
GP-23	263	0.72	BDL	1.17	58.7	28.9	10.3	BDL	0.04
GP-A01	180	BDL	0.79	0.68	56.3	10.76	2.86	BDL	BDL
GP-02	8.11	BDL	BDL	BDL	2.42	0.21	BDL	0.92	BDL
GP-34	188	1.30	BDL	1.08	101	7.00	2.40	BDL	BDL
GP-16	10.7	BDL	BDL	0.41	2.51	0.09	BDL	BDL	BDL
GP-14	6.32	BDL	BDL	0.69	0.12	BDL	BDL	BDL	BDL
GP-10A	37.3	BDL	BDL	0.30	5.91	1.40	0.43	BDL	BDL
GP-12	24.6	BDL	BDL	BDL	2.44	2.20	0.80	BDL	BDL
GP-24	0.10	BDL	BDL	0.003	0.05	0.07	0.02	BDL	BDL
GP-17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Well-P4	10.16	BDL	BDL	BDL	1.30	10.22	4.06	BDL	BDL
Well-JFP4	0.42	BDL	BDL	BDL	0.06	0.21	0.08	BDL	BDL

[a] BDL = below detection limit.

TABLE 4 Percent Distribution of Total Chlorinated VOCs in Wells [100 ´ (mmol/L)(mmol/L [total])]

Piezometer	1,1,1,2 TeCA	1,1,2 TCA	1,1-DCA	PCE	TCE	*cis*-DCE	*trans*-DCE	1,1 DCE	Vinyl Chloride
GP-18A	40.38	BDL[a]	BDL	4.45	39.98	9.86	5.33	BDL	BDL
GP-04	63.21	BDL	BDL	BDL	32.69	4.10	BDL	BDL	BDL
GP-06	96.31	1.10	0.38	1.10	1.11	BDL	BDL	BDL	BDL
GP-23	64.47	0.22	BDL	0.29	18.37	12.25	4.37	BDL	0.02
GP-A01	64.83	BDL	0.48	0.25	25.94	6.71	1.78	BDL	BDL
GP-02	61.65	BDL	BDL	BDL	23.49	2.76	BDL	12.09	BDL
GP-34	55.97	0.49	BDL	0.32	38.39	3.60	1.23	BDL	BDL
GP-16	73.91	BDL	BDL	2.89	22.18	1.03	BDL	BDL	BDL
GP-14	88.19	BDL	BDL	9.67	2.14	BDL	BDL	BDL	BDL
GP-10A	77.20	BDL	BDL	0.63	15.62	5.01	1.54	BDL	BDL
GP-12	74.79	BDL	BDL	BDL	9.46	11.55	4.21	BDL	BDL
GP-24	30.10	BDL	BDL	1.01	18.78	39.61	10.50	BDL	BDL
GP-17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Well-P4	27.83	BDL	BDL	BDL	4.53	48.41	19.23	BDL	BDL
Well-JFP4	41.81	BDL	BDL	BDL	7.44	36.5	14.25	BDL	BDL

[a] BDL = below detection limit.

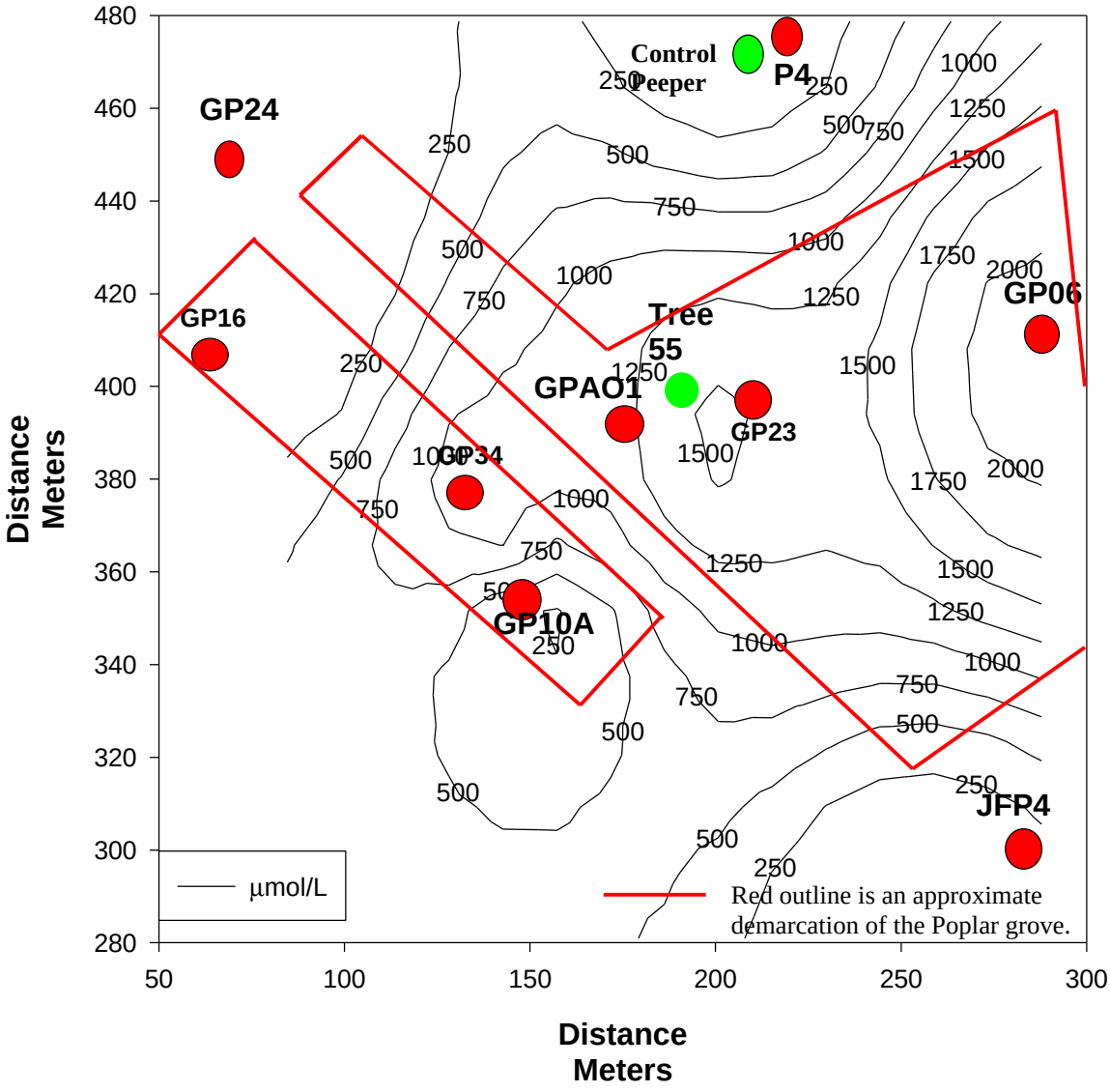

FIGURE 9 1,1,2,2-TeCA Contour Map of Poplar Grove for Piezometers 10-14 ft (3-4.3 m) Below Ground Surface

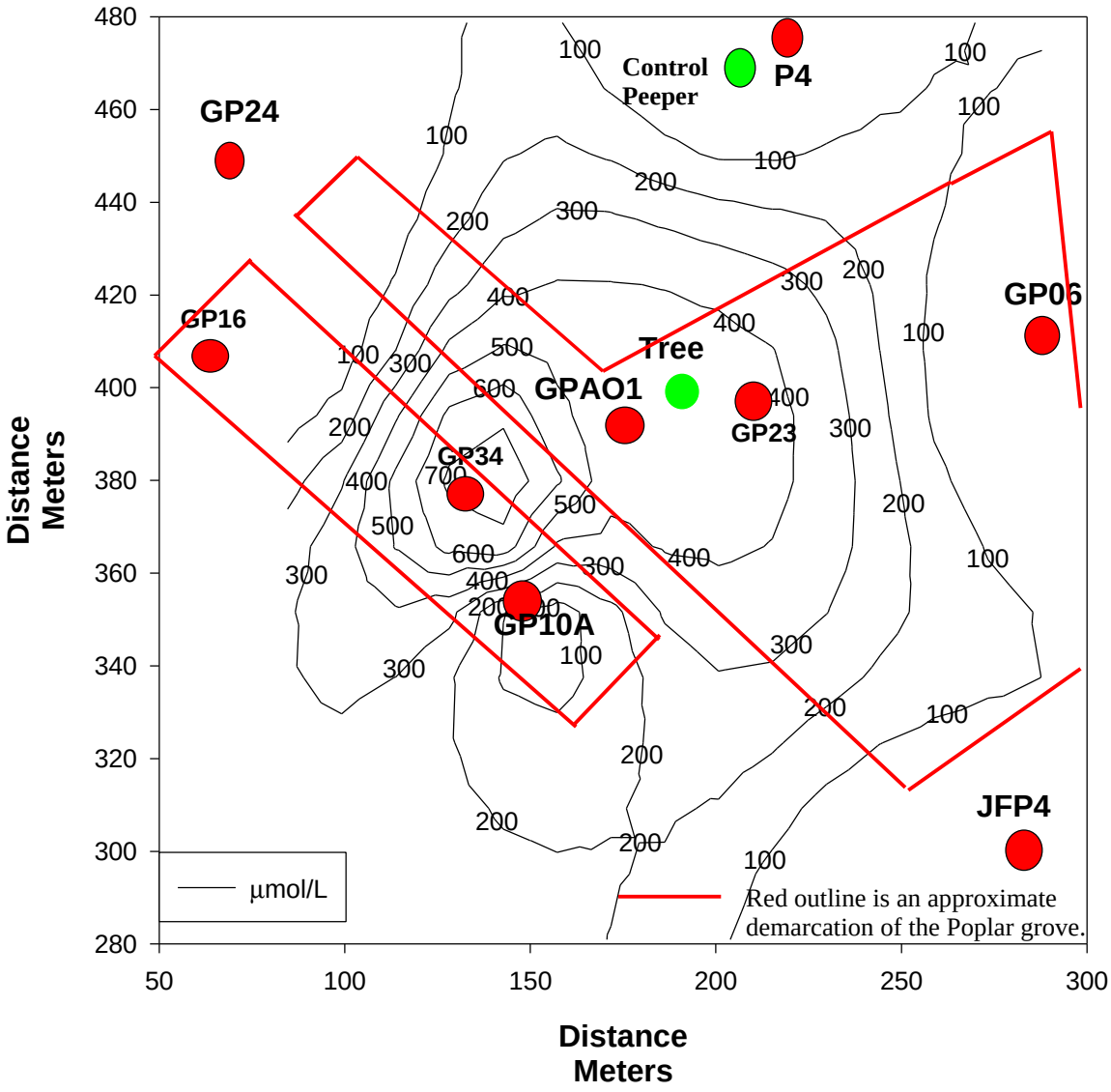

FIGURE 10 TCE Contour Map of Poplar Grove for Piezometers 10-14 ft (3-4.3 m) Below Ground Surface

