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Solvent Release into a Sandy Aquifer. 1. Overview of Source Distribution and Dissolution Behavior

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This paper describes some of the results from a field experiment at the Canadian Forces Base Borden, Ontario, Canada. Five liters of a chlorinated solvent mixture (2.0 L of trichloroethylene, 0.5 L of chloroform, and 2.5 L of tetrachloroethylene) was released into a sandy aquifer to create a heterogeneously distributed source. The dissolution and dissolved-phase plume development from this source were studied in detail along a cross-section downgradient of the source for a period of approximately 1 yr. At the conclusion of the experiment, the site was excavated to map the actual distribution of solvent residuals in the subsurface. Dissolved-phase concentrations exceeded 10% of the effective solubility of the individual components in the portion of the plume directly downgradient of the source, providing a strong indication of the presence of dense nonaqueous-phase liquids (DNAPLs). Dissolved-phase concentrations in several sampling points exceeded 50% of the effective solubility. However, even with detailed groundwater monitoring, it was not possible to determine the small-scale distribution of the DNAPL source. Lower dissolved concentrations occurred deeper than the DNAPL source zone, likely as a result of vertical groundwater flow caused by fluctuations in the water table elevation. Spatial delineation of the dissolved-phase plume downgradient of the source correlated generally to the lateral and vertical location of the DNAPL source. The distance between the DNAPL source and the downgradient sampling cross section could be determined from breakthrough curves for some of the sampling points but not for others because slow expansion of the DNAPL zone continued for some time during the dissolution experiment.

Introduction

Groundwater contamination by organic chemicals from sources such as leaking underground storage tanks, chemical spills, and waste disposal facilities has become a significant environmental problem. Chlorinated solvents are the organic contaminants detected most frequently in groundwater at such sites (*1*). Chlorinated solvents are liquid chemicals that have a relatively low solubility in water and a density greater than water (see Table 1) and are commonly referred to as dense nonaqueous-phase liquids or DNAPLs. When released into the subsurface environment, their high density and low solubility allow DNAPLs to penetrate downward through the unsaturated zone and into the groundwater zone as a separate liquid phase. Although chlorinated solvents have a relatively low solubility in water (200−10 000 mg L^{-1}), their solubility values can be from 10^4 to 10^6 times higher than health-based drinking water standards (5−25 μg L^{-1}) (Table 1 and ref *2*). During its migration through the subsurface, a portion of the DNAPL remains trapped as a residual in soil pores. DNAPL may also accumulate in zones, commonly layers or pools, where its further movement is limited by capillary forces. Groundwater that comes into contact with these DNAPL residual zones and accumulations will slowly dissolve the DNAPL. At many sites, dissolved contaminants released from such DNAPL zones have caused large and persistent plumes of groundwater contamination (*3*).

TABLE 1. Physical and Chemical Properties of the Chlorinated Solvents Relevant for This Study

compound	ρ^a (g cm^{-3})	S^b (mg L^{-1})	log (K_{ow})^c (−)	R^d (−)	H^e (−)
chloroform (TCM)	1.48	8700	2.0	1.0	0.10
trichloroethylene (TCE)	1.46	1400	2.3	1.1	0.27
tetrachloroethylene (PCE)	1.62	240	2.6	1.6	0.49

[a] ρ, density (*23*). [b] *S*, aqueous solubility at 23−24 °C (*24*). [c] K_{ow}, octanol/water partition coefficient (*25*). [d] *R*, retardation factor for Borden sand (*10*). [e] *H*, dimensionless Henry's law constant at 17.5 °C (*26*).

The research concerning DNAPL transport and dissolution in saturated and unsaturated porous media has focused on laboratory-scale experiments (*4*−*6*). Only a few field studies involving DNAPL released into the subsurface have been reported in the literature. One such field study involved two different releases of PCE (tetrachloroethylene) into an unsaturated zone to examine the migration of PCE in undisturbed unsaturated sediments (*7*). Two other studies involved PCE releases into the saturated zone (*8, 9*). Another field experiment was conducted to study the dissolution of chlorinated solvents in the groundwater and the plume evolution from a regularly shaped DNAPL source zone consisting of TCM (chloroform), TCE (trichloroethylene), and PCE emplaced in the groundwater zone (*10*).

Previous studies have not examined the dissolution from a heterogeneously distributed source consisting of a mixture of solvents or the possibilities of using detailed downgradient monitoring of the dissolved concentrations to gain information about the nature and spatial distribution of the DNAPL residual. Such information would be valuable in order to apply and/or optimize remedial measures.

The objectives of this field experiment are (i) to interpret the spatial distribution of DNAPL residual by monitoring dissolved concentrations downgradient from the source zone; (ii) to examine the dissolution of heterogeneously distributed DNAPL residual consisting of a mixture of chlorinated solvents; and (iii) to examine the enhanced dissolution of heterogeneously distributed DNAPL residual produced by an injection of a pulse of methanol/water.

This paper is the first of three and gives a description of the experimental site, field instrumentation, a tracer test, the DNAPL release, the monitoring of the dissolved phase, and the concluding excavation of the source zone. However,

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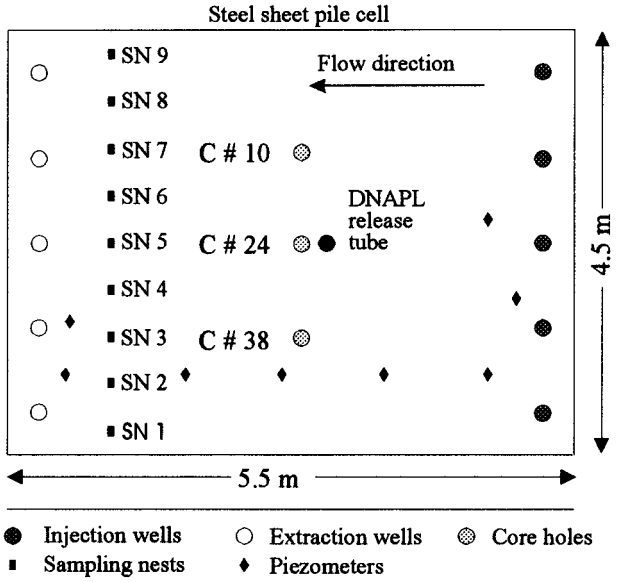

FIGURE 1. Plan view of the cell and the instrumentation. SN 1−9 are the locations of sampling nest 1 to 9; C # 10, 24, and 38 are the locations of the three soil cores used for permeameter tests.

the results will focus only on the first purpose of this experiment: to interpret the spatial distribution of DNAPL residual in the aquifer by monitoring dissolved concentrations downgradient of the source. The interpreted location of the source zone will be compared with the actual distribution of solvent residuals determined by the excavation. The second paper will focus on the results dealing with the dissolution of the solvent mixture. The third paper will present the results of the methanol/water mixture injection.

