



A PCE groundwater plume discharging to a river: influence of the streambed and near-river zone on contaminant distributions

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Abstract

An investigation of a tetrachloroethene (PCE) groundwater plume originating at a dry cleaning facility on a sand aquifer and discharging to a river showed that the near-river zone strongly modified the distribution, concentration, and composition of the plume prior to discharging into the surface water. The plume, streambed concentration, and hydrogeology were extensively characterized using the Waterloo profiler, mini-profiler, conventional and driveable multilevel samplers (MLS), Ground Penetrating Radar (GPR) surveys, streambed temperature mapping (to identify discharge zones), drivepoint piezometers, and soil coring and testing. The plume observed in the shallow streambed deposits was significantly different from what would have been predicted based on the characteristics of the upgradient plume. Spatial and temporal variations in the plume entering the near-river zone contributed to the complex contaminant distribution observed in the streambed where concentrations varied by factors of 100 to 5000 over lateral distances of less than 1 to 3.5 m. Low hydraulic conductivity semi-confining deposits and geological heterogeneities at depth below the streambed controlled the pattern of groundwater discharge through the streambed and influenced where the plume discharged into the river (even causing the plume to spread out over the full width of the streambed at some locations). The most important effect of the near-river zone on the plume was the extensive anaerobic biodegradation that occurred in the top 2.5 m of the streambed, even though essentially no biodegradation of the PCE plume was observed in the upgradient aquifer. Approximately 54% of the area of the plume in the streambed consisted solely of PCE transformation products, primarily *cis*-1,2-dichloroethene (cDCE) and vinyl chloride (VC). High concentrations in the interstitial water of the streambed did not correspond to high groundwater-discharge zones, but instead occurred in low discharge zones and are likely sorbed or retarded remnants of past high-concentration plume discharges. The high-concentration areas (up to 5529 µg/

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l of total volatile organics) in the streambed are of ecological concern and represent potential adverse exposure locations for benthic and hyporheic zone aquatic life, but the effect of these exposures on the overall health of the river has yet to be determined. Even if the upgradient source of PCE is remediated and additional PCE is prevented from reaching the streambed, the high-concentration deposits in the streambed will likely take decades to hundreds of years to flush completely clean under natural conditions because these areas have low vertical groundwater flow velocities and high retardation factors. Despite high concentrations of contaminants in the streambed, PCE was detected in the surface water only rarely due to rapid dilution in the river and no cDCE or VC was detected. Neither the sampling of surface water nor the sampling of the groundwater from the aquifer immediately adjacent to the river gave an accurate indication of the high concentrations of PCE biodegradation products present in the streambed. Sampling of the interstitial water of the shallow streambed deposits is necessary to accurately characterize the nature of plumes discharging to rivers. © 2004 Elsevier B.V. All rights reserved.

Keywords: Groundwater; Surface water; Contaminant plumes; Chlorinated hydrocarbons; Biodegradation; Sediments

1. Introduction

A National Priorities List characterization study for the United States estimates that 51% of 1218 hazardous waste sites impact surface water (USEPA, 1991) and at many of these sites chlorinated volatile organic compounds (VOCs) are migrating by groundwater flow to streams and rivers. Despite this relatively common occurrence, few published studies have characterized VOC plumes in detail to examine the processes that control how they discharge to a river. Some studies (Norman et al., 1986; Avery, 1994; Hess et al., 1989) examined VOC groundwater plumes discharging to rivers using seepage meters and piezometers and others have mapped plan-view distributions of VOCs in streambeds using diffusion samplers (Vroblesky et al., 1991, 1996; Savoie et al., 1999; Lyford et al., 1999; Church et al., 2002). These studies contain relatively little information concerning the hydrological and geological controls on plume characteristics and do not present the fine-scale vertical concentration data needed to evaluate how the plume has been changed by the near-river zone. Advection, biodegradation, and adsorption processes affecting a VOC plume discharging to a creek in a freshwater tidal wetland were investigated by Lorah et al. (1997) and Lorah and Olsen (1999), but only a portion of the plume was examined in vertical cross section and the studies did not examine the resulting streambed contamination in plan view. In this study, we attempt to provide a more holistic field study of a plume discharging to a river than appears to be available in the literature.

It is not clear to what extent conditions within the streambed will modify a contaminant plume prior to its discharge to the surface water. The area beneath and adjacent to a river or stream is potentially a very complex geological, hydrological, and biochemical zone (Huggenberger et al., 1998; Brunke and Gonser, 1997; USEPA, 2000; Conant, 2001, 2004; Woessner, 2000). Studies of uncontaminated sites show that conditions in the streambed may be spatially and temporally variable and subject to large hydraulic and geochemical gradients (Brunke and Gonser, 1997; Dahm et al.,

1998; Hendricks and White, 1991, 1995). As the plume passes through this zone, it is hypothesized that the geometry and chemical composition of the plume should change and that these changes would affect how the plume contaminates the streambed and surface water. One purpose of the current study was to investigate the geology near the river to determine if preferential flow paths or restrictions to flow existed that would control how and where the PCE groundwater plume discharged to the river. The concentration distribution in the streambed is relevant because ecologists view the streambed and near-stream groundwater/surface-water transition zone (which includes the hyporheic zone), as a unique habitat that plays an important role in the aquatic food-web and that provides other ecological functions related to the health of a stream (Hynes, 1970; Gibert et al., 1994; Boulton et al., 1998; Ward et al., 1998; USEPA, 2000). This study provides the first comprehensive assessment of a chlorinated solvent groundwater plume discharging into a river and shows that the near-stream zone substantially modifies the distribution, concentration, and composition of the plume prior to its reaching the surface water. The results of this study have important implications for the design of monitoring programs, evaluation of the ecological impacts of plumes, and the remediation of these discharges.

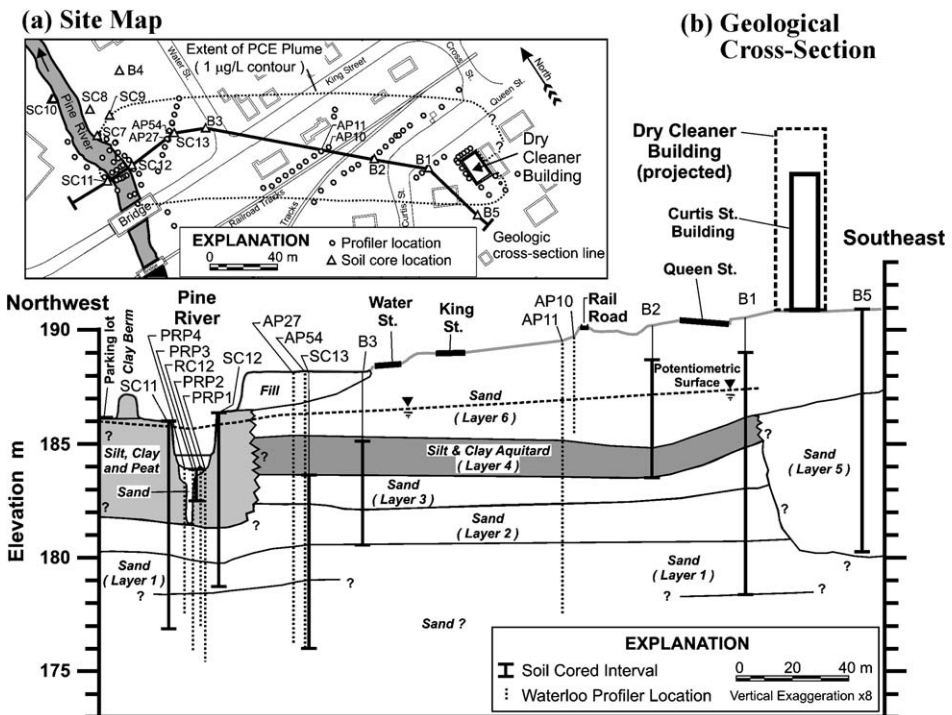


Fig. 1. (a) Site map showing outline of PCE groundwater plume, line of geologic cross section, soil coring locations, and Waterloo Profiler locations. (b) Geological cross section from the dry cleaner to the Pine River with stratigraphic layers numbered in accordance with Writt (1996).