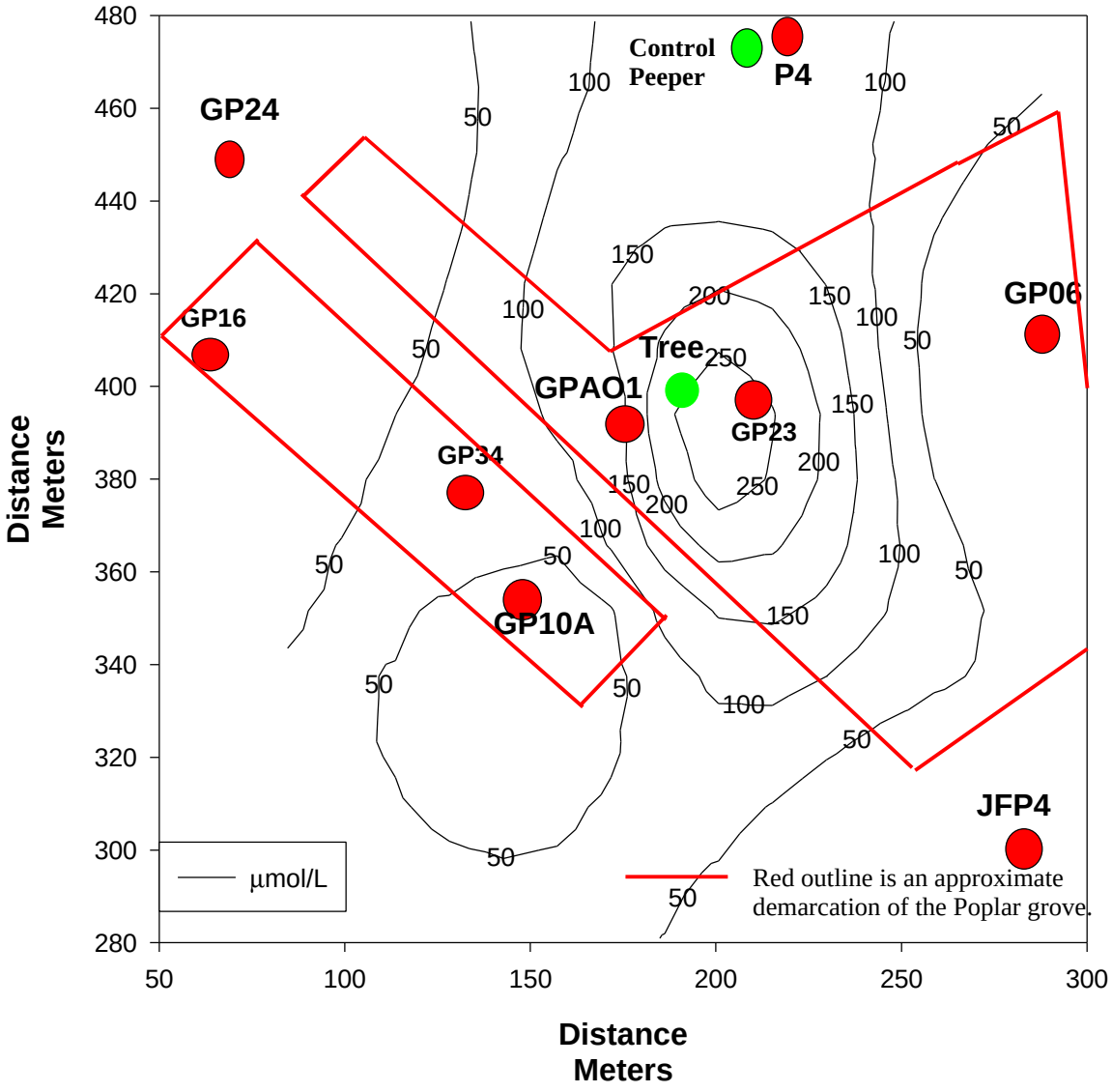

FIGURE 11 Cis-DCE Contour Map of Poplar Grove for Piezometers 10-14 ft (3-4.3 m) Below Ground Surface

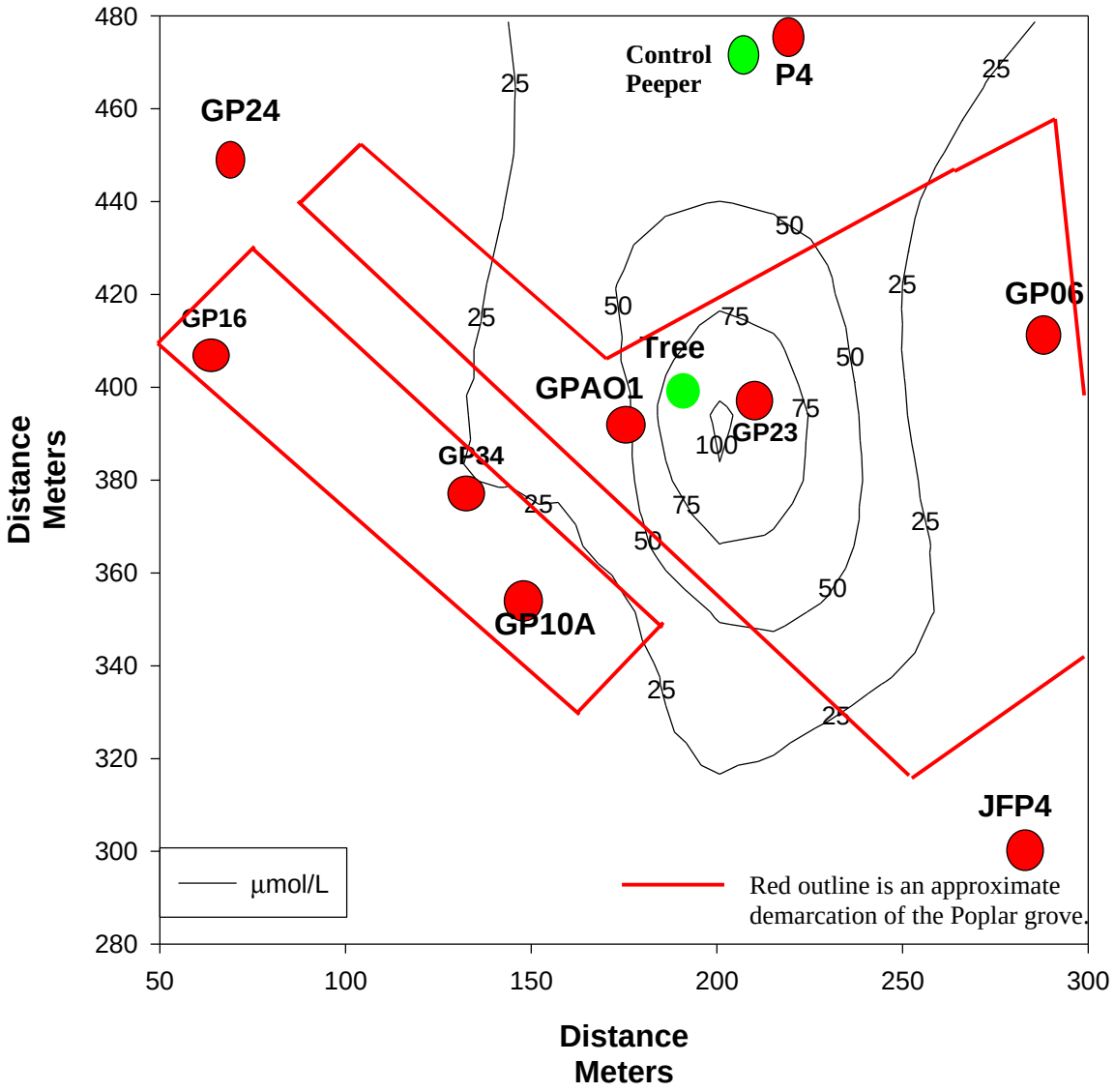

FIGURE 12 Trans-DCE Contour Map of Poplar Grove for Piezometers 10-14 ft (3-4.3 m) Below Ground Surface

3.1.3 Organic Acids

A series of organic constituents were analyzed that in previous studies have been identified as root exudates or as being derived from plant material. These constituents include certain organic acids (compounds that elute from an HPLC column designed to separate acidic constituents) and carbohydrates (a summation of compounds that elute on a column designed to separate carbohydrates). Groundwater monitoring wells were sampled to determine whether an increase of these two general groups of compounds could be observed upgradient and downgradient of the poplar grove. Results are summarized in Table 5. These data indicate that carbohydrates and several of the organic acids were present in these samples. The most commonly detected organic acids were lactate and acetate. Both are common by-products of anaerobic fermentation of organic matter. Levels of organic acids were on the order of several milligrams per liter for lactate and acetate, with several wells showing elevated concentrations of these compounds. These results do not suggest that a large mass of carbon is being released by the grove and subsequently affecting downgradient groundwater.

The comparison of the concentrations of the potential exudates between the wells and the dialysis samplers is of interest. Two prominent peaks were observed on the organic acid chromatograms that were not identified as one of the common organic acids. These peaks appeared to originate in the source areas upstream of the grove. They appeared to be conserved throughout their travel time through the grove. All that is known about these unidentified compounds is that they have acidic functional groups that allow them to pass through this column. These compounds are probably other unidentified contaminants or degradation products present in the source area.