Materials and Methods

Description of the Field Experiment. The field experiment was carried out in a sandy, unconfined, shallow aquifer at Canadian Forces Base Borden east of Toronto, Ontario, Canada. The aquifer is comprised of medium- to fine-grained lacustrine sand with occasional beds of coarse sand/gravel and of silt and exhibits distinct laminations or bedding features (*11*). Individual beds range from a few millimeters to several centimeters in thickness, and the beds are primarily horizontal (*11*). At the experimental site, the aquifer is about 2.3 m in thickness and is underlain by a 3 m thick clay aquitard.

The experiment was conducted in a 4.5 m × 5.5 m steel sheet pile cell. The sheet piles were vibrated about 0.3 m into the clay to create a contained segment of the aquifer. The joints of the steel sheet piles were sealed to reduce the permeability of the cell wall (*12*). Figure 1 shows a plan view of the cell and the instrumentation, and Figure 2 shows a cross section through the cell.

Groundwater flow through the cell was controlled by means of five injection wells and five extraction wells. The wells (0.05 m i.d., polyethylene) were installed by first water-boring a steel casing (0.1 m i.d.) to the desired depth about 2 m bgs (below ground surface). Then the well was inserted inside the steel casing, and the casing was removed leaving the well in place. The wells had 1.82 m long screens, ending 0.05 m from the bottom of the wells. The bottoms of the wells were located at 1.97 m bgs for the injection wells and at 1.87 m bgs for the extraction wells. Uncontaminated groundwater from the same aquifer was introduced into the injection wells to maintain a constant head of approximately 0.1 m bgs. Water was pumped from each extraction well at a constant rate of approximately 0.05 L min^{-1} (0.25 L min^{-1} in total) creating an average groundwater velocity of approximately 0.1 m day^{-1}, corresponding to the natural groundwater velocity at this site.

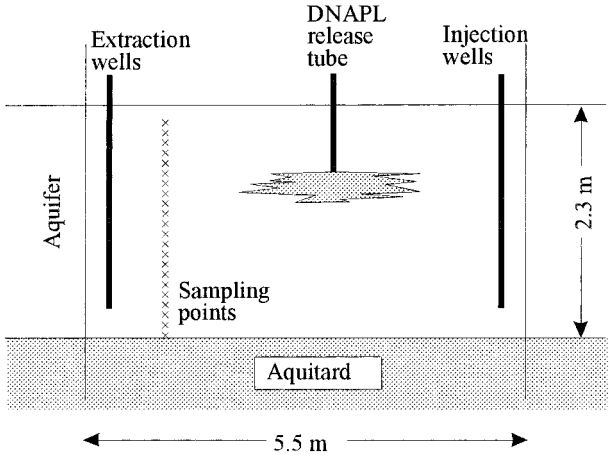

FIGURE 2. Cross section through the cell along the flow direction. The illustration of DNAPL in the figure does not represent the real distribution.

Eight piezometers were installed in the cell 153 days after the DNAPL release to measure the water table elevation (Figure 1). They were constructed of Teflon tubing (0.63 cm i.d.) and installed at a depth of 1.0 m with a 0.1 m long intake zone at the bottom end. The intake zone was made by slotting the tubes with a knife and wrapping with nylon screen (100 mesh). They were installed by driving a steel pipe down to the desired depth. A loose plug was connected to the drive end of the pipe to avoid sand entering the pipe during driving. A piezometer was then lowered into the pipe, which subsequently was removed leaving the piezometer (and the plug) in place. The water level in the piezometers were measured using a small electric water level tape.

A total of 195 stainless steel sampling points (0.63 cm o.d., 0.32 cm i.d.) were installed with a vertical spacing of 0.1 m and a horizontal spacing of 0.5 m to allow very detailed groundwater monitoring. The sampling points ranged in depth from 0.17 to 2.27 m. The bottom end of the sampling point was equipped with a stainless steel tip. The length of the screen on the sampling points was less than 1 cm and located approximately 0.03 m above the bottom of the sampling points. The sampling points were installed by pushing them down as far as possible manually, and then they were hammered down to the desired depth. The sampling points were located in a cross section approximately 0.7 m upgradient from the extraction wells (Figures 1 and 2). Each stainless steel tube was connected to a Teflon tube (0.32 cm o.d., 0.16 cm i.d.) above ground surface. Samples were collected using a sampling manifold and a peristaltic pump. The sampling manifold allowed collection of water samples that had only been in contact with Teflon and stainless steel.

Water samples were collected in 14.5 cm^3 glass vials capped with Teflon-coated silicone rubber septa and sealed with crimp-on aluminum caps. Approximately 80 cm^3 of water was purged from each sampling point prior to sampling. This purge volume proved sufficient to clean the sampling point and all the tubing, thus providing a representative water sample. During the entire experiment (291 days) about 7000 water samples were taken for chlorinated solvents, corresponding to approximately 0.5% of the total volume of water flow through the cell. Thus, the volume removed by sampling was insignificant as compared to the total flow. Water samples were collected approximately every second day during the first 20 days of the experiment, every

third day during the next 4 weeks, and weekly for the rest of the experiment.

Tracer Experiment. A tracer experiment was conducted prior to the solvent release to study the hydraulics and groundwater flow pathways of the aquifer. A 24-h pulse of sodium chloride with an average chloride concentration of 4100 mg L^{-1} was injected in all five injection wells. The chloride concentration was monitored at each sampling point to obtain breakthrough curves that were used to estimate the average groundwater velocity and travel time to each sampling point. The same sampling technique used for chlorinated solvents analysis was used for sampling water for chloride. A total of 5300 water samples was obtained during the tracer test.

Solvent Release. Five liters of a mixture of solvents (10% of TCM, 40% of TCE, and 50% of PCE by volume) was released into a tube (0.05 m i.d., polyethylene) located approximately 0.66 m bgs (Figures 1 and 2). This was approximately 0.05 m below the water table at the time of the solvent release. The tube was only open at the ends (i.e., unscreened). A red dye, Sudan IV (Fischer Scientific, Toronto, Ontario, Canada) was added to the solvent mixture at a concentration of 1 g L^{-1}. The dye is very hydrophobic, which means that the dye stays in the DNAPL phase. Due to the addition of the dye, the DNAPL was readily visible when the site was excavated. The addition of 1 g L^{-1} Sudan IV to the DNAPL does not significantly change the physical properties of the DNAPL (*5*). The solvents were released slowly into the injection tube to maintain a relatively constant DNAPL head (approximately 0.6 m) in the tube. The injection rate was approximately 0.4 L h^{-1} for the first 9.25 h, during which the constant head was maintained. At that time 3.7 L had been injected. After 9.25 h, the constant head was no longer maintained but decreased as a result of the injection. It took approximately 15.6 h to inject the remaining 1.3 L of solvents.

Methanol Injection. After 220 days, a 5.5-day pulse of 30% (vol/vol) methanol in water was injected in order to study the enhanced dissolution caused by the presence of methanol.