2. Description of study site and river

The study site is located in Angus, Ontario, Canada, approximately 75 km north–northwest of Toronto and near Canadian Forces Base Borden. A 60-m-wide dissolved-phase PCE groundwater plume extends 195 m downgradient to the Pine River from a dense nonaqueous phase liquid (DNAPL) source of PCE beneath a dry-cleaning facility (Fig. 1a). The groundwater at the site has likely been contaminated since at least the 1970s. The stratigraphy of the top 15 m of the deposits at the site is divided into five sand layers that consist primarily of fine to very fine sands and one 1- to 1.5-m-thick silty-clay aquitard layer at a depth of about 5 m (Writt, 1996) (Fig. 1b). Because the aquitard is absent near the dry cleaner, the DNAPL spilled there was able to reach and accumulate in the deeper sands. A high concentration (up to 43,318 $\mu\text{g/l}$) dissolved-phase PCE plume travels toward the river in the confined aquifer beneath the aquitard. Although several researchers had characterized the groundwater plume (Pitkin, 1994; Pitkin et al., 1994; Beneteau, 1996; Writt, 1996; Beneteau et al., 1999; Guilbeault et al., *in press*), the extent to which the aquitard, aquifer, or plume extended beneath or beyond the river was not determined. The only information regarding water quality beneath the river was from six shallow mini-piezometers installed in the streambed at about a 15-m spacing along the eastern edge of a 75 m reach of river downstream of the King Street bridge. Contamination was only detected at one of the six locations (AMP3) approximately 29 m north of the King Street bridge (see Fig. 2) where 221 $\mu\text{g/l}$ of PCE and 9.9 $\mu\text{g/l}$ of trichloroethene (TCE) were found (Pitkin, 1994).

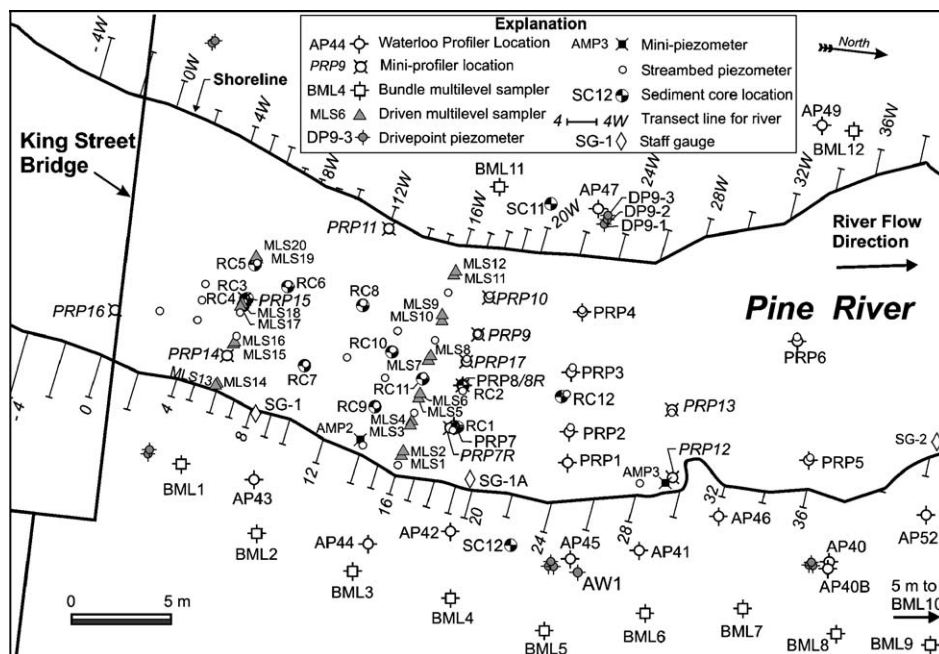


Fig. 2. Data location map for installations in and near the river.

The Pine River drains a basin that is about 348 km² in area and summer base flows at the study site are about 1 to 2 m³/s (Beebe, 1997; Burkard, 1990). The river is moderately-to-highly sinuous and has a channel with a low width-to-depth ratio, a high entrenchment ratio, and a slope of 0.0007 m/m (Beebe, 1997). At the study site, the river is relatively straight and the stream banks are about 1.2 to 2.5 m high and consist of silt, clay and peat deposits. The river is 11 to 14 m wide and in summer has an average depth of 0.5 m and maximum depth of about 1.1 m. The river is a high-quality cold-water habitat that supports a wide diversity of aquatic life and benthic taxa such as *Glossosoma* and *Leuctra* (Jones, 1999), trout and salmon.

3. Field methods

3.1. Characterization of geology and streambed sediments

The techniques used to characterize geology and streambed sediment at the site included: coring, Ground Penetrating Radar (GPR), and visual mapping of sediments. Seven cores of unconsolidated deposits were collected on land to a maximum depth of 12.2 m below ground surface (bgs) at locations SC7 to SC13 (Fig. 1a) using the piston-core-barrel method (Starr and Ingelton, 1992). Twelve cores were collected in the streambed at locations RC1 to RC12 (Fig. 2) by hand driving 0.051 m ID aluminum core tubes to a maximum depth of 1.8 m. Cored materials were logged and sediments classified. Hydraulic conductivities were determined for 178 subsamples of the streambed cores and 48 subsamples from aquifer materials at SC12 using a falling-head permeameter test method (Sudicky, 1986). The porosity and bulk density of each subsample was determined by using weight-to-volume calculations. Fraction of organic carbon (f_{oc}) analyses were performed on 52 samples from cores SC12, SC13, RC1, RC2, RC4, and RC11. Samples were analyzed using either the method of Tabatabai and Bremner (1970) or Churcher and Dickout (1987) which had detection limits of 0.05% and 0.008%, respectively.

The GPR survey was performed in October 1998 using a pulseEKKO IV GPR system (Sensors and Software, Mississauga, Ontario, Canada) with a pair of 200 MHz unshielded slab-antennae mounted in the bottom of a small inflatable boat. The GPR survey consisted of 16 transects across the Pine River (Fig. 3a). Visual mapping of the surficial geology of the streambed between transects –4 to –4W and 56–56W was done in July 1997, August 1998, and February 1999. Transect locations are used to identify locations in the streambed. For example, location 8–8W 4.5 m indicates that the transect is approximately 8 m downstream (north) of the King Street bridge (shown in Fig. 2) and the point is 4.5 m west of stake 8 (on the east bank) toward stake 8W (on the west bank).

3.2. Water level monitoring and stream gauging

To obtain a better understanding of groundwater/surface-water interactions, groundwater flow directions, and river stage/discharge relationships, several drivepoint piezometers, mini-piezometers, dataloggers and staff gauges were installed at the site. A total of

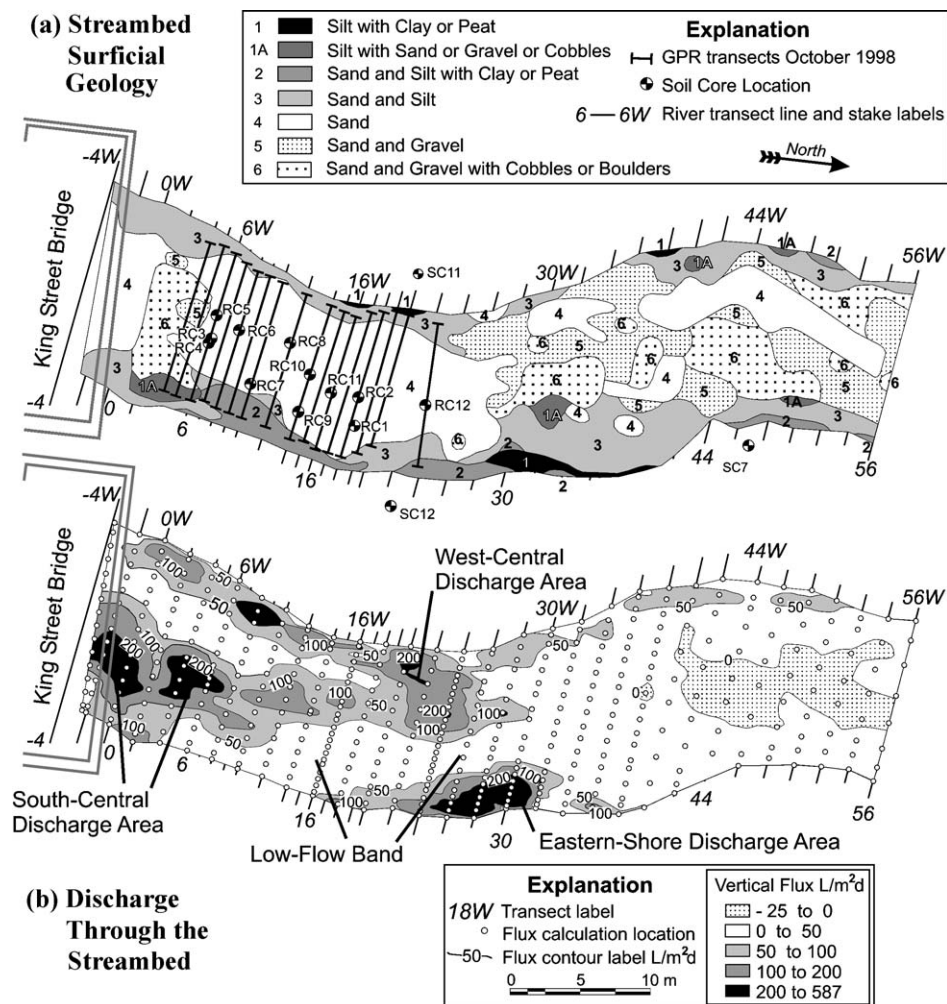


Fig. 3. (a) Map of surficial geology of the streambed and (b) map of vertical water fluxes through the streambed for February 1999.