TABLE 5 Concentrations (mg/L) of Organic Acids in Wells

Piezometer	Succinate	Lactate	Formate	Acetate	Propionate	Butyrate	Benzoate	Carb.
GP-18A	<0.5	3.4	<0.5	<0.5	<0.5	<0.5	<0.5	1.9
GP-04	<0.5	3.1	<0.5	0.53	<0.5	<0.5	<0.5	2.1
GP-06	<0.5	4.3	<0.5	<0.5	<0.5	<0.5	<0.5	3.4
GP-23	<0.5	2.9	<0.5	<0.5	<0.5	<0.5	<0.5	6.0
GP-A01	<0.5	23.4	<0.5	9.6	8.3	<0.5	<0.5	34.9
GP-02	<0.5	4.2	<0.5	0.58	<0.5	<0.5	<0.5	5.1
GP-34	<0.5	6.1	<0.5	1.9	<0.5	<0.5	<0.5	11.1
GP-16	<0.5	5.0	<0.5	2.1	<0.5	<0.5	<0.5	7.1
GP-14	<0.5	3.1	<0.5	12.7	<0.5	<0.5	<0.5	21.1
GP-10A	<0.5	4.2	<0.5	<0.5	<0.5	<0.5	<0.5	7.5
GP-12	<0.5	5.0	<0.5	1.3	<0.5	<0.5	<0.5	9.2
GP-24	<0.5	3.0	<0.5	<0.5	<0.5	<0.5	<0.5	4.1
GP-17	<0.5	3.2	<0.5	<0.5	<0.5	<0.5	<0.5	2.3
Well-P4	<0.5	4.2	<0.5	<0.5	<0.5	<0.5	<0.5	2.9
Well-JFP4	<0.5	3.3	<0.5	<0.5	<0.5	<0.5	<0.5	4.1

3.2 DIALYSIS SAMPLER RESULTS

3.2.1 Control Dialysis Sampler

The control dialysis sampler sampled from a depth of 5.9 to 9.8 ft (1.80 to 3.00 m) BGS. Of the chlorinated VOCs analyzed, PCE, 1,2-DCA, 1,1-DCE, CA, and VC were not found in any samples at concentrations above 50 ppb (Tables 6 and 7; Figure 13). This result is similar to the distribution found in Well P4, with the exception of 1,1-DCA. Total concentrations of chlorinated VOCs generally decrease with depth. In general, the chlorinated VOC profile reflects a degraded, rather than a nondegraded, distribution (Figure 14). *Cis*-1,2-DCE is the dominant compound found throughout the depth profile, and constitutes 54 to 75% of the total molar concentration of chlorinated VOCs. *Trans*-1,2-DCE is also found throughout the profile at significant concentrations (9 to 15%), while possible parent compounds (1,1,2,2-TeCA, 1,1,1,2-TeCA, and TCE) remain at less than 10% throughout the profile. Differences in concentrations between *cis*-1,2-DCE and *trans*-1,2-DCE are probably due to degradation of TCE, which preferentially forms cis-1,2-DCE, while dihaloelimination forms more equal (3:2:1) amounts of *cis*-1,2-DCE and *trans*-1,2- DCE (Lorah and Olsen 1999).

Of interest is the presence of the lower chlorinated ethanes (1,1,2-TCA and 1,1-DCA), neither of which is present in well P4. It appears that in the depths sampled by the dialysis sampler, reductive dechlorination (as opposed to dihaloelimination) of parent alkanes is also occurring. This result could be due to a difference in microbial consortia between the depths at which the dialysis sampler sampled and the depths sampled by well P4 (the screen for well P4 is from 5 to 20 ft BGS) or some environmental condition that promotes one pathway over the other. One possible explanation is the presence of 1,1,1,2-TeCA in the dialysis samples but not in the well or piezometer samples. It is possible that this compound is more susceptible to degradation by reductive dechlorination than dihaloelimination. This explanation is partly supported by the visual correlation between concentrations of these three compounds. Increases or decreases in molar concentrations are inversely mirrored by changes in the progeny products. Changes in 1,1,1,2-TeCA are inversely mirrored in changes in trans-1,2-DCE. Overall, the distribution is remarkably similar throughout the depth sampled, with the exception of the distribution of 1,1,2-TCA.

Figure 15 compares the concentration and percent distribution of chlorinated VOCs between well P4 and the control dialysis sampler. The well is located within 5 ft (1.5 m) of the dialysis sampler insertion point. However, it samples a deeper stratum and has a large well screen. A significant difference does exist in the concentrations of 1,1,1,2-TeCA, 1,1,2-TCA, and 1,1-DC between the dialysis sampler and the well. Water from P4 contains higher concentrations of most compounds, and approximately 50% more total chlorinated VOCs. These differences are likely due to the sampled interval and the existing variability in the formation.

TABLE 6 Concentrations of Chlorinated VOCs in the Control Dialysis Sampler

Cell	Depth of Cell (cm)	1,1,2,2-TeCA (µmol/L)	1,1,1,2-TeCA (µmol/L)	1,1,2-TCA (µmol/L)	1,1-DCA (µmol/L)	TCE (µmol/L)	*cis*-1,2-DCE (µmol/L)	*trans*-1,2-DCE (µmol/L)	Cl^- (mmol/L)
C1	187	30.12	10.54	50.76	8.33	8.85	165.1	30.73	36.5
C2	194.5	BDL	BDL	23.64	11.25	9.46	183.8	42.19	37.1
C3	202	10.84	10.96	18.94	5.21	4.31	118.3	17.71	36.6
C4	209.5	5.36	3.92	5.00	6.88	4.54	100.0	25.21	19.8
C5	217	3.80	9.76	20.53	BDL	4.23	105.2	24.38	22.6
C6	224.5	8.86	6.45	22.35	8.54	5.00	116.7	30.52	26.8
C7	232	7.35	5.84	14.17	17.19	8.85	185.4	37.81	26.1
C8	239.5	2.29	8.61	5.38	7.60	3.08	113.5	28.54	20.5
C9	247	9.04	9.28	5.38	5.31	3.46	121.6	19.06	29.3
C10	254.5	3.43	11.39	BDL	8.75	2.77	165.6	30.94	40.0
C11	262	1.33	8.73	12.8	BDL	BDL	81.35	16.56	16.9
C12	269.5	BDL	6.02	5.00	BDL	BDL	65.31	10.10	16.9
C13	277	2.29	7.95	6.89	5.83	BDL	102.1	20.00	13.3
C14	284.5	BDL	6.93	4.85	3.23	BDL	64.58	10.94	12.6
C15	292	2.29	7.95	11.82	2.60	BDL	53.44	9.38	12.4
C16	299.5	4.22	4.22	1.74	2.60	BDL	45.83	9.17	7.31

TABLE 6 (Cont.)

Cell	Depth of Cell (cm)	1,1,2,2-TeCA (mg/L)	1,1,1,2-TeCA (mg/L)	1,1,2-TCA (mg/L)	1,1-DCA (mg/L)	TCE (mg/L)	*cis*-1,2-DCE (mg/L)	*trans*-1,2-DCE (mg/L)	Cl^- (mg/L)
C1	187	5.00	1.75	6.70	0.80	1.15	15.85	2.95	1270
C2	194.5	BDL	BDL	3.12	1.08	1.23	17.64	4.05	1300
C3	202	1.80	1.82	2.50	0.05	0.56	11.36	1.70	1280
C4	209.5	0.89	0.65	0.66	0.66	0.59	9.6	2.42	693
C5	217	0.63	1.62	2.71	BDL	0.55	10.10	2.34	792
C6	224.5	1.47	1.07	2.95	0.82	0.65	11.20	2.93	938
C7	232	1.22	0.97	1.87	1.65	1.15	17.80	3.63	912
C8	239.5	0.38	1.43	0.71	0.73	0.40	10.90	2.74	717
C9	247	1.50	1.54	0.71	0.51	0.45	11.67	1.83	1020
C10	254.5	0.57	1.89	BDL	0.84	0.36	15.90	2.97	1400
C11	262	0.22	1.45	1.69	BDL	BDL	7.81	1.59	594
C12	269.5	BDL	1.00	0.66	BDL	BDL	6.27	0.97	591
C13	277	0.38	1.32	0.91	0.56	BDL	9.80	1.92	467
C14	284.5	BDL	1.15	0.64	0.31	BDL	6.20	1.05	440
C15	292	0.38	1.32	1.56	0.25	BDL	5.13	0.90	435
C16	299.5	0.70	0.70	0.23	0.25	BDL	4.40	0.88	256

TABLE 7 Percent of Total Chlorinated VOCs in the Control Dialysis Sampler [100 ´ (mmol/L)/(mmol/L [total])]

Cell	Depth of Cell (cm)	1,1,2,2-TeCA	1,1,1,2- TeCA	1,1,2-TCA	1,1 -DCA	TCE	*cis*-1,2-DCE	*trans*-1,2-DCE
C1	187	9.89	3.46	16.67	2.74	2.91	54.23	10.09
C2	194.5	BDL	BDL	8.74	4.16	3.50	67.98	15.61
C3	202	5.82	5.88	10.17	2.80	2.31	63.52	9.51
C4	209.5	3.55	2.59	3.31	4.56	3.01	66.27	16.71
C5	217	2.26	5.81	12.23	BDL	2.52	62.66	14.52
C6	224.5	4.46	3.25	11.27	4.31	2.52	58.81	15.39
C7	232	2.66	2.11	5.12	6.21	3.20	67.03	13.67
C8	239.5	1.35	5.10	3.18	4.5	1.82	67.17	16.88
C9	247	5.22	5.36	3.11	3.07	2.00	70.23	11.01
C10	254.5	1.54	5.11	BDL	3.93	1.24	74.30	13.88
C11	262	1.10	7.23	10.6	BDL	BDL	67.36	13.71
C12	269.5	BDL	6.97	5.78	BDL	BDL	75.56	11.69
C13	277	1.58	5.48	4.75	4.02	BDL	70.38	13.79
C14	284.5	BDL	7.65	5.36	3.57	BDL	71.34	12.08
C15	292	2.62	9.09	13.51	2.98	BDL	61.09	10.72
C16	299.5	6.22	6.22	2.57	3.84	BDL	67.62	13.52