Excavation of the Site. The site was excavated 291 days after the DNAPL release in order to determine the actual DNAPL distribution in the soil. Photos were taken to map the DNAPL distribution, and soil samples were obtained for analysis of TCM, TCE, and PCE. The soil was excavated in 0.05-m vertical increments between 0.5 and 0.95 m bgs and in 0.1-m increments down to 1.35 m bgs. Photos were taken of every layer containing visible DNAPL, and soil samples were obtained from every second layer containing visible DNAPL. The soil samples were obtained using a stainless steel 1.8 cm^3 piston sampler. The samples were taken immediately after the excavation of a layer and approximately 0.02 m below the surface in order to avoid sampling where solvents may have evaporated. The samples were transferred to 25 cm^3 glass vials that contained 20 cm^3 of methanol. The vials were capped immediately with Teflon-coated silicone septa and screw caps. The samples were stored in a cooler in the field and later in a laboratory refrigerator at 4 °C until they were analyzed. More than 200 soil samples were taken during the excavation.

Soil Cores. Forty-nine 2.5 m long soil cores were collected in a 0.5-m grid from the experimental site. The cores were obtained in aluminum tubes (0.1 m i.d.) that were driven down using either a regular or an electrical hammer. Where there was a possibility for the core to penetrate locations with solvent residuals, the cores were taken in 0.5 m long pieces, and then the soil around them was removed as the excavation progressed. In that way the migration of contamination along the outside of the core tubes was minimized/controlled. Three of the cores were subdivided into 0.05-m pieces and used for measurements of the hydraulic conductivity by a falling head permeameter technique on small repacked soil columns. The hydraulic conductivities were measured in the laboratory at room temperature (approximately 20 °C) and corrected to the field temperature (10 °C) by multiplying with a factor of 0.77 (*13*). The other cores may be used later for detailed study of the hydraulics of the site.

Analytical Procedures. Chloride was analyzed using a specific chloride electrode (Markson model 92014 digital pH/MV/temp meter, with an Orion chloride combination electrode, model 96178).

Water samples were analyzed for chlorinated solvents on a Varian 3400 gas chromatograph equipped with an electron capture detector (GC−ECD). The gas chromatograph setup was the following: detector temperature 300 °C, column temperature 70 °C, and injector temperature 100 °C. The column from J&W Scientific was 30 m long with an inside diameter of 0.69 mm; the phase was DB624, and the film thickness was 3 μm. The data acquisition was done on a Varian 4400 integrator. Depending upon the actual concentration in the water sample, the sample was either directly extracted in the sampling vials with pentane containing internal standard (dibromoethane) or an aliquot of sample was diluted with organic-free water in another vial and then the diluted sample was extracted with pentane. The pentane phase was analyzed by direct injection.

Soil samples (1.8 cm^3) were extracted with 20 cm^3 of methanol. Dibromoethane was added to each soil−methanol mixture as an internal standard, and the samples were shaken for at least 2 h. The less contaminated samples were analyzed directly by GC−ECD, whereas the more contaminated samples were diluted in methanol containing an internal standard before they were analyzed.

Results

Hydraulic Conditions of the Experiment. The average hydraulic heads in the five injection wells and the five extraction wells are shown in Figure 3. The head in the injection wells was kept constant during the entire experiment at a level of 0.087 m ± 0.004 m bgs. However, the water level in the extraction wells varied between 1.154 and 0.160 m bgs during the experiment. Figure 4 shows the water table and the average heads in the injection and the extraction wells at days 160, 237, and 269. It is evident that the water table fluctuated significantly during the experiment due to the clogging and re-development of primarily the injection wells.

The solid lines in Figure 4 show the best fit of a straight line to the head in the piezometers for each set of data. Theoretically, the water table in an unconfined aquifer should not be a straight line; however, the deviation from the real solution for an unconfined aquifer is not significant. The slope of the lines give the hydraulic gradient in the cell. The average gradient was 0.023 ± 0.0024. The average head in the middle of the cell was estimated to be 0.48 m ± 0.20 m bgs. Based on the average head in the middle of the cell, the average height of the saturated zone (excluding the capillary fringe) was calculated to be 1.82 m. Since, the total pumping rate (0.25 L min^{-1}), the width of the cell (4.5 m), and the porosity of the aquifer (0.33 (*14*)) are known, the average hydraulic conductivity of the aquifer can be estimated as 2.2 × 10^{-5} m s^{-1}. Furthermore, the average groundwater velocity was calculated to be 0.13 m day^{-1}, which is comparable to the natural groundwater velocity at Borden of 0.091 m day^{-1} (*14*).

Tracer Test. Figure 5 shows the estimated groundwater velocities at the sampling points. Each velocity was estimated from a breakthrough curve of chloride using a moment technique (*15*). The estimated velocities varied between 0.048 and 0.21 m day^{-1} with a geometric mean of 0.097 m day^{-1}

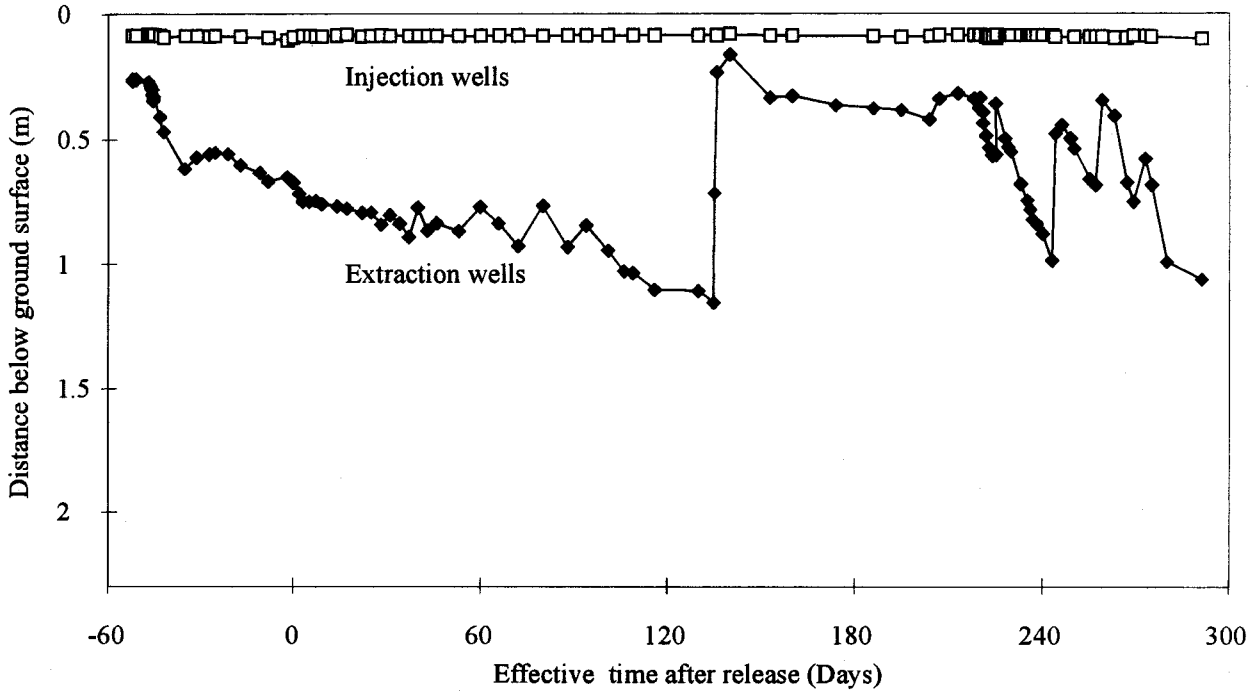

FIGURE 3. Average head in the injections wells (□) and in the extraction wells (■).