41 drivepoint piezometers were installed at 20 locations (DP1 to DP20) on land to depths of between 2.5 and 8.0 m bgs. Monthly water-level measurements were made in all land-based piezometers for a period of 13 months starting in July 1998. In July 1998, a drivepoint well AW1 was installed in the confined aquifer 27 m north of the bridge and 3.8 m east of the river and the water levels were monitored to within 0.005 m on a 15-min interval until November 1999, using a Solinst Model 3001, M5 Levellogger™ (Solinst Limited Canada, Georgetown, Ontario).

Piezometers were also installed at 40 locations in the streambed. Three pairs of mini-piezometers were installed in the streambed at locations between 55 and 72 m downstream of the bridge in June 1996 using the method of Lee and Cherry (1978). Thirty-four

drivepoint piezometers made of 0.021 m OD PVC pipe were also installed (Fig. 2) to depths of 0.65 to 0.70 m in the streambed. Slug testing of the drivepoint piezometers was performed in November and December 1998, and hydraulic conductivity was determined using the Hvorslev (1951) variable-head method. Prior to each slug test, the hydraulic-head difference between the river and the piezometer was measured to within 0.001 m using a potentiomanometer similar to that described by Winter et al. (1988).

Manual measurements of stream stages began in 1996 and stages were eventually recorded on a 15-min interval between March 1998 and June 1999, using a Solinst, Model 3001, M5 Levelogger™ placed in a stilling well in the river at PRP1 (Fig. 2). Discharge was measured eight times at the site using a Swoffer Model 2100-STD flowmeter. A stage/discharge relationship was developed for the site using this data.

3.3. Plume delineation

Sampling devices used to characterize and delineate the subsurface water quality at the site were: the Waterloo Profiler, mini-profiler, bundle multilevel samplers, and “driveable” multilevel samplers. Early in the study (June and November 1996), a few drivepoint piezometers and mini-piezometers were also used for sampling. Table 1 summarizes the

Table 1
Summary of sampling of groundwater and streambed interstitial water

Sampling device	Sample location names	Number of locations	Number of GW samples	Maximum depth of sampling (m)	Vertical sampling interval (m)	Date of sampling
Drivepoints and mini-piezometers	DP1 to DP6, SP1, SP2, SP3	12	25 ^a	8	NA	6/96
Drivepoints and mini-piezometers	DP1, DP2, DP8, DP9, SP1	5	13 ^a	7.6	NA	11/96
Waterloo Profiler	AP40 to AP52	13 ^b	175	11.5	0.25 or 0.50	7/96 to 8/96
Waterloo profiler	AP96-1 to AP96-10	10	81	12	0.3 to 1.0	6/96 to 8/96
Waterloo profiler	AP53 to AP55	3	21	12.2	0.6 to 1.5	11/97 to 12/97
Waterloo profiler	PRP1 to PRP8	8	106	8.5	0.1 to 0.5	8/96 to 11/96
Mini-profiler	PRP7R, PRP8R, PRP9R, PRP10 to PRP17	11	104	2.1	0.15 to 0.6	8/97 or 10/97 ^c
Mini-profiler	Plan-view mapping	80	80	0.3	NA	8/98
Driveable multilevels	MLS3, MLS4, MLS7, MLS8, MLS17, MLS18	6	41	4.5	0.15 or 0.3	11/98
Driveable multilevels	MLS1 to MLS20	10	139	5.4	0.15 or 0.3	3/99
Bundle multilevel samplers	BML1 to BML12	12	106	9.5	0.5	3/99

NA—not applicable, only sampled at one depth.

^a Includes multiple piezometers sampled at a location (e.g., shallow, intermediate and deep levels).

^b Location AP40 profiled in two parts AP40 and AP40B but counted as one location.

^c PRP17 was sampled in 8/98.

characteristics of these devices and a description of their sampling and construction can be found in Conant (2001).

The Waterloo Profiler method of obtaining vertical profiles of water quality (Pitkin et al., 1999) was used at 34 locations to collect approximately 383 groundwater samples. Thirteen of these profile locations (AP40 to AP52) were along profiler transects 5 and 6, which were within 4 m of the east and west sides of the Pine River, respectively (most locations are shown in Fig. 2). Another 10 locations in the upgradient confined aquifer were profiled to further characterize high-concentration areas and delineate the lateral edges of the PCE plume along previously profiled transects by Pitkin (1994) and Writt (1996). Three locations were profiled along transect 4 near AP27 (see Fig. 1a) and next to previously profiled locations by Writt (1996) to reassess a high-concentration plume area 29 to 37 m east of the river. Eight locations (PRP1 to PRP8) were also profiled in the streambed (Fig. 2) and the holes sealed with bentonite.

A “mini-profiler” was used to obtain vertical profiles and determine the plan-view distribution of groundwater quality in the streambed. The mini-profiler was a soil vapor probe (Hughes et al., 1992) that was modified to collect water and was a 0.0064 m OD, 0.003 m ID stainless-steel tube, 2.6 m in length, having a 0.01-m-long screen. The mini-profiler was used for vertical profiling at PRP7R, PRP8R, PRP9R, and PRP10 to PRP17 (Fig. 2). In August 1998, a 1.8-m-long mini-profiler was used at 80 locations to map the horizontal extent of the plume at a depth of 0.3 m below the streambed. Samples were collected on approximately a 2 by 4 m grid starting at transect –4 to –4W (beneath the King Street bridge) and ending at transect 44–44W, with two additional samples collected on transect 52–52W.

Twelve bundle multilevel samplers, designated BML1 to BML12, were installed along the banks of the river (Fig. 2). BML1 to BML10 were installed in a row on the east side of the river and roughly parallel to profiler transect 5 to assess possible changes in the location and position of the plume. The BMLs were constructed in a similar manner to those used by Mackay et al. (1986) and described by Bianchi-Mosquera and Mackay (1992). Each BML sampler consisted of a 10-m-long center stalk with 8 to 11 sampling points at the bottom having a vertical spacing of 0.5 m.

Because of the large upward hydraulic gradient between the confined aquifer and the river, there was concern that the installation of multilevel samplers deep in the streambed could pierce the semi-confining deposits and result in vertical water flow along the installations and preferential pathways for the aquifer contamination to reach the river. Therefore, two new types of driveable multilevel samplers (MLS) were developed for use in the streambed that eliminated the need for a larger diameter temporary casing to install samplers and thereby minimized the possibility of vertical water flow along the installation. The MLS sampling ports were flush with the outside of a stainless steel or PVC pipe that was driven directly into the streambed using an electric jack hammer. Therefore, the hole that was created to install the multilevel sampler was exactly the same size as the device and so there was no annular space that needed to be sealed to prevent vertical flow up the borehole. The 0.034 m OD stainless-steel type was a modified version of the multilevel sampling device used by de Oliveira (1997) and had nine sampling ports spaced 0.3 m apart and were driven down to a maximum depth of 5.6 m. The 0.042 m OD PVC type of driveable multilevels were 1.52 m in length and had 10 sampling ports spaced

0.15 m vertically along their length. The stainless steel and PVC type driveable multilevel samplers (MLS1 to MLS20) were permanently installed in pairs at 10 locations along transects 6–6W and 16–16W (Fig. 2).