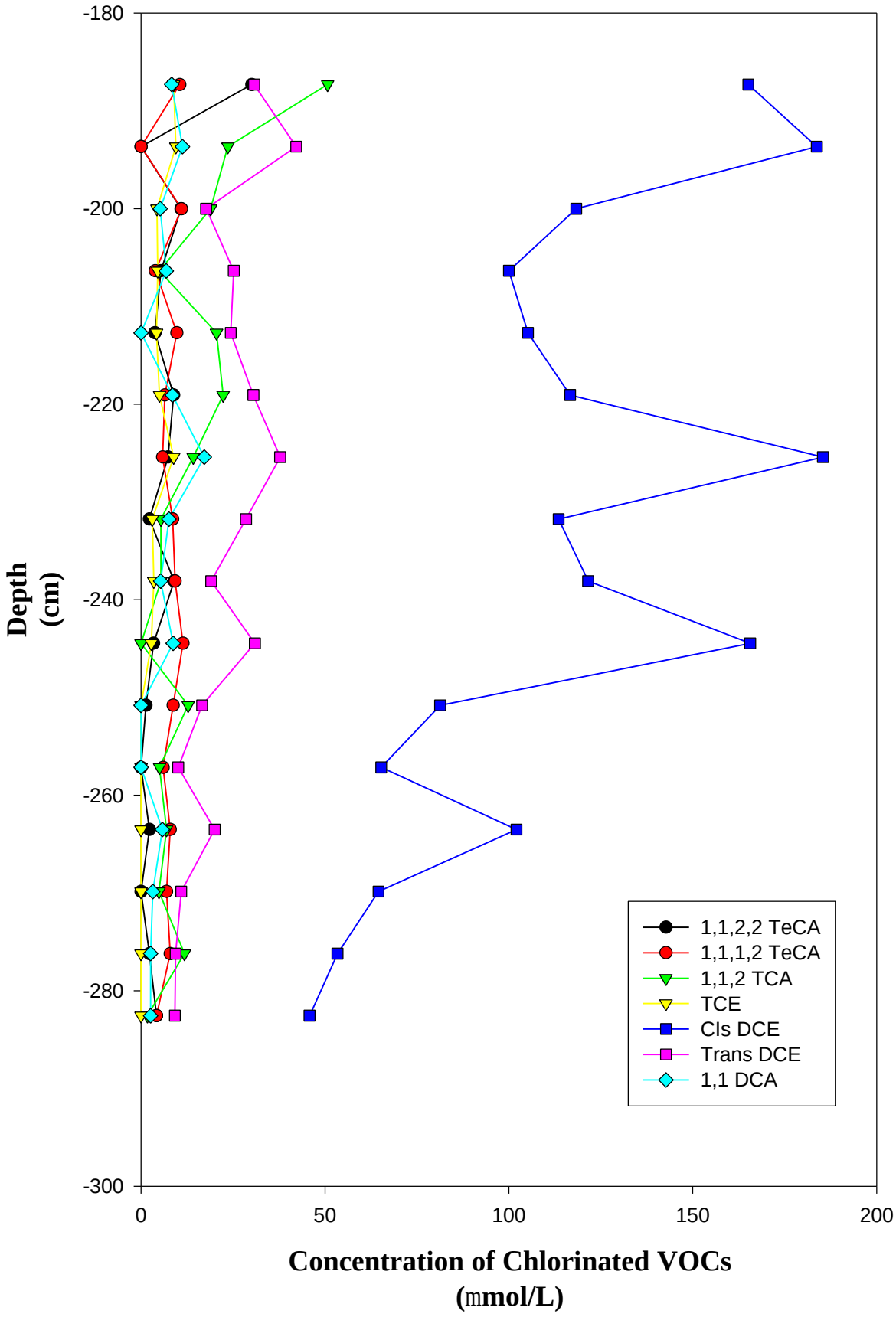

FIGURE 13 Concentration of Chlorinated VOCs in Dialysis Sampler from the Control Site

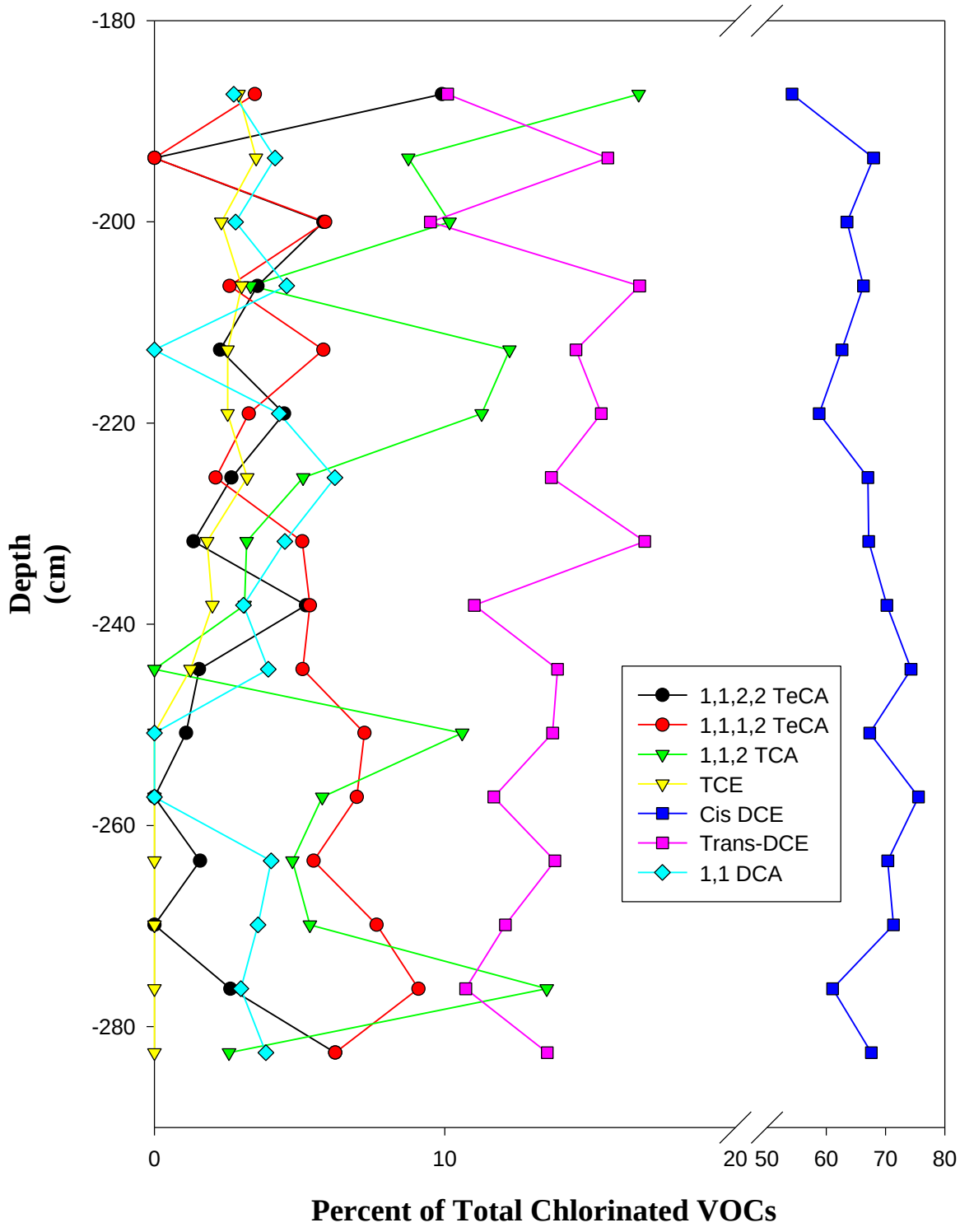

FIGURE 14 Percent of Total Chlorinated VOCs Distribution in Control Dialysis Sampler

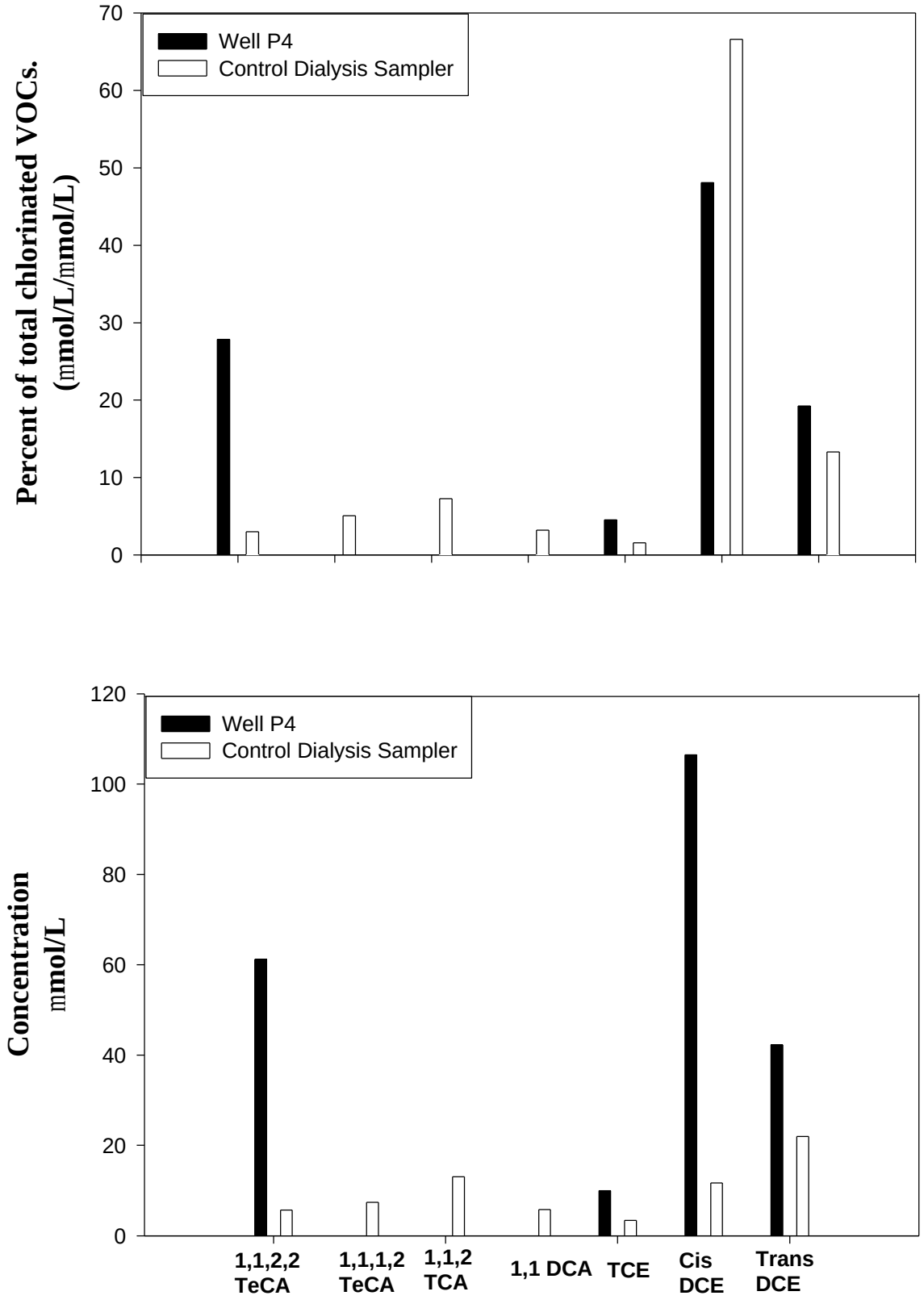

FIGURE 15 Concentration and Percent Distribution Comparison of Chlorinated VOCs in Well P4 versus the Average of the Control Dialysis Sampler

The vertical distribution of VOCs in the control dialysis sampler serves as a useful baseline for comparison of the dialysis sampler inserted near tree 55. Wells or piezometers are unlikely to be able to detect variations caused by plant root interactions. Therefore, comparing concentrations and percent distributions between dialysis samplers inserted in unvegetated and vegetated areas should give an indication of the importance of microscale effects caused by roots.

Concentrations of dissolved gases (ethene, ethane, and methane) in the dialysis sampler indicate that reductive dechlorination is occurring in the region sampled (Table 8). Relatively high concentrations of ethene and ethane were measured, indicative of complete biodegradation of chlorinated ethenes and ethanes in the region of the control dialysis sampler. Similarly, methane was detected in relatively high concentrations, providing evidence of completely reducing conditions near this region.

Concentrations of organic acids and the summed carbohydrates measured in the control dialysis sampler were similar to those measured in the wells (Table 9). Although some differences do exist, it is reasonable to assume that these differences represent the natural variability of these substances in the surficial aquifer. Chloroacetic acids (mono-, di-, and trichloroacetic acids) were not detected. These acids are potential degradation products of chlorinated ethenes in poplar trees.