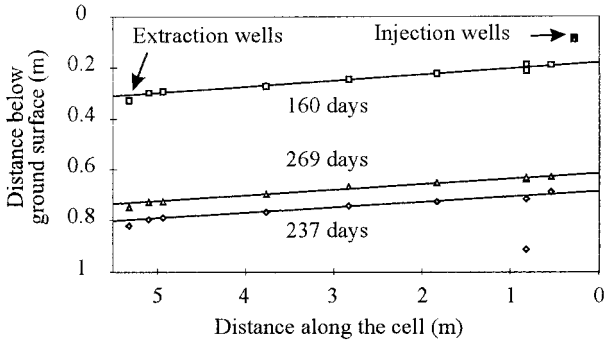

FIGURE 4. Hydraulic head in the piezometers and the average head in the extraction wells and in the injection wells at day 160 (□), day 237 (◇), and day 269 (△). The straight lines are the best fit to the head data of the piezometers.

and an arithmetic mean of 0.10 m day^{-1}. The velocities for sampling nests 1−3 do not vary substantially with depth. The velocities estimated for the other six nests are relatively constant down to about 1.7 m bgs, where the velocities increase toward the bottom of the aquifer. Based on the average hydraulic gradient of 0.023, the range of groundwater velocities can be converted to a range of hydraulic conductivities between 8.0×10^{-6} and 3.5×10^{-5} m s^{-1} with a geometric mean of 1.6×10^{-5} m s^{-1}.

Hydraulic Conductivities from Soil Cores. The hydraulic conductivity was measured on 0.05 m long soil samples obtained from three soil cores. The location of the cores are shown in Figure 1. The hydraulic conductivities based on the soil cores ranged from 1.1×10^{-5} to 8.0×10^{-5} m s^{-1} with a geometric mean of 2.6×10^{-5} m s^{-1} and an arithmetic mean of 2.8×10^{-5} m s^{-1}, which compare well with the hydraulic conductivities estimated from the tracer experiment. The three hydraulic conductivity profiles from the cores (data not shown) show the same trend as the tracer experiment, e.g., increasing hydraulic conductivity toward the bottom for cores 24 and 10 (corresponding to sampling nests 5 and 7 (Figure 5)), and also show higher hydraulic conductivity in the upper portion of the cores.

Dissolved Concentrations. Figure 6 shows the relative concentrations of TCM, TCE, and PCE for some representative sampling points (location SN-5, sampling point 505 (0.57 m bgs), 507 (0.77 m), and 509 (0.97 m)). Sampling points 505, 507, and 509 represent the upper, middle, and lower portions, respectively, of the core of the dissolved plume. The relative concentration is the measured concentration divided by the effective solubility of the compound of interest for the initial solvent mixture. The effective solubility is the aqueous solubility of the compound times the initial mole fraction of the compound in the DNAPL phase (*16*) (1020 mg L^{-1} for TCM, 589 mg L^{-1} for TCE, and 111 mg L^{-1} for PCE).

After 40 days, the relative concentrations measured at sampling point 505 were about 0.5, corresponding to 50% of the initial effective solubility limits. At about 100−130 days, TCM and TCE concentrations declined, likely in response to the declining water table, which would have left the upper portion of the DNAPL source in the unsaturated zone. When the water table rebounded after 130 days, submerging the DNAPL zone, the dissolved concentrations increased to levels higher than those observed during the early part of the experiment. Based on the location of the DNAPL, the water table elevations, and the expected thickness of the capillary fringe, the DNAPL zone was in the unsaturated zone for only a short time. Starting at about 160 days, TCM declined relative to TCE in response to the preferential dissolution of the more soluble TCM from the DNAPL source. This occurred because the mole fraction of TCM in the remaining DNAPL source was decreased, which in turn reduces the solubility of TCM. There was no apparent effect on the dissolved concentrations due to the fluctuations in the water table at sampling point 507. Concentrations were reasonably constant until about 140 days when TCM concentration declined in response to the preferential dissolution. For sampling point 509, the dissolved concentrations were high while the water table dropped until 130 days but declined dramatically when the water table rebounded. The changes in dissolved concentrations observed in these sampling points illustrate that the dissolved plume varied slightly in elevation as the water table fluctuated. Dissolved concentrations approached (>50%) the effective solubility for TCM, TCE, or PCE at least for some time during the experiment in the sampling points in the

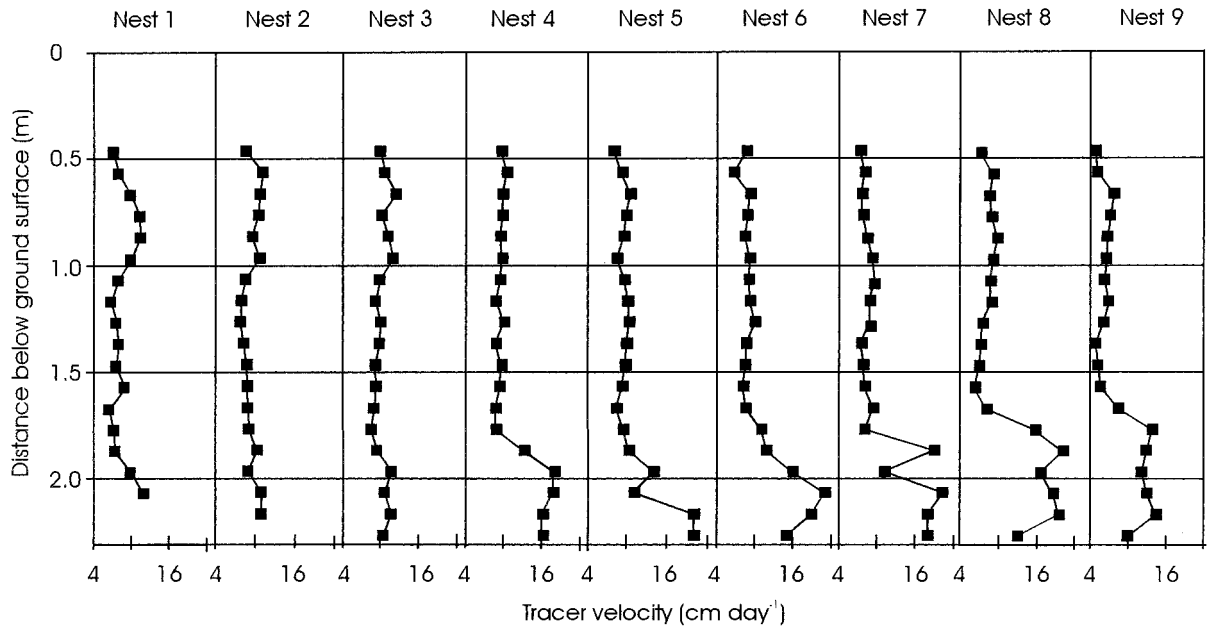

FIGURE 5. Estimated groundwater velocities for the sampling points.

core of the plume (sampling points 404−409, 506−510, and 604−608). The increase in concentrations after 220 days is due to the methanol injection.