Water samples collected from these devices were analyzed at the University of Waterloo for VOCs [i.e., PCE and its seven anaerobic degradation products: TCE, 1,1-dichloroethene (11DCE), 1,2-*trans*-dichloroethene (tDCE), 1,2-*cis*-dichloroethene (cDCE), vinyl chloride (VC), ethene, and ethane]. Analyses for PCE and TCE were performed using a Hewlett Packard 5890 Series II gas chromatograph equipped with an Ni⁶³ electron capture detector (ECD). Minimum detection limits for PCE and TCE were 0.7 and 0.9 µg/l, respectively. Analyses for cDCE, tDCE, 11DCE, and VC were performed using a Hewlett Packard 5890 Series II gas chromatograph equipped with an HNU photoionization detector (PID). Minimum detection limits were as follows: for cDCE (1.0 µg/l), tDCE (1.4 µg/l), 11DCE (1.4 µg/l) and VC (0.7 µg/l). Analyses for ethene and ethane were performed using a Hewlett Packard 5790A gas chromatograph equipped with a flame ionization detector (FID). Minimum detection limits for ethene and ethane were 0.5 µg/l.

3.4. Surface-water sampling

Between June 1996 and March 1999, 71 surface-water samples were collected from various locations within the study reach and analyzed for VOCs. The majority of water samples were collected by hand in 40 or 25 ml glass vials as grab samples from 0.02 to 0.05 m above the streambed. Other samples were collected during profiling of the streambed by placing the Waterloo Profiler or a mini-profiler tip just above the streambed and using a peristaltic pump and sampling manifold.

3.5. Sediment quality sampling

Total PCE and TCE concentrations in soils and sediments were determined for samples collected during coring activities. Forty-one samples were obtained from cores SC11 and SC12 by cutting them open in the field and immediately subsampling them with a stainless-steel mini-corer and extruding the samples into vials containing methanol. Samples of the methanol from each vial were extracted with pentane and analyzed for PCE and TCE using the ECD method previously described. The minimum detection limits for the method were 0.23 micrograms of PCE per gram of dry sediment (µg/g) and 0.22 µg/g for TCE. Twenty-five samples from RC1 to RC4 were subjected to a new core sampling technique to simultaneously determine both the interstitial pore water and total contaminant concentrations from which the sorbed concentration could be determined (Conant, 2001). Aluminum core tubes containing sediments were immediately capped and holes were drilled through the aluminum walls on a 0.15 m vertical spacing for sampling. A glass syringe was used to extract water from the sediment at each drilled hole and then a mini-corer was used to collect a sediment sample at the same location. A total of 25 sediment samples were analyzed for PCE, TCE, and cDCE using a new method where the methanol used to preserve and extract the sample was directly injected into the gas chromatograph with the ECD instead of extracting the methanol with pentane. The method

improved the minimum detection limits to 0.006, 0.002, and 0.11 $\mu\text{g/g}$ for PCE, TCE, and cDCE, respectively, and did not foul the column or result in carry-over. Water samples could be collected from only 11 of the 25 locations because some deposits were too fine grained to obtain water using the syringe. Water samples from the sediments were analyzed for VOCs using the same methods used for previous water samples.

4. Results and discussion

4.1. Geology

Geological investigations were designed to answer specific questions including: (1) does the aquitard found to the east of the river extend under the river; (2) if the aquitard extends under the river, has the river eroded down through it; (3) do the shallow fluvial deposits emplaced by the river affect near stream groundwater flow and result in preferential discharge locations or restrictions to flow; and (4) is the discharge through the streambed controlled by the deeper deposits?

Soil cores showed that the silty-clay aquitard found to the east of the river was not present beneath or near the river. Near the river, “semi-confining deposits” were present instead of the aquitard. The lower sands of the confined aquifer extend beneath these semi-confining deposits and beyond the river (see Fig. 1b). The semi-confining deposits found in SC7 to SC12 consisted of about a 5-m-thick sequence of finely bedded silts, peat, and clay that contain woody fragments and infrequent sand stringers. The semi-confining deposits under the river found in cores RC1, RC2, RC7, RC9, RC11, and RC12 ranged from a gray to darker gray silt with a small amount of clay to a gray to olive-gray clay or silty clay. Table 2 summarizes the results of the permeameter tests on sediment samples and includes hydraulic conductivity data, anisotropic ratios, average porosities, and average bulk densities for the semi-confining deposits and other deposits at the site. Results of falling head permeameter tests indicated that the semi-confining deposits have hydraulic conductivities equal to or lower than those reported by Witt (1996) for the silty (i.e., less clayey) upper portion of the adjacent aquitard. Slug testing of five piezometers screened in the semi-confining deposits in the streambed also had low vertical hydraulic conductivities (K_v) that ranged from 9.34×10^{-4} to 4.44×10^{-6} cm/s with a mean value of 6.90×10^{-6} cm/s. Because the semi-confining deposits are more heterogeneous and include some higher hydraulic conductivity materials than the clay aquitard, they allow more water to pass through them than the aquitard.

The GPR survey indicated that the semi-confining deposits were absent in some areas and that preferential pathways (e.g., geological windows with relatively high-hydraulic-conductivities) existed between the underlying aquifer sands and the river. Semi-confining deposits extended from the east bank to about a third of the way across the river (approximately 4.0 to 4.5 m) along transects 14–14W through 24–22W. GPR and coring showed that less than 0.8 m of sandy materials overlies the semi-confining deposits in those areas. These sandy deposits become considerably thicker (i.e., 2.5 to over 3.1 m thick) in the center of the river. The cross-sectional areas of these sandy

Table 2
Hydraulic conductivity, porosity, and bulk density determined for different types of deposits

Layer name ^a	Deposits	Hydraulic conductivity (cm/s) from permeameter measurements ^b					Anisotropic ratio (K_A/K_H)	Average porosity (%)	Average bulk density ^c (g/cm ³)	Number of samples
		Maximum	Minimum	K_A	K_G	K_H				
1	Sand	2.07×10^{-2}	9.91×10^{-3}	1.25×10^{-2}	1.25×10^{-2}	1.24×10^{-2}	1.00	30.9	1.83	19
2	Sand	2.39×10^{-2}	9.69×10^{-3}	1.47×10^{-2}	1.43×10^{-2}	1.36×10^{-2}	1.08	32.8	1.78	24
3 ^d	Sand	7.88×10^{-2}	9.11×10^{-3}	3.00×10^{-2}	2.48×10^{-2}	2.05×10^{-2}	1.46	37.0	1.67	17
4 (Aquitard) ^d	Silty clay	2.06×10^{-2}	3.23×10^{-4}	3.67×10^{-3}	1.55×10^{-3}	9.75×10^{-4}	3.77	NA	NA	8
5 ^d	Sand	5.26×10^{-2}	1.61×10^{-3}	1.84×10^{-2}	1.28×10^{-2}	8.09×10^{-3}	2.28	NA	NA	26
6 ^d	Sand	5.02×10^{-2}	1.05×10^{-3}	1.86×10^{-2}	1.30×10^{-2}	7.29×10^{-3}	2.55	NA	NA	19
Streambed sands	Sand	3.89×10^{-2}	1.73×10^{-3}	1.68×10^{-2}	1.53×10^{-2}	1.34×10^{-2}	1.25	39.6	1.60	167
Semi-confining deposits (under river) and peat	Silt, clay,	4.29×10^{-4}	2.36×10^{-5}	1.89×10^{-4}	1.12×10^{-4}	7.62×10^{-5}	2.49	62.6	0.99	10

K_A —depth weighted arithmetic mean, K_G —geometric mean, K_H —depth weighted harmonic mean.

NA—not estimated.

^a See geologic cross section (Fig. 1b) for layer number designations and locations.

^b All hydraulic conductivity values corrected to 10 °C.

^c Bulk density calculated assuming a solids density of 2.65 g/cm³.

^d Data from (or calculated from) Writt (1996).

deposits are somewhat “u-shaped” and are consistent with the infilling of an older and deeper river channel that can be seen along several GPR transects including 16–16W (Fig. 4a). Fig. 4b shows a small preferential groundwater flow path in a sandy zone through the semi-confining deposits between MLS8 and MLS10. In cores where the contact between sandy materials and the semi-confining deposits was encountered, the sands had hydraulic conductivities 32 to 382 times greater than the underlying semi-confined deposits. The streambed sand deposits had a geometric mean hydraulic conductivity (K_G) of 1.53×10^{-2} cm/s which is similar to the value obtained for the sands of the confined aquifer (Table 2). In the southern GPR transects near the bridge (4–4W to 10–10W), nearly the entire width of the river appears to be sandy at depth and these fluvial deposits serve as a preferential flow zone for groundwater discharge (Fig. 4c and d).