TABLE 8 Concentrations of Dissolved Gases in Control Dialysis Sampler Cells

Cell	Depth of Cell (cm)	Ethene (ppbw)	Ethane (ppbw)	Methane (ppmw)	CO_2 (ppmw)
C1	187	31.05	29.43	1.66	6.32
C2	194.5	31.59	29.91	1.54	5.40
C3	202	34.61	29.83	1.71	6.59
C4	209.5	17.61	14.13	6.28	4.55
C5	217	23.49	20.35	6.11	5.77
C6	224.5	22.00	18.90	6.46	4.99
C7	232	45.89	41.73	6.25	8.29
C8	239.5	21.14	20.51	1.21	5.18
C9	247	41.26	40.31	1.58	7.49
C10	254.5	21.31	21.39	3.95	3.99
C11	262	29.49	26.29	1.55	6.09
C12	269.5	36.26	31.72	2.24	7.48
C13	277	29.15	25.49	2.86	6.55
C14	284.5	18.36	15.02	3.81	3.81
C15	292	10.39	8.40	0.83	2.07
C16	299.5	11.34	7.06	0.87	3.49

TABLE 9 Concentrations of Organic Acids and Carbohydrates in Control Dialysis Sampler Cells

Cell	Depth of Cell (cm)	Concentrations (mg/L)							
		Succinate	Lactate	Formate	Acetate	Butyrate	Propionate	Benzoate	Carbohydrates
C1	187	<0.5	19.74	<0.5	6.52	<0.5	11.40	<0.5	8.4
C2	194.5	<0.5	29.02	<0.5	<0.5	<0.5	9.99	<0.5	3.5
C3	202	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
C4	209.5	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
C5	217	<0.5	19.86	<0.5	5.23	<0.5	6.30	<0.5	4.6
C6	224.5	<0.5	13.01	<0.5	7.58	<0.5	5.59	<0.5	12.8
C7	232	<0.5	27.36	<0.5	11.54	<0.5	16.11	<0.5	19.8
C8	239.5	<0.5	20.26	<0.5	7.85	<0.5	7.37	<0.5	4.5
C9	247	<0.5	18.60	<0.5	23.71	<0.5	15.59	<0.5	16.8
C10	254.5	<0.5	19.45	<0.5	9.59	<0.5	12.57	<0.5	12.4
C11	262	<0.5	17.49	<0.5	20.99	<0.5	16.22	<0.5	13.9
C12	269.5	<0.5	17.03	<0.5	28.14	<0.5	24.46	<0.5	17.5
C13	277	<0.5	20.82	<0.5	25.60	<0.5	23.32	<0.5	5.2
C14	284.5	<0.5	18.19	<0.5	4.44	<0.5	11.25	<0.5	1.5
C15	292	<0.5	22.60	<0.5	6.47	<0.5	6.44	<0.5	6.8
C16	299.5	<0.5	16.40	<0.5	4.94	<0.5	<0.5	<0.5	6.5

3.2.2 Tree 55 Dialysis Sampler

The dialysis sampler inserted in the poplar grove at tree 55 sampled from 7.4 to 11.3 ft (2.25 to 3.45 m) BGS. This depth was chosen on the basis of water levels in wells near the sampler insertion point. The top of the dialysis sampler was approximately 12 in. (30 cm) below the water level. Examination of the core removed by the Geoprobe™ during insertion revealed the presence of roots above and within the sample zone. The top 6 ft (1.8 m) of the core (0-6 ft [0-1.8 m] BGS) was very dry and consisted mainly of silty sands, clays, and silt layers (Figure 16). Saturated sediments appeared to start at approximately 7 ft (2.13 m) BGS, with a moist but visually nonsaturated layer of clayey silt directly above this layer. The sample zone was completely saturated and consisted mainly of sand with a silty sand layer in the top portion (Figure 16). Of particular interest were the root systems, visually identified at approximately 9 ft (2.74 m) BGS. In addition, from approximately 9.3 to 11 ft (2.85 to 3.34 m) BGS a deeply red colored sand was identified with metal precipitate or debris, presumably iron present at the bottom of the boring (Figures 16 and 17).

The same chlorinated VOCs detected in the control dialysis sampler were detected in the tree 55 dialysis sampler. No 1,2-DCA, 1,1-DCE, PCE, or VC was present at concentrations exceeding 250 ppb (Tables 10 and 11). A number of cells did not yield sufficient water to test (cells at 246 cm, 313.5 cm, and 336 cm). With the exception of the last cell, which was cracked, the other cells were saturated when installed. The cell at 246 cm corresponds closely to the identified depth of a root. Uptake of water from the cell by the root system is a possible explanation for this loss of volume.

FIGURE 16 Photograph of Geoprobe™ Core Taken from the Insertion Point of Tree 55 Dialysis Sampler

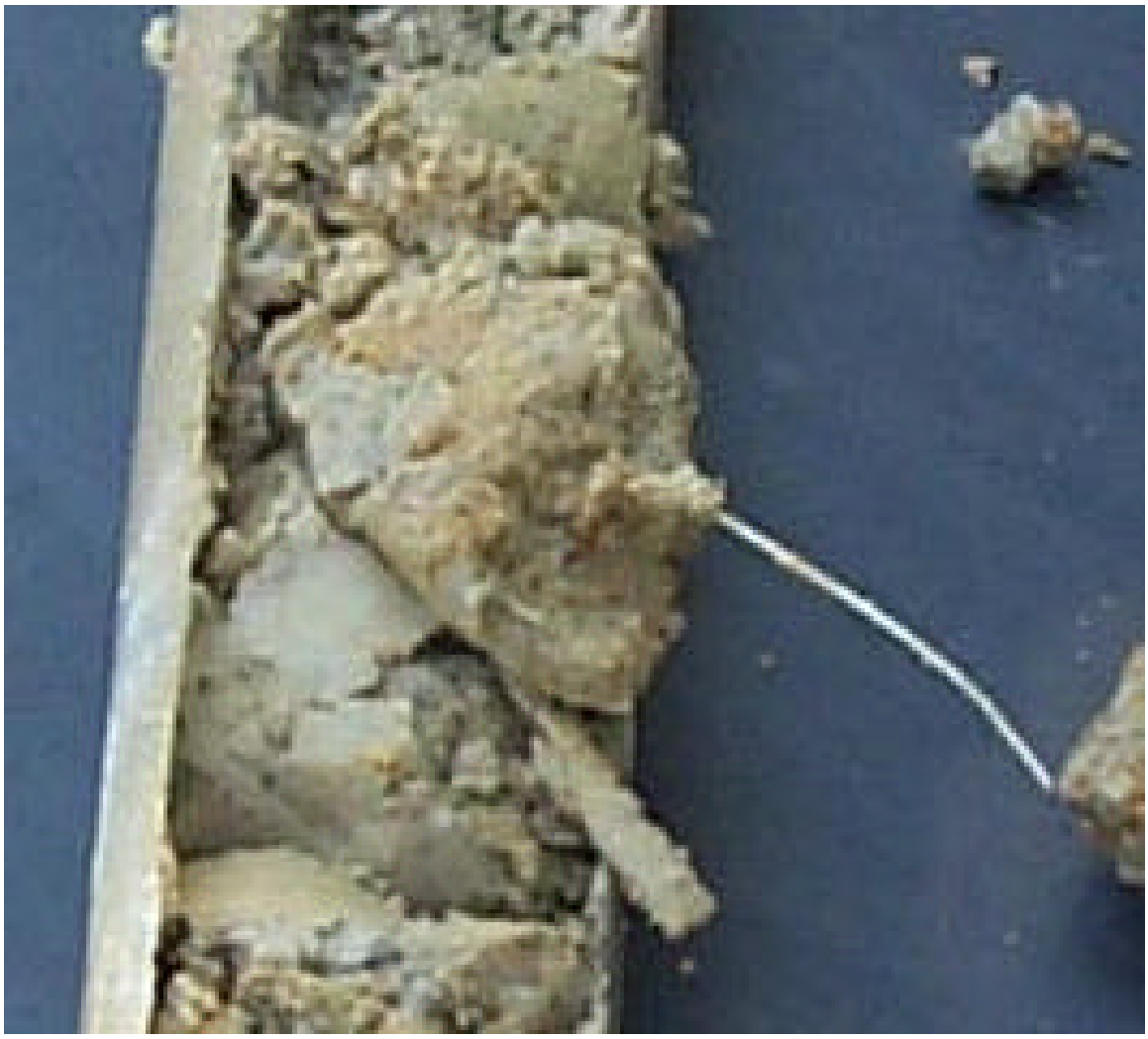

FIGURE 17 Closeup of Root Found in Soil Core Taken from the Insertion Depth of the Tree 55 Dialysis Sampler

TABLE 10 Concentration of Chlorinated VOCs in the Tree 55 Dialysis Sampler

Cell	Depth of Cell BGS (cm)	1,1,2,2-TeCA (µmol/L)	1,1,1,2-TeCA (µmol/L)	1,1,2-TCA (µmol/L)	1,1-DCA (µmol/L)	TCE (µmol/L)	*cis*-1,2-DCE (µmol/L)	*trans*-1,2-DCE (µmol/L)	Cl^- (mmol/L)
P1	231	227.1	7.83	6.52	0.42	41.54	54.9	16.98	N/S
P2	238.5	14.76	7.59	4.09	1.77	21.77	30.83	6.67	N/S
P3	246	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P4	253.5	8.37	7.65	8.79	1.46	16.38	24.9	4.69	3.78
P5	261	47.53	7.89	1.52	0.83	10.08	18.13	2.92	2.91
P6	263.5	50.0	6.87	2.58	1.15	11.46	15.21	3.33	2.71
P7	268.5	142.65	8.25	3.56	4.9	56.23	56.88	17.92	1.47
P8	276	115.96	5.84	7.20	4.27	44.15	53.75	14.27	1.72
P9	283.5	116.0	7.53	BDL	4.27	41.54	52.08	13.85	1.92
P10	291	113.2	8.61	14.24	4.48	51.00	59.38	16.46	1.85
P11	298.5	36.63	4.46	18.94	BDL	10.54	14.79	BDL	2.34
P12	306	7.05	BDL	10.15	BDL	6.15	8.33	BDL	1.87
P13	313.5	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P14	321	BDL	BDL	4.47	BDL	5.62	15.42	BDL	1.64
P15	328.5	BDL	4.82	BDL	0.42	5.38	11.98	BDL	1.65
P16	336	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S

TABLE 10 (Cont.)