Contour plots were constructed using the PC-program Surfer (Surfer Access System version 4.07, Golden Software Inc.). An inverse distance method was used to interpolate between the sampling points. Figure 7 shows contour plots for relative concentrations of TCM, TCE, and PCE 88, 195, and 266 days after the solvents release. The outer contour of 0.001 corresponds to concentrations of TCM, TCE, and PCE of 1.0, 0.59, and 0.11 mg L^{-1}, respectively. The figure reveals that the area of the TCM plume decreased significantly during the experiment and that the maximum concentration of TCM decreased as well. The area of the TCE plume did not change significantly over the time of the experiment, whereas both the area of the PCE plume and the maximum concentration of PCE increased during the experiment. The concentration gradients at the periphery of the three plumes seem to be relatively high, especially at the bottoms of the plumes where the concentrations changed by 2 orders of magnitude over a distance of 0.3 m. This indicates that the vertical and lateral dispersion is relatively low in the aquifer. The maximum depth that significant dissolved concentrations were observed was approximately 1.7 m bgs

The breakthrough curves for all the sampling points were used to estimate the time for breakthrough of the first compound (in most cases TCM). The time for breakthrough is defined as the time to reach 50% of the initial maximum concentration of the compound of interest. The retardation of TCM in this aquifer has been shown to be insignificant (a retardation factor of 1, see Table 1). Therefore, the time for TCM breakthrough can be used to estimate the distance from the sampling points to the closest point of DNAPL residual assuming that the flow lines are horizontal and the estimated groundwater velocities based on the tracer experiment represent the velocities of TCM. It must also be assumed that the rate of DNAPL infiltration and migration was rapid as compared to the groundwater flow. Figure 8 shows the estimated distances for the sampling points where dissolved solvent concentrations were observed. For sampling nests 4−6, the distance from the sampling points to the nearest location of solvent residuals varied between 1.5 and 4 m. Those distances are reasonable according to the likely geometry of the source zone. In general, the distances increased with depth for sampling nests 4−6, suggesting that the DNAPL may have moved toward the injection wells during the apparent downward migration of the DNAPL.

For sampling nest 7, the estimated distances are comparable with the distances for sampling nests 4−6 at a depth of 0.67−0.87 m. However, the distances for the two most-shallow sampling points in sampling nest 7 are slightly higher than the maximum possible distance of 4.5 m considering the geometry of the cell. For sampling nests 2 and 3, the estimated distances were larger than the cell, ranging from 4.5 to 25 m. A likely explanation for this is that the DNAPL phase continued to move during the experiment and did not reach the location upgradient sampling nests 2, 3, and 7 till later in the experiment. Another observation that supports this explanation is that for most of the sampling points in sampling nests 2, 3, and 7, no TCM was observed. TCM is the compound that should be removed first due to the preferential dissolution of TCM. DNAPL that moved into the area of sampling nests 2, 3, and 7 later in the experiment may already have been depleted of TCM. Nevertheless, it appears that the estimated distances may be used to "locate" the nearest location of DNAPL residual for many of the sampling points. They may be characterized as the sampling points for which the time for DNAPL to reach the corresponding layer is short as compared to the travel time for the dissolved phase from the location of the DNAPL phase to the sampling points.

Excavation. The overall geometry of the distribution of DNAPL residuals that remained in the subsurface at the end of the experiment is shown in Figure 9. Illustrative photos of the release are shown in ref *17*. The DNAPL was released from the bottom of the tube at a depth of 0.66 m. Most of the DNAPL was present in layer 2 at 0.55 m bgs. The DNAPL-contaminated zones were much smaller in the other four layers. No DNAPL was observed below layer 5 at 0.70 m bgs. DNAPL was observed around the DNAPL release tube up from the bottom of the tube to a depth of 0.30 m, but the tube was stained red up to a depth of 0.20 m. These observations indicate that DNAPL had migrated upward outside the tube to shallow depth and then migrated laterally outward into the sand.

Figure 9 reveals that most of the DNAPL was distributed above the bottom of the tube; only layer 5 is below the bottom of the tube. The horizontal spreading of the DNAPL at