The surficial geology of the streambed was visually mapped in July 1997, August 1998, and February 1999. Erosion and deposition of sediments over time can change the geomorphology, topography, and composition of streambeds, yet the map of the surficial geology for February 1999 (Fig. 3a) was remarkably similar to the previous mappings. Between the King Street bridge and transect 30–30W, 56.3% of the area of the streambed consisted of fine to very fine sand and 13.7% consisted of sand and gravel with or without cobbles and boulders. Downstream of transect 30–30 W, in an area of a gentle riffle, the streambed material was even coarser. Fluvially deposited silty materials were primarily found along the edges of the river during each mapping. Although erosion and deposition cause the topography to vary by as much as 0.45 m at some locations, the semi-confining deposits typically were not visible at the streambed surface and only outcropped as very small areas along the stream banks.

4.2. Groundwater flow and discharge through the streambed

Fig. 5a shows the potentiometric surface for drivepoints screened in the confined aquifer for November 1998, which corresponds to the lowest monthly water-level conditions observed between July 1998 and August 1999. During those 13 months, the pattern of groundwater flow was very similar and water levels in individual piezometers changed less than 0.4 m. The section of river extending 40 m downstream of the bridge appears to be an area of groundwater discharge and so the plume should not flow past the river except possibly to reach the area near DP9. Deep piezometer DP9-3 (which was confirmed to be installed and operating properly) consistently had the lowest hydraulic head observed in the confined aquifer (hence the concentric contours around it) and appears to be near an area of discharge from the confined aquifer up into the overlying unconfined system. A geologic window through the semi-confining deposits at or near DP9-3 is likely the cause of the low hydraulic head at DP9-3, since hydraulic heads in the unconfined deposits were lower than the hydraulic heads in the confined aquifer.

Water levels measured in piezometers screened in the confined aquifer near the river were artesian and were 0.5 to 1.5 m higher than those in the river. Between July 1998 and June 1999, the vertical hydraulic gradient between the confined aquifer at AW1 and the river at PRP1 was always upward at between 0.29 and 0.42 m/m and indicated

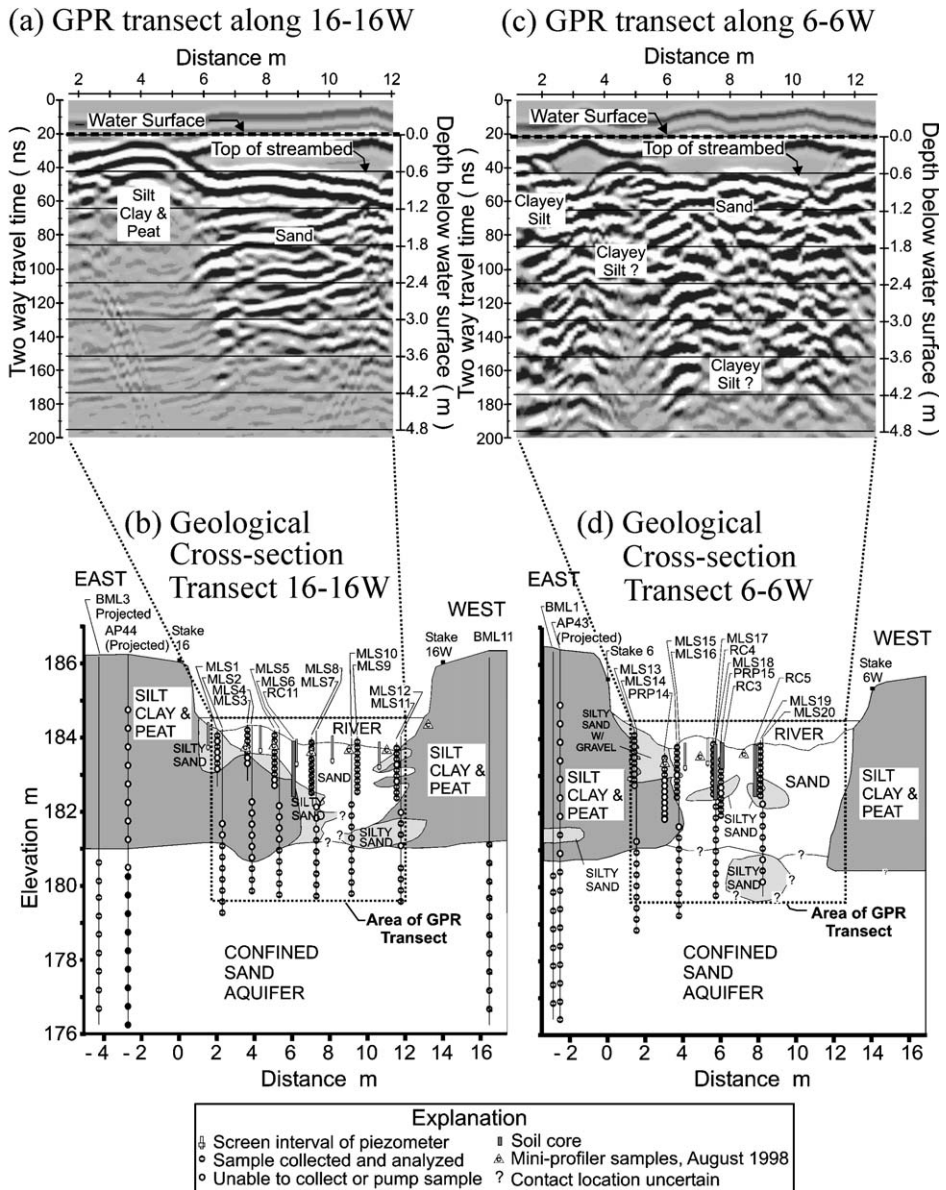


Fig. 4. (a) GPR transect and (b) geologic cross section along river transect 16–16W. (c) GPR transect and (d) geologic cross section along river transect 6–6W. GPR survey performed in October 1998. Note: two way travel times based on a single radar velocity of 0.055 meters per nanosecond (m/ns) and a topography correction has been applied to compensate for the water velocity of 0.033 m/ns.

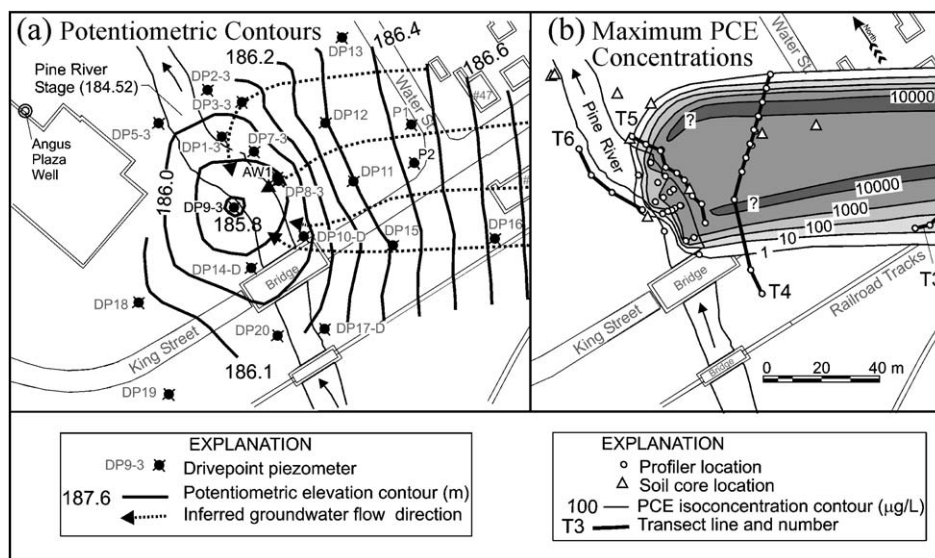


Fig. 5. (a) Potentiometric contour map for the confined aquifer November 1998. (b) Contour map of maximum PCE concentrations in groundwater at each vertical profile location. Concentration data from this study and from Pitkin (1994), Writt (1996), and Guilbeault et al. (in press).

groundwater discharges to the river even during storm runoff events and the modest spring runoff. During this time, the flow in the Pine River was between 1.4 and 6.9 m^3/s and the river stage varied by 0.84 m. The lack of gradient reversals during flooding events indicates that uncontaminated surface water does not flow down into the underlying sand aquifer and so cannot displace contaminated groundwater there, except possibly during more extreme flooding situations than were observed during this period of time.