Cell	Depth of Cell BGS (cm)	1,1,2,2-TeCA (mg/L)	1,1,1,2-TeCA (mg/L)	1,1,2-TCA (mg/L)	1,1-DCA (mg/L)	TCE (mg/L)	*cis*-1,2-DCE (mg/L)	*trans*-1,2-DCE (mg/L)	Cl^- (mg/L)
P1	231	37.7	1.3	0.86	0.04	5.4	5.27	1.63	N/S
P2	238.5	2.45	1.26	0.54	0.17	2.83	2.96	0.64	N/S
P3	246	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P4	253.5	1.39	1.27	1.16	0.14	2.13	2.39	0.45	132
P5	261	7.89	1.31	0.2	0.08	1.31	1.74	0.28	102
P6	263.5	8.3	1.14	0.34	0.11	1.49	1.46	0.32	94.8
P7	268.5	23.68	1.37	0.47	0.47	7.31	5.46	1.72	51.5
P8	276	19.25	0.97	0.95	0.41	5.74	5.16	1.37	60.5
P9	283.5	19.26	1.25	BDL	0.41	5.4	5.0	1.33	67.4
P10	291	18.79	1.43	1.88	0.43	6.63	5.7	1.58	64.8
P11	298.5	6.08	0.74	2.5	BDL	1.37	1.42	BDL	82.0
P12	306	1.17	BDL	1.34	BDL	0.8	0.8	BDL	65.5
P13	313.5	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P14	321	BDL	BDL	0.59	BDL	0.73	1.48	BDL	57.7
P15	328.5	BDL	0.8	BDL	0.04	0.7	1.15	BDL	58.0
P16	336	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S

TABLE 11 Percent of Total Chlorinated VOCs in the Tree 55 Dialysis Sampler [100 ´ (mmol/L)/(mmol/L [total])]

Cell	Depth of Cell (cm)	1,1,2,2 TeCA	1,1,1,2 TCA	1,1,2-TCA	1,1 DCA	TCE	*cis*-1,2-DCE	*trans*-1,2-DCE
P1	231	63.92	2.20	1.83	0.12	11.69	15.45	4.78
P2	238.5	16.87	8.68	4.68	2.02	24.88	35.25	7.62
P3	246	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P4	253.5	11.59	10.59	12.17	2.02	22.68	34.36	6.49
P5	261	53.47	8.88	1.70	0.94	11.34	20.39	3.28
P6	263.5	55.19	7.58	2.84	1.26	12.65	16.79	3.68
P7	268.5	49.13	2.84	1.23	1.69	19.36	19.59	6.17
P8	276	47.25	2.38	2.93	1.74	17.99	21.9	5.81
P9	283.5	19.31	3.20	BDL	1.82	17.65	22.13	5.89
P10	291	42.34	3.22	5.33	1.68	19.08	22.21	6.16
P11	298.5	42.91	5.22	22.19	BDL	12.35	17.33	BDL
P12	306	22.24	BDL	32.04	BDL	19.42	26.3	BDL
P13	313.5	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P14	321	BDL	BDL	17.53	BDL	22.02	60.45	BDL
P15	328.5	BDL	21.32	BDL	1.84	23.83	53.01	BDL
P16	336	N/S	N/S	N/S	N/S	N/S	N/S	N/S

No generalizations can be made about the profile of VOCs as was observed in the control dialysis sampler. Distributions of compounds varied markedly with depth (Figure 18). Total concentrations of chlorinated VOCs range from a high of 355 µmol to a low of 22 µmol (Table 10). Three compounds dominate: 1,1,2,2 TeCA, TCE, and cis-1,2-DCE. Concentrations of cis-1,2-DCE are higher than TCE at all depths suggesting substantial degradation of TCE. 1,1,2,2-TeCA concentrations change dramatically with depth. Through much of the dialysis sampler, there appears to be as much parent compound (1,1,2,2-TeCA) as combined daughter products (*cis*-1,2-DCE, *trans*-1,2-DCE, 1,1 DCA and 1,1,2-TCA). However in cells adjacent to the two cells that were missing water (246 and 315 cm BGS) the amount of 1,1,2,2-TeCA decreases with corresponding increases in *cis*-1,2-DCE and 1,1,2 DCA (Figure 19).

Of interest is the comparison of the distribution of chlorinated VOCs detected in nearby wells with those detected in the tree 55 dialysis sampler. Figure 20 compares the concentrations and percent distribution at piezometer GP-A01 and GP-23 with those found at depths representative of various distributions in the dialysis sampler. Much higher concentrations of chlorinated VOCs were measured in both wells than in the tree 55 dialysis sampler. Examination of the percent distribution indicated that P1 and P8 cells, representative of nondegraded profiles and high concentrations of VOCs, were quite similar to the piezometer distribution profile. Dialysis sampler cells near suspected or known root systems had extremely low concentrations and highly degraded percent distribution profiles, very dissimilar to those of the wells. This finding strongly suggests a microscale influence as could be produced from a root system.

Concentrations of dissolved gases (ethene, ethane, and methane) were much lower in the tree 55 sampler than observed in the control dialysis sampler (Table 12). These findings are strong indicators that the environment of the poplar rhizosphere is less reducing than the upgradient surficial aquifer, perhaps encouraging the oxidation of progeny products.

Concentrations of organic acids and the summed carbohydrates in the tree 55 dialysis sampler were similar to those measured in the wells (Table 13). Although some differences do exist, it is reasonable to assume that those differences represent the natural variability of these substances in the surficial aquifer. Measurements of chloroacetic acids (mono-, di, and trichloroacetic acids) were all inconclusive. Strictly speaking, measurements were below the lowest point on the calibration curve, but a measurable peak was observed with the same retention time and identifying ions as dichloroacetic acid. A larger water sample was needed to increase the detection of this compound. A sufficiently large water sample to analyze for this compound should be collected in future analyses.