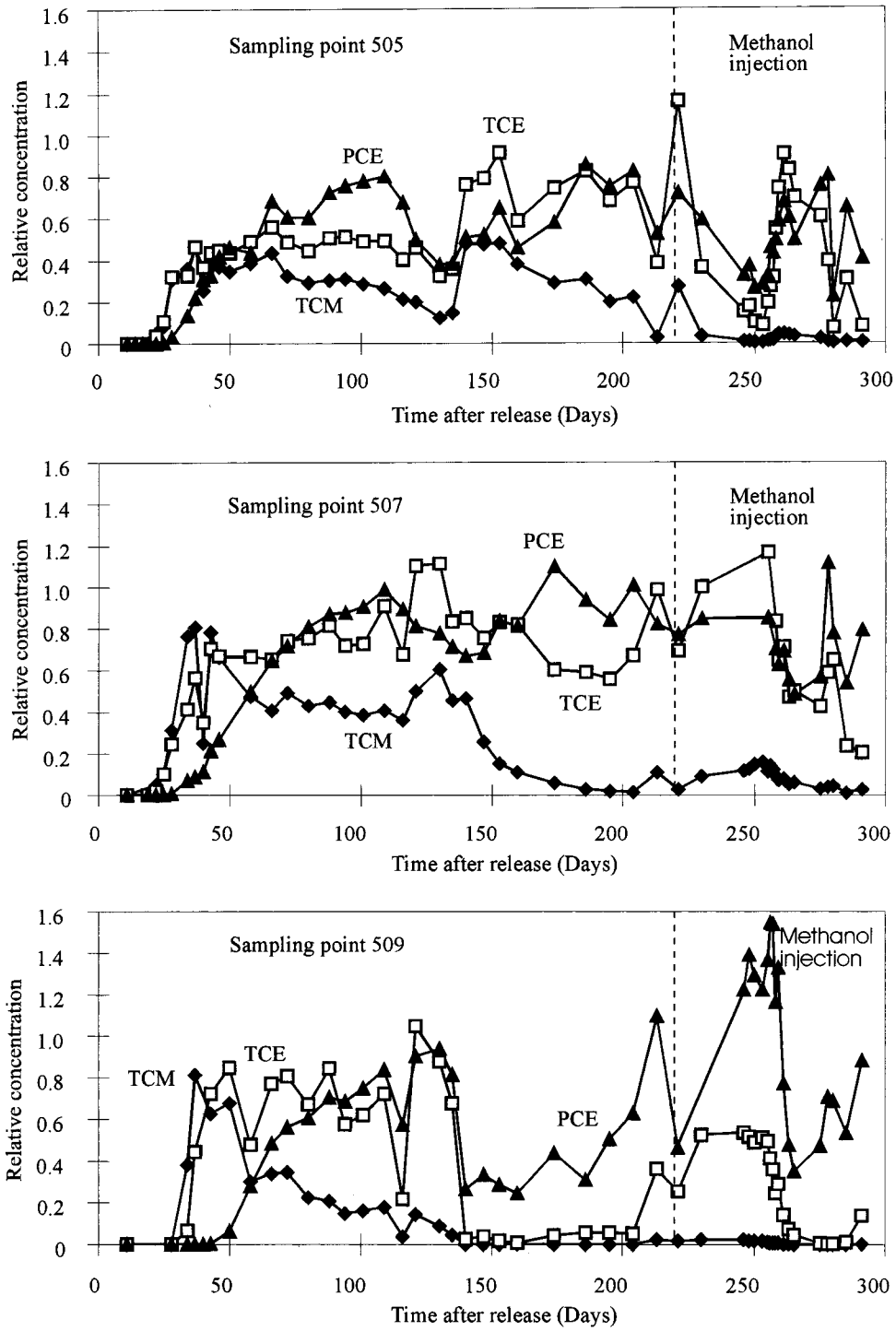

FIGURE 6. Relative concentration of TCM (◆), TCE (□), and PCE (▲) vs time for three sampling points located in sampling nest 5. Sampling point 505 is located 0.57 m below ground surface; sampling point 507 is 0.77 m below ground surface, and sampling point 509 is 0.97 m below ground surface. A relative concentration of 1.0 corresponds to 1020 mg L^{-1} of TCM, 589 mg L^{-1} of TCE, and 111 mg L^{-1} of PCE.

approximately 0.55 m bgs was attributed to a zone of slightly higher permeability. The sand above 0.55 m had a higher hydraulic conductivity (7.4×10^{-5} m s^{-1}) than the sand below (1.7×10^{-5} m s^{-1}), which facilitated the horizontal migration of the DNAPL at that specific depth.

The thickness of the main DNAPL pool was less than 1 cm. At three different locations DNAPL moved downward from this layer: into a sand back-filled core hole, along the outside of a core tube, and along the outside of a stake. These observations indicate that the DNAPL-contaminated zone contained mobile DNAPL and that the DNAPL was present not only as residual but also as an accumulation or a pool at some locations. The cores were taken just before and during the excavation, and the stakes were installed just prior to the excavation, which indicates that the downward movement occurred within a few days.

Discussion

Source Distribution and Mass Balance. The actual distribution determined by visual examination during excavation of the cell revealed that most of the DNAPL accumulated as a pool in layer 2 at 0.55 m bgs. DNAPL accumulations and residuals were distributed on a very small scale, on the order of 0.5 cm or less, due to small-scale variations in geology and

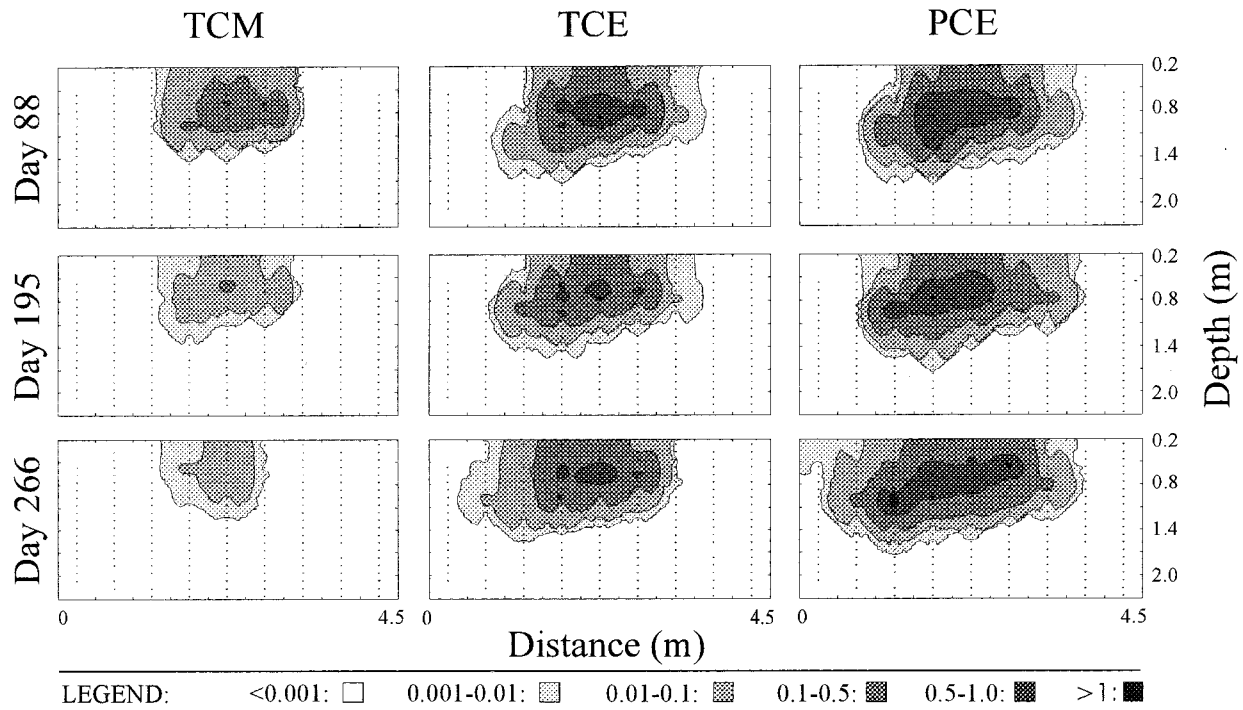

FIGURE 7. Contour maps for TCM, TCE, and PCE at days 88, 195, and 266. The contours shown are relative concentrations of 0.001, 0.01, 0.1, 0.5, and 1.0. A relative concentration of 1.0 corresponds to 1020 mg L^{-1} of TCM, 589 mg L^{-1} of TCE, and 111 mg L^{-1} of PCE.

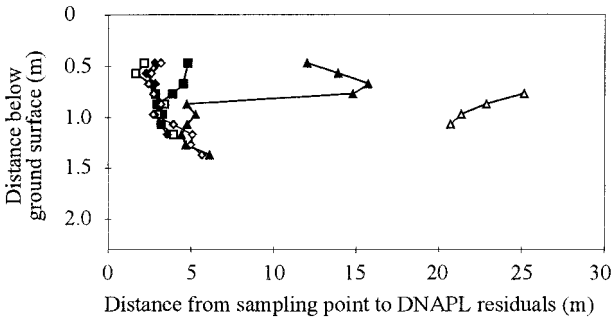

FIGURE 8. Calculated distances from the sampling points to the closest location of solvent residuals for all the sampling points where significant dissolved concentration were observed. See text for details on calculations. (△) is the sampling points in sampling nest 2, (▲) in sampling nest 3, (◇) in sampling nest 4, (◆) in sampling nest 5, (□) in sampling nest 6, and (■) in sampling nest 7.

hydraulic conductivity. These geological variations were not visible to the eye but were evident as a result of the DNAPL distribution. This is consistent with observations from other field experiments (*7*−*9*).