Flow in the shallow streambed deposits was spatially variable and complex. Darcy's law calculations using water-level measurements and slug-testing results from 34 streambed piezometers showed that the vertical flux (q_v) ranged from 0.029 to 446 liters per square meter of streambed per day ($\text{l}/\text{m}^2 \text{ day}$) to perhaps as much as 7060 $\text{l}/\text{m}^2 \text{ day}$ at one location. This variability was primarily a function of the wide range in hydraulic conductivity of materials in which the piezometers were screened. Water levels measured in streambed piezometers at low river flow conditions in November and December 1998 all showed upward flow of water with head differences between the screens and the river of between 0.002 and 0.233 m with a median value of 0.01 m. Streambed temperature mapping combined with q_v values obtained from piezometer data allowed a very detailed plan-view map of the discharge to be created at this site (Conant, 2004). The pattern of discharge is shown for February 1999 (Fig. 3b) and was very similar in pattern to that for July 1998 (not shown). The mapping identified three high-discharge zones referred to as the west-central, eastern-shore, and south-central discharge areas where vertical fluxes are near or exceeded 200 $\text{l}/\text{m}^2 \text{ day}$. A low-flow band ($< 50 \text{ l}/\text{m}^2 \text{ day}$) was also identified that separated the eastern-shore discharge area from the other two high-discharge areas. A substantial area of recharge was also identified in the riffle downstream of transect 30–

30W. Springs, low-to-moderate discharge zones, and no-discharge zones were also observed at the site.

The streambed discharge in Fig. 3b showed no direct correlation with the streambed surficial geology in Fig. 3a. However, GPR, soil core data, and slug testing data show that the south-central and west-central discharge areas are consistent with the geology at depth. The geological windows through the semi-confining deposits appear to control the pattern of discharge in the streambed. The plan-view mapping of water levels and flow lines drawn for the confined aquifer (Fig. 5a) was also consistent with having discharge occurring in the streambed at the three high-discharge locations and not at the riffle area to the north.

4.3. The upgradient groundwater plume

Characterization of the upgradient land-based plume traveling toward the river provided information on the nature of the contamination that might be found beneath the river. Maximum PCE concentrations encountered in vertical profiles at each Waterloo Profiler location were used to create a plan-view map for the plume (Fig. 5b). The plume shown in Fig. 5b is also based on information from an additional 49 profile points (not shown) that are just east of the area shown (locations are shown in Fig. 1a). Within the plume are two narrow (5 to 10 m wide) high-concentration ($>10,000$ $\mu\text{g/l}$) “cores” (terminology from Cherry, 1996) that extend from the DNAPL source area to the river and are within a 60-m-wide lower concentration “fringe” that is generally less than 1000 $\mu\text{g/l}$. Profiling along transect 6 in July 1996 showed that the entire plume discharges to the river prior to reaching its western shore except near DP9 where 2.5 $\mu\text{g/l}$ of PCE was detected at AP47. The presence of PCE in that area was confirmed by sampling drivepoint piezometers DP9-2 and DP9-3 in November 1996 that detected 5.1 and 26.3 $\mu\text{g/l}$ of PCE, respectively, and when 2.1 $\mu\text{g/l}$ of PCE was detected at BML11 in March 1999. The location of the plume near DP9 and in the upgradient aquifer was consistent with the groundwater flow paths shown in Fig. 5a.

To determine the PCE concentration distribution about to reach the river, the plume in the confined aquifer was characterized in cross section beneath the eastern river bank immediately adjacent to the Pine River. PCE concentrations for transect 5 performed in 1996 and the BML1 to BML10 transect sampled in 1999 are shown at a 1:1 scale in Fig. 6b and c, respectively, and the transect locations are shown in Fig. 6a. In both transects, plume concentrations varied vertically by factors of 100 to 1000 over distances of less than 1 to 2 m. The PCE groundwater plume along transect 5 was generally 5 to 7 m thick and approximately 45 m wide but was only about 4 to 5 m thick in the BML transect. The plume was found only in the confined aquifer and was not observed in the semi-confining deposits except for low concentrations (<10 $\mu\text{g/l}$) found in AP45 and AP46 (Fig. 6b). In transect 5, the peak concentrations in the plume (>1000 $\mu\text{g/l}$) were found in a continuous band that was 1.0 to 1.5 m thick along nearly the full width of the plume. The two plume cores ($>10,000$ $\mu\text{g/l}$) shown in Fig. 5b were either not intersected by the sampling array or were not present. However, the two highest concentrations for transect 5 were 8707 $\mu\text{g/l}$ at AP40 and 6643 $\mu\text{g/l}$ at AP43 which were located where the plume cores should have been. When the BML

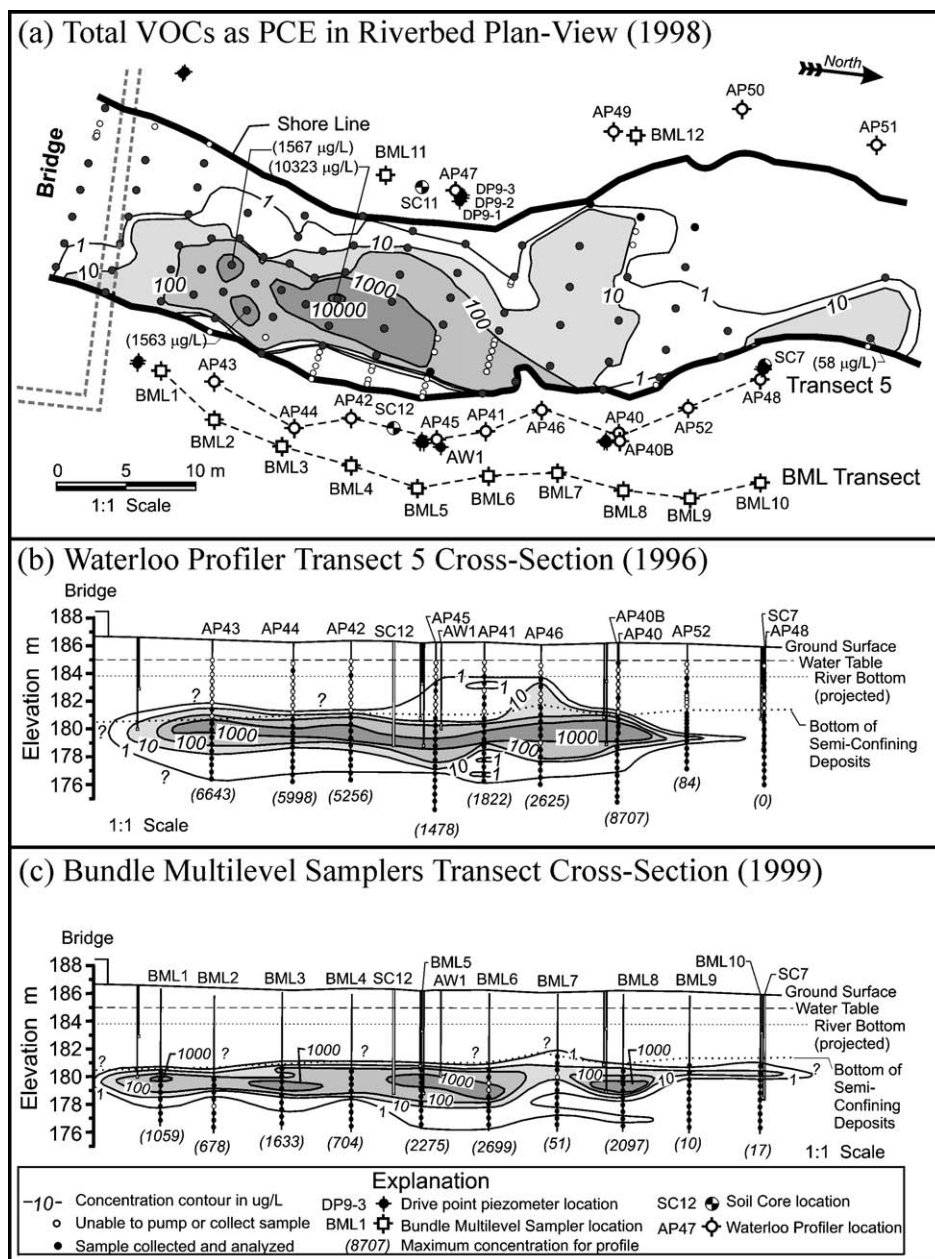


Fig. 6. (a) Plan-view of total VOCs concentrations expressed as equivalent PCE in streambed at a depth of 0.3 m in August 1998. (b) Cross section view of PCE concentrations along transect 5 sampled with Waterloo Profiler in July–August 1996. (c) Cross-sectional view of PCE concentrations along BML transect sampled in March 1999. All figures are at same 1:1 scale.