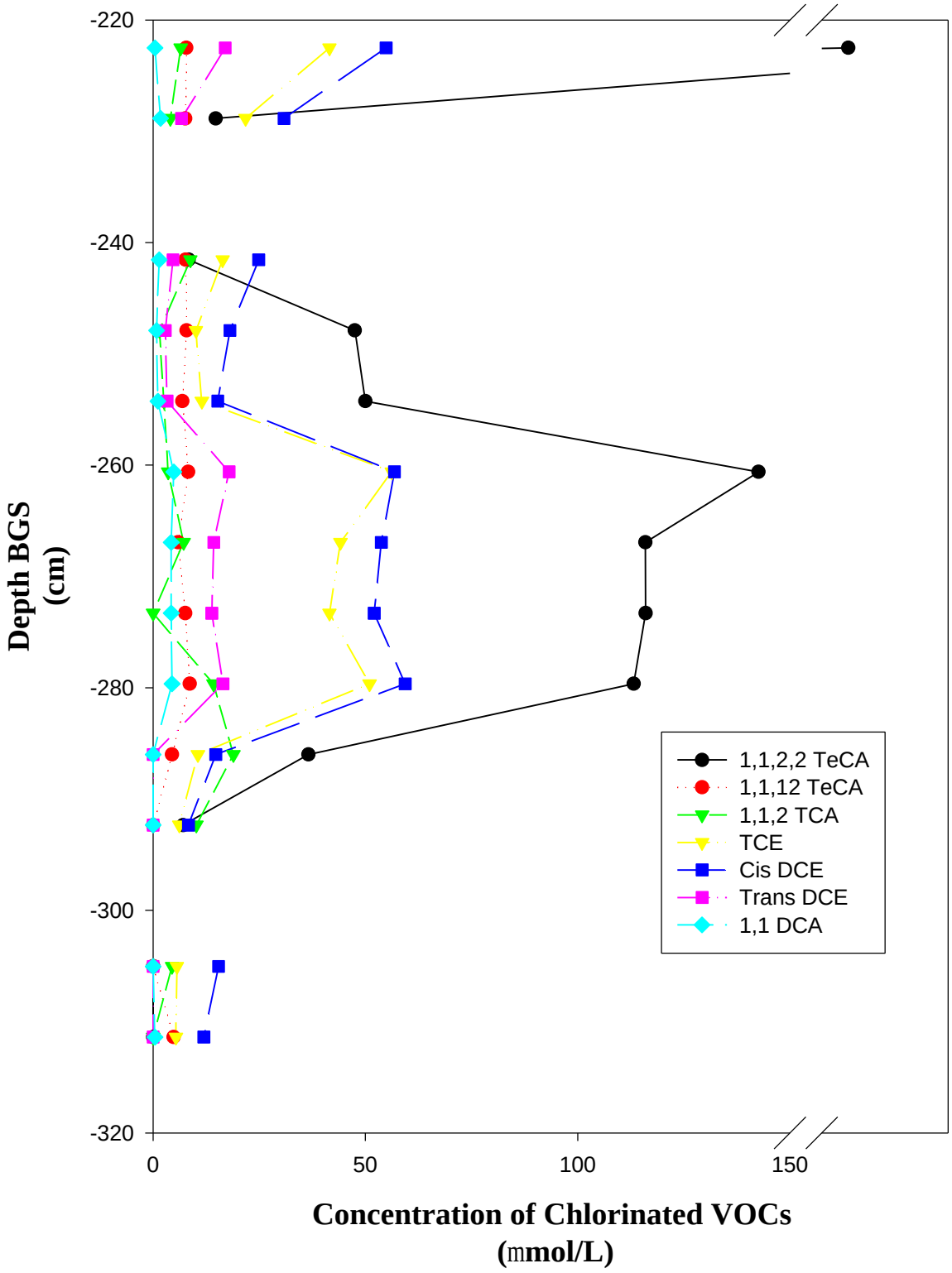

FIGURE 18 Concentration of Chlorinated VOCs in Tree 55 Dialysis Sampler

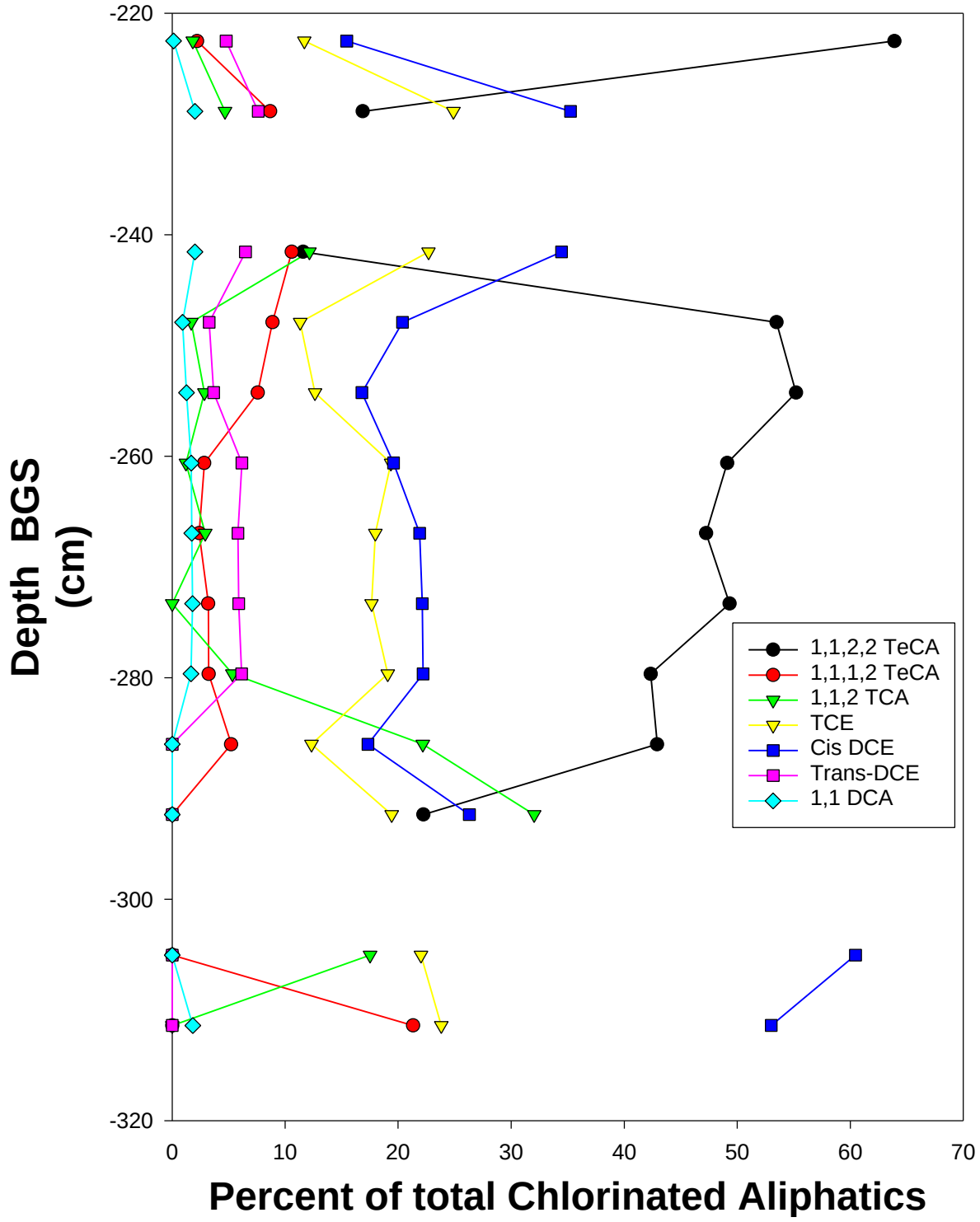

FIGURE 19 Percent of Total Chlorinated VOCs Distribution in the Tree 55 Dialysis Sampler

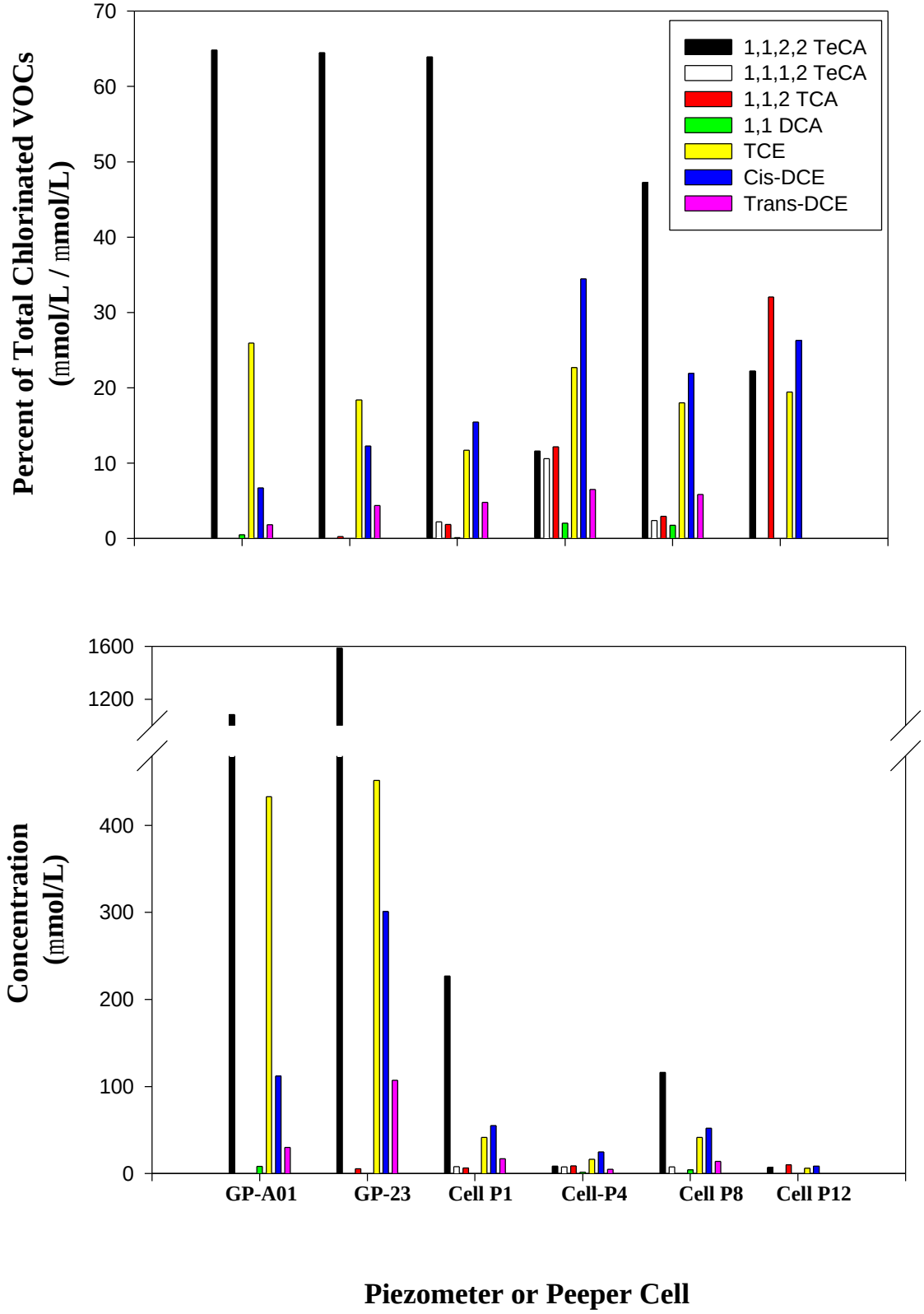

FIGURE 20 Comparison of the Concentration and Distribution of Chlorinated VOCs between Selected Cells of the Tree 55 Dialysis Sampler and Nearby Piezometers

TABLE 12 Concentrations (parts per million or billion by weight) of Dissolved Gases in Tree 55 Dialysis Sampler Cells

Cell	Depth of Cell (cm)	Ethene (ppbw)	Ethane (ppbw)	Methane (ppmw)	CO_2 (ppmw)
P1	231	NS	NS	NS	NS
P2	238.5	NS	NS	NS	NS
P3	246	NS	NS	NS	NS
P4	253.5	NS	NS	NS	NS
P5	261	3.16	<0.5	0.28	2.45
P6	263.5	2.61	<0.5	0.28	3.50
P7	268.5	7.60	4.68	0.75	3.33
P8	276	15.32	7.95	2.45	4.20
P9	283.5	23.09	15.87	1.50	5.09
P10	291	21.60	11.68	1.24	3.74
P11	298.5	1.72	13.68	0.73	2.18
P12	306	7.28	4.16	0.64	1.17
P13	313.5	4.65	<0.5	0.28	1.25
P14	321	7.63	5.97	0.89	0.75
P15	328.5	NS	NS	0.28	NS
P16	336	NS	NS	0.28	NS

TABLE 13 Concentrations of Organic Acids in Tree 55 Dialysis Sampler Cells

Cell	Depth of Cell (cm)	Concentrations (mg/L)							
		Succinate	Lactate	Formate	Acetate	Butyrate	Propionate	Benzoate	Carbohydrates
P1	231	<0.5	23.84	<0.5	4.85	<0.5	18.33	<0.5	8.2
P2	238.5	<0.5	19.42	<0.5	4.31	<0.5	17.37	<0.5	6.8
P3	246	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P4	253.5	<0.5	14.61	<0.5	3.33	<0.5	17.08	<0.5	7.3
P5	261	<0.5	20.74	<0.5	9.00	<0.5	11.68	<0.5	6.2
P6	263.5	<0.5	21.21	<0.5	6.94	<0.5	1.04	<0.5	3.0
P7	268.5	<0.5	21.13	<0.5	5.93	<0.5	<0.5	<0.5	12.5
P8	276	<0.5	20.81	<0.5	4.35	<0.5	<0.5	<0.5	18.4
P9	283.5	<0.5	23.86	<0.5	8.30	<0.5	6.36	<0.5	1.5
P10	291	<0.5	15.91	<0.5	5.09	<0.5	<0.5	<0.5	4.2
P11	298.5	<0.5	18.07	<0.5	6.97	<0.5	1.71	<0.5	16.8
P12	306	<0.5	21.48	<0.5	6.01	<0.5	2.54	<0.5	14.7
P13	313.5	<0.5	24.14	<0.5	20.24	<0.5	32.84	<0.5	6.3
P14	321	<0.5	23.39	<0.5	6.22	<0.5	8.27	<0.5	7.4
P15	328.5	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
P16	336	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S

4 CONCLUSIONS AND RECOMMENDATIONS

This study reports the first high-resolution dialysis sampling data from the root zone of poplar trees used for phytoremediation. The approach was developed as an improved method of performance monitoring for phytoremediation technologies. Dialysis samplers were designed and installed in the rhizosphere of one of the existing trees (tree 55) and in an upgradient location without vegetation at the J-Field Area of Aberdeen Proving Ground.

For these samplers, depressions (or cells) were drilled in a solid Plexiglas rod. Deionized water was placed in the cells, and the cells were covered with a membrane filter sheet (0.45 μm). After the sampler was inserted into the ground, constituents in the groundwater diffused across the membrane into the dialysis sampler cell. After a period of equilibration, samplers were retrieved and the water in each cell was sampled and analyzed. Because the sampler can be constructed to any specification, the resolution or spacing of the samples can be specified in the design.

The data collected from the control and tree 55 samplers revealed several results of note:

1. The VOC depth profile from the control location was relatively constant, with variability on the order of 10%. Both the relative composition of the chlorinated VOC profile and the absolute concentration were relatively constant throughout the sampler depth.

2. The upgradient control dialysis sampler samples showed strong evidence of reductive dechlorination. The evidence included: high concentrations of ethane, ethane, and methane; and a high ratio of progeny products (*cis*-1,2-DCE) to parent compounds (1,1,2,2-TeCA and TCE). The results were consistent with previous monitored natural attenuation sampling in this location of the surficial aquifer.

3. In the tree 55 dialysis sampler, the VOC depth profile was highly variable in both absolute concentration and the relative concentration of parent and progeny products. This variability was enhanced in the vicinity of several "dry" cells in the dialysis sampler, presumably because of the strong suction of nearby roots. This highly variable profile is indicative of highly spatially variable biodegradation and uptake near the active roots. The scale of this variability appears to be centimeters, emphasizing the importance of these high-resolution samplers.