Soil samples containing visible DNAPL were taken from layers 1, 3, and 5. Due to a preferential dissolution of TCM from the DNAPL phase, the soil samples had very low TCM concentrations relative to TCE and PCE; therefore, it was difficult to obtain accurate concentrations for TCM. The average residual saturation of DNAPL was 3.6% of the pore space based on the soil samples containing visible DNAPL. Based on the spatial distribution of DNAPL (Figure 9), the volume of soil in layers 1−5 containing visible DNAPL was estimated to be 133.3 L. Using a porosity of 0.33, the total volume of solvents present as DNAPL was estimated to be 1.58 L (Table 2), which corresponds to 31.6% of the amount released.

The estimated mass of visible DNAPL described in the previous paragraph may be underestimated because the average residual concentration (3.6%) used does not account for the DNAPL pool in layer 2. However, based on photos, the thickness of that pool was estimated to be approximately 0.5 cm, and the pool area was estimated to be about 2.2 m^2. Assuming an average residual saturation of 20% of the pore space (*9*), the total amount of DNAPL in that pool was estimated to be 2.2 L (Table 2). The volume of DNAPL in the remaining layers was estimated using the average residual saturation of 3.6% of the pore space based on soil samples obtained from layers 1, 3, and 5 and a total volume of contaminated soil in layers 1, 3, 4, and 5 of 23 L. The total volume of DNAPL in these layers was estimated to be 0.27 L. Based on these calculations, approximately 2.5 L of DNAPL was present in the aquifer at the end of the experiment corresponding to 50% of the released solvent.

Soil samples were obtained below layer 5 to obtain information about the mass of solvents in the soil sorbed to the soil particles and dissolved in the aqueous phase. A total of 22 soil samples was taken from each of the layers 7 and 10−14 (0.80, 0.95, 1.05, 1.15, 1.25, and 1.35 m bgs). The average concentrations in the soil samples, assuming that all the mass was in the aqueous phase, were 4.0 mg L^{-1} for TCM, 37.5 mg L^{-1} for TCE, and 55.7 mg L^{-1} for PCE, which gives a total concentration of 97.2 mg L^{-1}. Using these average concentrations and the volume of contaminated soil that those concentrations represent, the total equivalent volume of solvents present in the aquifer at the end of the experiment as sorbed and dissolved phases below layer 5 was estimated to be 0.006 L for TCM, 0.057 L for TCE, and 0.076 L for PCE, producing a total volume of 0.14 L (Table 2) corresponding to 2.8% of the released solvent.

The total mass of solvents removed from the cell with the effluent water (Figure 10) was 1.62 L (0.44 L of TCM, 0.91 L of TCE, and 0.27 L of PCE) corresponding to 32.3% of the total volume of solvents released (Table 2).

The total volume of DNAPL accounted for was 3.34 or 4.23 L depending upon the method used for estimating the volume of solvents still present as DNAPL in the subsurface. These estimates represent 67% and 87%, respectively, of the total volume of 5 L of DNAPL released to the cell.

The discrepancy in the mass balance is likely due to the difficulty in quantifying the remaining DNAPL mass by soil

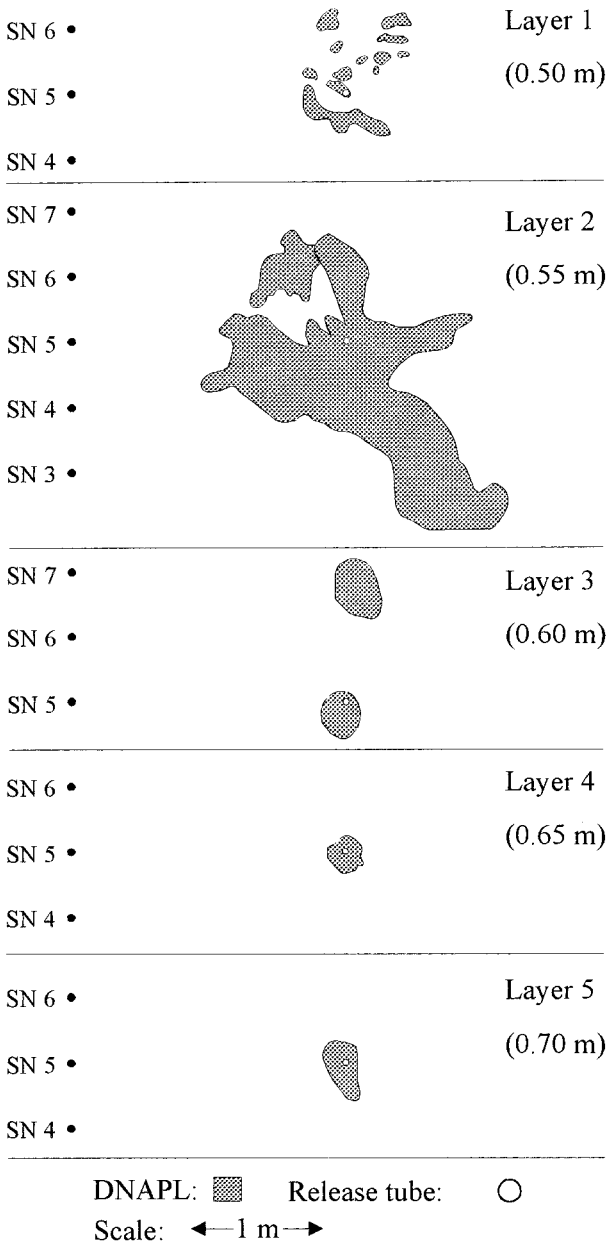

FIGURE 9. Observed locations of solvents residual in five different layers in the subsurface based on visual inspection during the excavation of the site.

sampling due to the extreme small-scale spatial variability in the DNAPL distribution. It is unlikely that significant mass was removed from the site by other processes such as (bio)-degradation or volatilization. Biodegradation seems unlikely because the aquifer is aerobic (*14*), and the conditions necessary for biodegradation of the chlorinated solvents (*18, 19*) are not present.

Volatilization may have caused some removal of mass, since the chlorinated solvents are volatile compounds, and the DNAPL was present, at least temporarily, in the unsaturated zone. The degree of loss of the three solvents by volatilization from the groundwater would be proportional to their Henry's law constants, which for TCM, TCE, and PCE are 0.1, 0.27, and 0.49, respectively (Table 1). As a result, PCE would be lost preferentially to TCE and TCM. TCE would be lost preferentially to TCM. It would be expected that a significant loss of solvent by volatilization from the water or from the DNAPL would be evidenced by changes in dissolved concentrations in the shallow sampling points at times when the water table was lowest. However, the results from sampling point 505 (Figure 6) or the other shallow sampling points do not suggest any preferential loss of PCE or TCE as compared to TCM. Consequently, there does not appear to have been significant loss of solvent due to volatilization.