transect was sampled in 1999, the area with greater than 1000 $\mu\text{g/l}$ of PCE was discontinuous, and the peak PCE concentration for the entire cross section was only 2699 $\mu\text{g/l}$ detected at BML6. Using the contaminant distributions shown across the entire transects in Fig. 6b and c, it was estimated that approximately 19.7 grams of PCE per day (g/day) was flowing toward the river in 1996 but only 7.7 g/day of PCE was traveling toward the river in 1999. These PCE mass discharges are both less than the 58.5 to 146.2 g/day estimated for transect 4 in 1995 based on data from Writt (1996). These differences in the plume over time could be an artifact of: how the sampling array intersected the plume; seasonal changes in the dissolution of the DNAPL source; depletion of the DNAPL source over time; or possibly changes in the flow field caused by profiler holes through the aquitard along transects 1 to 4 that were not sealed during previous studies. This decline in concentration (and mass discharge) over time was also observed at the three profiler locations along transect 4 (near AP27) which had peak PCE concentrations of 109 to 7305 $\mu\text{g/l}$ in 1997 and were considerably lower than the 6096 to 13064 $\mu\text{g/l}$ observed by Writt (1996) at the same locations in 1995. Concentrations observed along the BML transect (BML1 to BML9) in 2001 (Hunkeler et al., in press) were also consistent with this overall trend of declining concentrations and had only two samples with PCE concentrations exceeding 1000 $\mu\text{g/l}$.

The plume in the confined aquifer upgradient of the river was composed almost entirely of PCE with only minor detections of PCE transformation products; therefore, observed declines in PCE concentrations over time are not thought to be caused by anaerobic biodegradation, particularly since the aquifer is not very reducing (anaerobic to possibly nitrate reducing). Analyses of samples of dissolved-phase PCE from the confined aquifer for ratios of ^{37}Cl and ^{13}C isotopes (Beneteau et al., 1999; Hunkeler et al., in press) confirmed that biodegradation of PCE was not a significant process. Some small amounts of degradation products were detected in the plume near the top of the confined aquifer, in the organic rich materials of the semi-confining deposits, and along the northern edge of the plume near the river. For example, along the BML transect low concentrations of cDCE ($<14.5 \mu\text{g/l}$) and TCE ($<9.5 \mu\text{g/l}$) were detected in the top 2 to 4 sampling points in the aquifer at BML7, BML9, and BML10 and 26.8 $\mu\text{g/l}$ of TCE was found at the top most point in the aquifer at BML1. Low levels of PCE degradation products (but no PCE) were also detected in drivepoint piezometers and one streambed piezometer in the area north and west of BML10 which is an area where the PCE plume would have traveled through had it not curved southward to meet the river (Fig. 5a and b). These concentrations are perhaps remnants from a time when the plume had traveled through that area.

4.4. Contamination of interstitial water in the streambed

Fig. 6a shows in plan-view the equivalent PCE concentrations for interstitial water samples collected from the shallow streambed using the mini-profiler in August 1998. The figure shows that the size, configuration, concentration, and composition of the plume found at a depth of 0.3 m in the streambed deposits were significantly different than the PCE concentrations in the upgradient plume shown in cross sections at the

same 1:1 scale along transect 5 and the BML transect (Fig. 6b and c). The major difference was the change in composition caused by anaerobic transformation of PCE to TCE, cDCE, tDCE, 11DCE, VC, ethene and ethane. To directly compare the contaminated area of the streambed to the PCE concentrations found in the confined aquifer, total VOCs detected in the streambed (i.e., PCE and its anaerobic degradation products) were converted to equivalent PCE concentrations.

The plan-view area of contamination in the streambed delineated by the 1 $\mu\text{g/l}$ equivalent PCE contour in Fig. 6a is 469 m^2 or about 2.3 to 3.2 times larger than in the two cross sections (Fig. 6b and c) and the area enclosed by the 10 $\mu\text{g/l}$ contour is about 2.9 to 3.8 times larger. The plume has a similar north–south dimension in both the streambed and aquifer, but is much wider in the streambed than its vertical thickness in the aquifer. This widening is not consistent with the narrowing of flow lines and focusing of flow at the shoreline normally encountered when groundwater discharges to surface water or when flowing through localized areas of preferred discharge (e.g., the eastern-shore discharge area). At some locations, the plume discharges over the full width of the river even though the river is receiving uncontaminated groundwater discharge from the west at some locations. Although plumes normally do not discharge over the full width of the river, that pattern of contamination has been observed where other VOC plumes discharge to rivers (Norman et al., 1986; Savoie et al., 1999; Lyford et al., 1999). The ability of the plume to pass beyond the center of the river may also be a result of higher overall groundwater discharge from the east compared to that from the west. This inequity in flow causes groundwater from the west to discharge primarily along the 50 to 100 l/m^2 day areas along the western edge of the river (Fig. 3b). The overall widening of the plume is primarily a result of the plume traveling up through low hydraulic conductivity semi-confining deposits at depth (see Fig. 7a and b), which requires larger areas (and/or higher gradients) to transmit equal quantities of water through them. Low hydraulic-conductivity layers and anisotropy of geological deposits have been shown to cause similar widening of groundwater discharge areas for flow to a lake (Guyonnet, 1991). Preferential discharge of water from the confined aquifer up into the unconfined deposits near DP9 also caused the plume to spread and reach the western shore while preventing groundwater flow from the west from reaching the river's edge at this location. Although three main areas of preferred groundwater discharge exist in the streambed, these areas have not caused the plume to split up into separate isolated sections and the plume is currently one contiguous area of contamination. It is possible that when the plume initially reached the river decades ago, it might have split up and discharge preferentially through these three separate areas but since then sufficient time has elapsed to allow it to penetrate the intervening lower hydraulic conductivity deposits. However, hyporheic mixing and recharge of surface water into the streambed did occasionally result in small uncontaminated areas being observed within the footprint of the plume in the streambed (e.g., at MLS9 in Fig. 7b).

The internal distribution of concentrations in the plume in plan-view in the streambed had distinct differences when compared to concentrations observed in cross section along transect 5 and the BML transect. The pattern of equivalent PCE