4. Analysis of dissolved gases from tree 55 dialysis sampler indicated a less favorable environment for reductive dechlorination than in the control location. Progeny product ethane and ethene concentrations were substantially lower and methane concentrations were also low. These findings are strong

indicators that the environment of the poplar rhizosphere is less reducing than the upgradient surficial aquifer, perhaps encouraging the oxidation of progeny products.

5. Measurements of potential root exudates (organic acids and carbohydrates) in both dialysis samplers and upgradient and downgradient wells did not indicate that a large input of carbon is occurring as water is passing through the grove.

6. Monochloro-, dichloro- and trichloroacetic acids were measured because these compounds have been identified as degradation products of chloroethenes in poplars. Results were below detection in the control location. In the tree 55 dialysis sampler, measurements were inconclusive. Strictly speaking measurements were below the lowest point on the calibration curve, but a measurable peak was observed with the same retention time and identifying ions as dichloroacetic acid. More water was needed to increase the detection of this compound. Sufficient water for this analysis should be collected in future analyses.

In summary, these results suggest that the impact of the rhizosphere on the chlorinated VOCs is spatially variable and needs to be studied further on the measurement scale employed in this study. The initial measurements using this sampling technique suggest that the rhizosphere is a less reducing environment. The results represent only one tree with possibly an underdeveloped root system compared with other trees in the grove. Further studies should utilize this measurement technique to assess spatial changes in chlorinated VOCs as groundwater moves through the entire grove.

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APPENDIX A:

STANDARD OPERATING PROCEDURES FOR SELECTED ANALYTICAL TECHNIQUES

CFR Biotechnologies, Inc.

GC-MS ANALYSIS FOR VOLATILE ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 This method is a quantitative procedure for volatile organic compounds (VOCs) from waters and soils using gas chromatography equipped with a mass-selective detector.

2.0 SUMMARY OF METHOD

2.1 The method utilized is SW 846 Method 8260B with the modifications listed below.

3.0 MODIFICATION

3.1 Reduced analyte list- For each application, the analyte list is reduced to only those compounds that are of interest. For example, if solvents are of interest, only the subset of chlorinated solvents (ethenes and ethanes) are analyzed.

3.2 The column utilized is a narrow-bore (0.25 mm) DB-5 column with a thin-film thickness (0.25 micron). This is not one of the 4 recommended columns but is very similar to the 1 micron DB-5 column recommended as column 3. We obtain satisfactory results meeting all criteria with this DB-5 column using cryofocusing (to -80°C) as described in the method. Use of this column allows us to switch between VOA and semi-VOA analyses without the need to vent the GC-MS system and change the column.

4.0 APPARATUS AND MATERIALS

As described in Method 8260B.

5.0 REAGENTS

As described in Method 8260B.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

As described in Method 8260B.

7.0 PROCEDURE

As described in Method 8260B.

8.0 QUALITY CONTROL

As described in Method 8260B.

9.0 REFERENCES

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CFR Biotechnologies, Inc.

HPLC ANALYSIS FOR ORGANIC ACIDS AND OTHER ROOT EXUDATES

1.0 SCOPE AND APPLICATION

1.1 This method is a quantitative procedure for organic acids in water using the high-pressure liquid chromatograph with a diode array detector. This modification of the method is designed to detect additional analytes that could be classified as root exudates from vegetation.

2.0 SUMMARY OF METHOD

2.1 Two aliquots of the sample are removed. One aliquot of sample is preserved with phosphoric acid and filtered through a 0.2 μm syringe filter. This is termed the *acid* sample. The other is filter through a 0.2 μm syringe filter and not preserved. This is termed the *sugar* sample. The filtrate is injected onto the HPLC and response compared with an external standard calibration curve for quantitation. For the acid sample, the organic ions analyzed by this technique include mugineic acid, malate, citrate, oxalate, lactate, succinate, benzoate, butyrate, acetate, formate and propionate. For the sugar sample, peak locations and areas are quantified. Identity of the compounds is pursued using other techniques, if necessary.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents and glassware. All these materials must be routinely demonstrated to be free from contaminants by running laboratory reagent blanks.

3.2 The UV-VIS detector on the HPLC is sensitive to all dissolved organic compounds and has high sensitivity to aromatic compounds. For example, response to benzoate is 10x higher than non-aromatic organic acids. Therefore, aromatic contaminants can provide a potent source of interferences.

4.0 APPARATUS AND MATERIALS

4.1 Balance: analytical, capable of accurately weighing 0.0001 gm

4.2 High performance liquid chromatograph: An analytical system complete with HPLC suitable for low-level analysis including all required accessories including syringes, analytical columns, gases, detectors, pumps, mobile phases and data system for measuring peak heights and areas.

4.2.1 Detector: Diode array detector

4.2.2 HPLC column: For the acid sample, Supelco C-610H (sulfonated polystyrene/divinylbenzene, spherical, 9 um), 25 cm length, 4.6 mm id) or equivalent column. For the sugar sample, a ZORBAK Eclipse XDB Reversed Phase HPLC column is used.)

4.3 Vials and caps: 2 mL for HPLC autosampler

4.4 Volumetric flasks: 10- 50- and 100-mL with ground glass stopper or Teflon-lined screw cap

4.5 Pasteur pipets: Disposable

4.6 0.2 um syringe filters: Whatman or equivalent

5.0 REAGENTS

5.1 Water: HPLC grade or equivalent

5.2 Phosphoric acid: ACS grade or equivalent

5.2.1 Mobile phase: 0.1% in HPLC-grade water- filtered through 0.45 μm filter and degassed using vacuum system

5.2.2 Preservation solution: 8 N solution of H_3PO_4 in HPLC water

5.3 Stock standard solution (0.1 g/100 mL): Stock standards must be prepared from pure standard materials.

5.3.1 Prepare stock materials by accurately weighing 0.01 grams of pure material. Dissolve the material in HPLC grade water in a 100 mL volumetric flask. Preserve with phosphoric acid solution: 50 uL 8N H_3PO_4 per 10 mL of solution. Store at 4°C.

5.4 Standard mixture #1: a low level standard curve is used for field samples. Standards are prepared by dilution of the stock solutions above to the following levels: 0.5 mg/L, 1.0 mg/L, 5 mg/L, 10 mg/L and 20 mg/L

5.5 Standard mixture #2: a high level standard curve is used for high level field samples and for the treatability studies. Standards are prepared by dilution of the stock solutions above to the following levels: 10 mg/L, 20 mg/L, 50 mg/L, 100 mg/L and 200 mg/L

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Water samples are collected from purged groundwater wells and transferred to clean glass bottles. Samples for organic acid analyses should be cooled to 8°C if filtration cannot be performed in the field. When possible, an aliquot of sample (5-10 mL) should be filtered through a 0.2 um syringe filter and preserved with phosphoric acid as described above.

6.2 When preserved, samples are stable indefinitely (Batelle, 1998). CFR runs samples within 21 days of preservation.

7.0 PROCEDURE

7.1 Sample preparation: Allow the preserved sample to reach room temperature and pipet 1 mL into an HPLC autosampler vial.

7.2 HPLC conditions: Flowrate: 0.5 mL/minute, column temperature: 40°C isothermal, injection volume: 150 uL

7.3 Analysis:

7.3.1 **Calibration:**

7.3.1.1 External standard calibration: The HPLC must be calibrated every 24 hours for half of full-scale response when injecting 150 uL of standard mixture #1 or #2

7.3.2 **HPLC analysis:** Inject the same volume of sample as was injected for the standards used to perform the external standards calibration. HPLC conditions must be the same for standard and sample.

7.4 Interpretation of chromatogram: The chromatogram is interpreted by the analyst for peak identification, the presence of peak splitting and the baseline. If the data system has not correctly performed these tasks, corrective action in the form of adjustment of the baseline and the integration parameters is performed.

8.0 QUALITY CONTROL

8.1 Blanks: Reagent water blanks are run daily to ensure the integrity of he analysis system

8.2 Matrix spikes/matrix spike duplicates (MS/MSD): Matrix spikes and matrix spike duplicates are used to assess accuracy and precision of the method daily. The MS level is at 2x the lowest standard. Percent recoveries should be within 25% of expected. Relative percent difference should be less than 25% or corrective action is initiated.

8.3 Continuing calibration check: External standard calibration is performed daily as described above. If the % difference of the continuing calibration check is >20%, samples are not run and the instrument and standards are assessed and problems corrected.

9.0 REFERENCES

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CFR Biotechnologies, Inc.

GC-MS ANALYSIS FOR TCE METABOLITES IN WATER

1.0 SCOPE AND APPLICATION

1.1 This method is a quantitative procedure for measuring water-soluble TCE metabolites using gas chromatography equipped with a mass-selective detector. The Method is based on Standard Methods 6233 (Disinfection byproducts) with the modifications listed in Section 3.0 below.

2.0 SUMMARY OF METHOD

2.1 The method utilizes GC-MS to analyze three metabolites di- and trichloroacetic acid and trichloroethanol following derivitization using diazomethane in MTBE.

3.0 MODIFICATION

3.1 Reduced analyte list- For each application, the analyte list is reduced to only those compounds that are of interest. In this case, the chloroacetic acids and trichloroethanol.

3.2 Trichloroethanol and parent TCE are measured on a separate sample aliquot from the chloroacetic acids. Details of this separate measurement are provided below.

3.3 GC-MS is utilized instead of electron capture detection. While this raises the detection limit, it provides the ability to confirm detection of these analytes without relying on retention times solely.

4.0 APPARATUS AND MATERIALS

4.1 Details for the apparatus are provided in the attachment (Method 6223) for the chloroacetic acid analyses. The same materials are utilized for the trichloroethanol analysis.

5.0 REAGENTS (Details in attachment)

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Water samples are collected from purged groundwater wells and transferred to clean 40 mL VOA vials without headspace.

6.2 It is assumed that holding times are similar to VOAs from Method 8260B.

7.0 PROCEDURE

7.1 Extraction. Water samples for chloroacetic acid analysis are extracted using concentrated H_2SO_4 and MTBE as described in the attached method 6233. For the trichloroethanol, a separate 10 mL aliquot is extracted with 4 mL of MTBE and the mixture vortexed for 30 s. 3 mL of the MTBE is drawn off and dried over 2 g of Na_2SO_4 for 2 hours at room temperature. One milliliter of the MTBE extract will be spiked with 10 uL of an internal standard (25 mg/mL of dibromochloropropane in MTBE). This extract will contain TCE and trichloroethanol.

7.2 Analyses will be conducted on a 1 uL subsample of the extract on a GC-MS using the temperature program described in Method 6223.

8.0 QUALITY CONTROL (details in attached method)

9.0 REFERENCES

APHA-AWWA-WEF, *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992, A.E. Greenberg, L.S. Clesceri and A.D. Eaton (eds.).