Magnitude of the Dissolved-Phase Concentrations. In the portion of the plume directly downgradient from the source, dissolved-phase concentrations exceeded 10% (i.e., 0.1 relative concentration) of the effective solubility of the individual components, providing a strong indication of the presence of DNAPL (*17*). Dissolved concentrations exceeded 50% of the effective solubility at several sampling points. During the course of the experiment, the magnitude and extent of the TCM concentrations declined as a result of preferential removal of the TCM by dissolution from the DNAPL. Modeling of the preferential dissolution of the more soluble DNAPL components and the potential of using temporal changes in dissolved concentration ratios to estimate DNAPL mass (*20*) in this experiment will be the subject of a future paper.

Spatial Delineation of the Dissolved-Phase Plume. Spatial delineation of the dissolved-phase plume downgradient from the source correlated generally to the lateral and vertical location of the DNAPL source. Lateral and vertical extent of the plume where a relative concentration of 0.1 was exceeded corresponded closely to the lateral and vertical location of the DNAPL source. However, because of the small scale of the DNAPL layers (i.e., ~0.5 cm or less) even the very detailed monitoring of dissolved concentrations in the downgradient sampling points could not discern the presence of the different DNAPL layers within the source zone.

Lower dissolved concentrations were also observed beyond the extent of the DNAPL source. The deepest location of DNAPL was 0.70 m bgs (Figure 9), and the deepest sampling point where significant dissolved concentrations were observed was 1.7 m bgs (Figure 7). Dissolved concentrations at the margins of the plume fluctuated, in apparent response to fluctuations in the elevation of the water table. It is likely that the fluctuations in the water table caused vertical hydraulic gradients within the cell that enhanced the vertical spreading of the dissolved plume.

It is unlikely that DNAPL had actually migrated down to a depth of 1.7 m and that all the solvents located deeper than 0.7 m were completely dissolved before the excavation. If all the deeper DNAPL had been dissolved, the dissolved concentrations in the deeper sampling points should have declined during the depletion of the DNAPL, and this was not observed. Similarly, it is unlikely that the density of the dissolved plume caused the vertical migration of the plume. The density effect can be evaluated by examining the excess density ratio, which is the ratio between the density difference between the displaced fluid and the displacing fluid and the density of the displaced fluid. Water in equilibrium with a DNAPL with the initial composition used in this study has a total concentration of dissolved solvents of 1720 mg L^{-1} (initial condition). During the experiment, approximately 30% of the released volume (predominantly TCM and TCE) was dissolved, which would change the theoretical total equilibrium concentration to 668 mg L^{-1} at the end of the experiment. These very high concentrations were observed at only a few sampling points. The maximum density ratio at the beginning of this experiment was 1.7×10^{-3}, and this ratio would have declined with time. Several field and laboratory experiments have revealed that total concentrations in the order of 1000 mg L^{-1} (corresponding to a density ratio of approximately 1×10^{-3}) may be sufficient to cause sinking of dissolved plumes in homogeneous media (*21, 22*). However, greater density ratios would be necessary to cause sinking of plumes in layered media like the Borden aquifer.

TABLE 2. Mass Balances for the Released Solvents[a]

	comments on the calculations	volume (L)
total released		5.0 (0.5, 2.0, 2.5)
removed with effluent water	32.3% of the total vol	1.62 (0.44, 0.91, 0.27)
dissolved or sorbed DNAPL still in the aquifer	av total concn: 97.2 mg L^{-1}, total vol of water: 2218 L	0.14 (0.006, 0.057, 0.076)
remaining in DNAPL phase (all 5 layers)	vol of DNAPL-contaminated soil: 133.3 L, av total concn: 3.6% (0.003%, 0.77%, 2.83%) of pore vol	1.58 (0.001, 0.34, 1.24)
remaining in DNAPL phase (only layer 2)	total area (2.2 m^2) of layer 2 covered with a pool (height of 0.5 cm; concn of 20% of pore vol	2.2
remaining in the DNAPL phase (all 5 layers excluding layer 2)	vol of DNAPL-contaminated soil: 23 L, av total concn: 3.6% of pore vol	0.27

[a] Refer to the text for details regarding the mass balance calculations. The numbers in parentheses correspond to the concentration of TCM, TCE, and PCE.

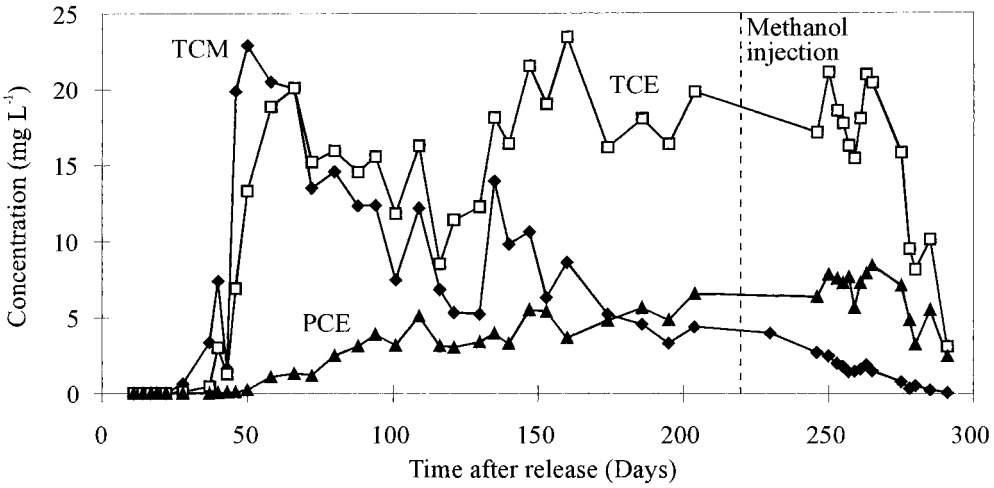

FIGURE 10. Observed effluent concentration of TCM (◆), TCE (□), and PCE (▲) vs time.

The predictions of the location of the DNAPL based on the breakthrough curves of TCM for some of the individual sampling points gave reasonable estimates of the distance between the DNAPL source and the sampling point, especially for those sampling points where TCM was observed first. However, estimates of the distance between the DNAPL and the sampling points were not possible for most of the sampling points in sampling nests 2 and 3 in which dissolved concentrations were not observed until rather late in the experiment. The late arrival of the dissolved plume at these locations suggests that the DNAPL moved during the experiment. It is not known whether the continued DNAPL migration was a result of slow continued movement along relatively low permeability pathways or whether the DNAPL was remobilized during the experiment.

In general, this field experiment has shown that the dissolved-phase plume emitted from the DNAPL source exceeded 10% of the effective solubility of the DNAPL components across the lateral and vertical extent of the source zone, so that the general location of the source zone could be determined. However, even with detailed groundwater monitoring it was not possible to determine the small-scale distribution of the DNAPL source. Lower dissolved concentrations occurred deeper than the DNAPL source zone, likely the result of vertical groundwater flow caused by fluctuations in the water table elevation. Delineation of source zones by groundwater monitoring at real sites of DNAPL contamination will be challenging because DNAPL zones may be larger and more complicated, fluctuations in groundwater levels and flow direction may be greater, and monitoring will be less detailed than described in this experiment.

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