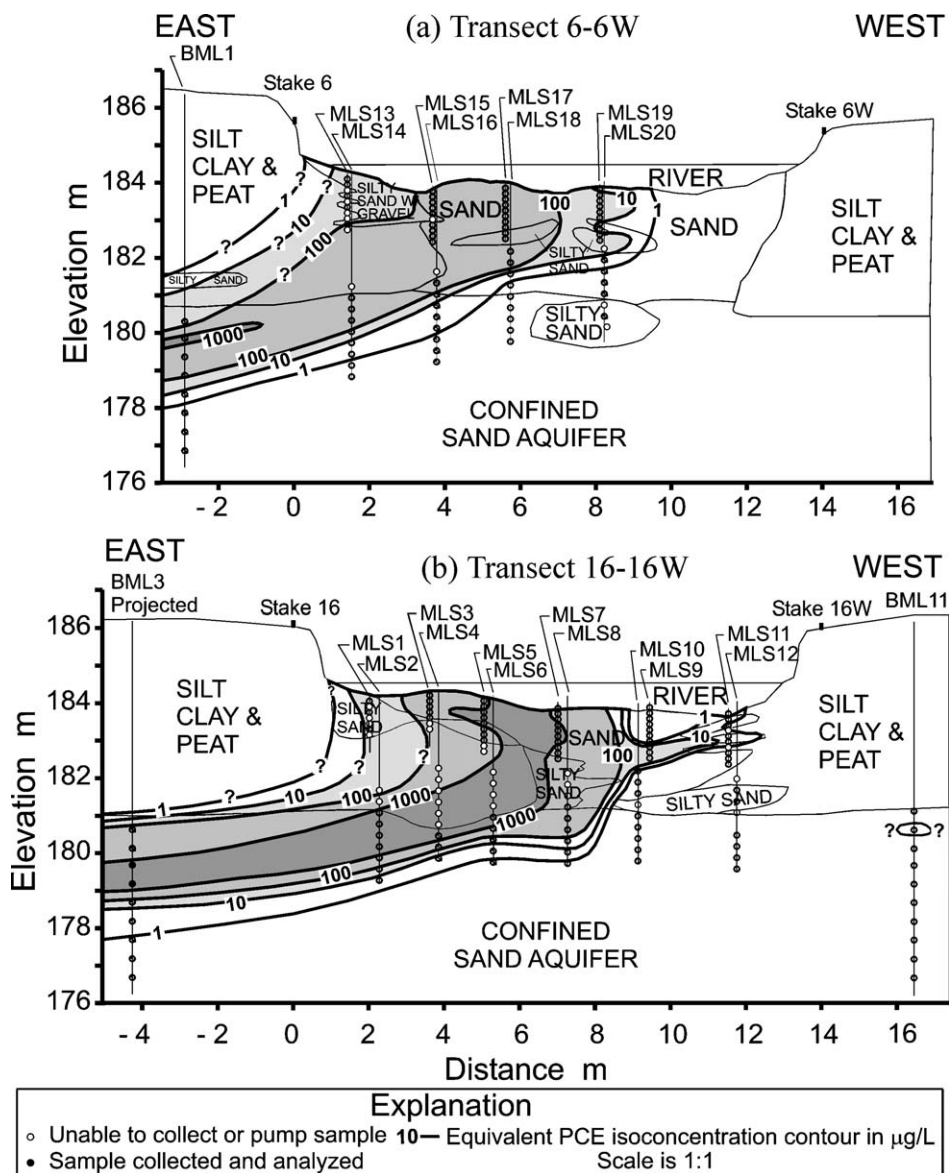


Fig. 7. Total VOCs expressed as equivalent PCE concentrations for MLS and BML points sampled in March 1999 along (a) transect 6-6W and (b) transect 16-16W.

concentrations in the streambed was complex and changed by a factor of 100 to 10,000 over lateral distances of less than 1 to 3.5 m. The areas of the streambed enclosed by the 100 and 1000 $\mu\text{g/l}$ contours (Fig. 6a) did not closely resemble the distributions seen in cross section in the aquifer (Fig. 6b and c). Of the two cross

sections, the BML results obtained from the 1999 sampling are a better match to the streambed concentration distribution, except that high concentrations at BML8 (2097 $\mu\text{g/l}$) to the north are not found in the shallow streambed (concentrations in the streambed were <100 $\mu\text{g/l}$ in that area). Deeper sampling in the streambed at PRP5, PRP6, PRP12, and PRP13 detected maximum concentrations of PCE that were only 2794, 7.3, 841, and 214 $\mu\text{g/l}$, respectively, and also failed to locate the discharge location of the northern plume core seen in Fig. 5b or the 8707 $\mu\text{g/l}$ of PCE observed at AP40. The size of the northern core likely was too small to be detected by the sampling array and/or discharged through a small preferential pathway. The relatively small amount of PCE biodegradation products in the area suggests the core did not disappear as a result of biodegradation. The highest equivalent PCE concentration found during the plan-view mapping occurred at 16–16W 7.0 m where 10,323 $\mu\text{g/l}$ was detected and consisted of 5529 $\mu\text{g/l}$ of degradation products (no PCE) of which 83.5% was cDCE. This high-concentration area may be where the southern high-concentration plume core is discharging to the river but it is more likely a retarded remnant of when the core discharge to that area in the past. Because the southern core was not detected when sampling transect 5 or the BML transect, the core may no longer be present in that area.

The greatest change in the plume was caused by biodegradation that was restricted to the sub-streambed zone. After traveling about 195 m to reach the river with essentially no biodegradation of PCE occurring, the plume is suddenly transformed as it travels through the top 2.5 m of the streambed. Fig. 8a–c shows the distribution of PCE, cDCE, and VC at a depth of 0.3 m in the streambed in August 1998. Peak concentrations of PCE, TCE, cDCE, VC, ethene, and ethane observed in the streambed were 1433, 82, 4619, 823, 100.7, and 76.8 $\mu\text{g/l}$, respectively. At approximately 54% of the locations detecting VOCs in the streambed, PCE had been completely transformed to degradation products. The area of the plume still containing PCE was also 54% (coincidentally) of the total VOC plume area and was limited to three separate and distinct areas corresponding to the three high-discharge areas in the streambed. PCE appears to have been primarily transformed to cDCE (Fig. 8b) with little or no accumulation of TCE (i.e., only five locations had TCE concentrations exceeding 7.8 $\mu\text{g/l}$) and only rare detections of 11DCE or tDCE. This pattern of degradation products is indicative of anaerobic biodegradation processes (Wiedemeier et al., 1999). Further biodegradation of cDCE to VC, ethene, and ethane appears to be limited to areas having the highest equivalent PCE concentrations in Fig. 6a. Large changes in concentrations of degradation products occur on a scale of meters to centimeters both vertically and horizontally. For example, 3639 $\mu\text{g/l}$ of PCE with about 557 $\mu\text{g/l}$ of degradation products were found at PRP8R at a depth of 1.2 m, but at a depth of 1.05 m the PCE concentration was only 125.6 $\mu\text{g/l}$ and degradation products, of which 90% was cDCE, totaled about 3377 $\mu\text{g/l}$ (Fig. 9b). Clearly the streambed has reduced the amount of PCE discharging to the river while increasing the mass of transformation products that is discharging. The overall amount of contamination reaching the river might even be further reduced by other biodegradation processes that mineralize cDCE and VC but have gone undetected because the by-products are carbon dioxide and water (Bradley and Chapelle, 1998).

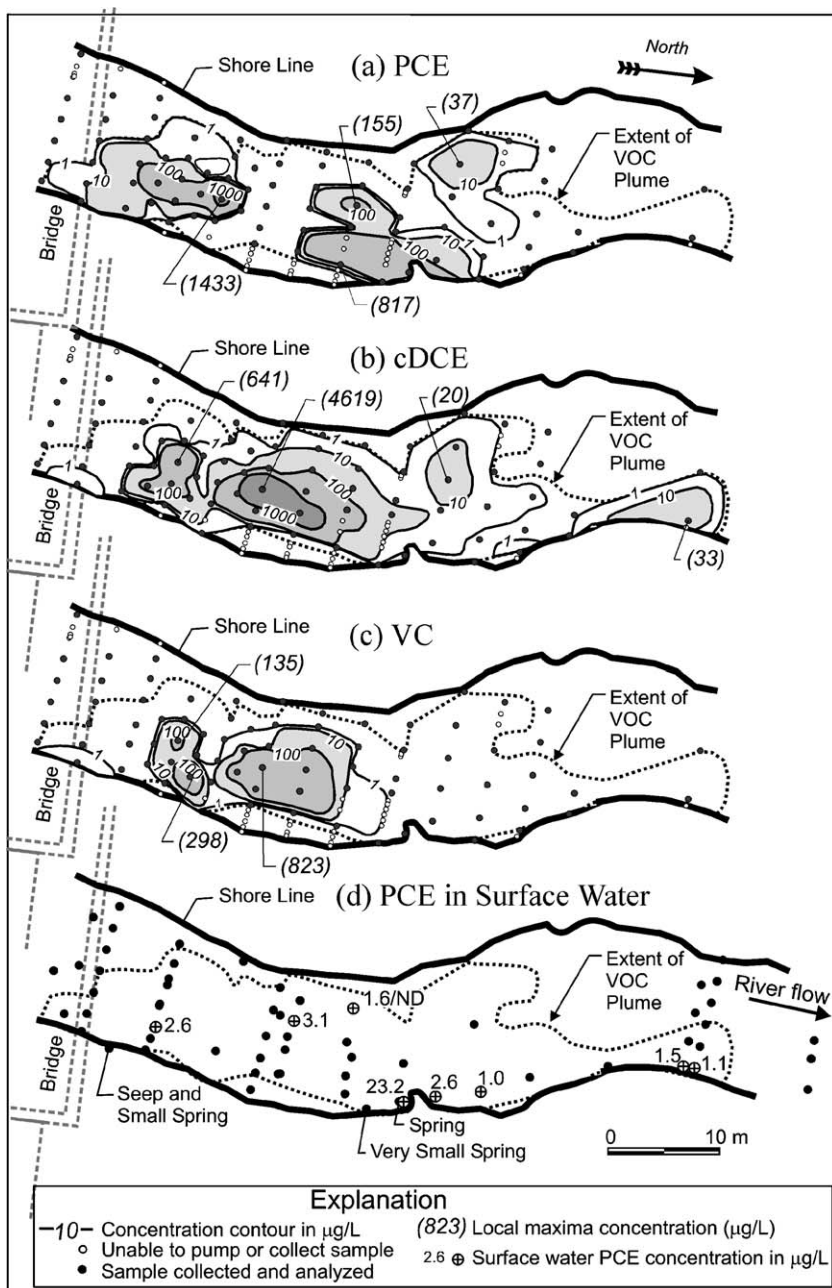


Fig. 8. Plan-views of contaminant concentrations in the interstitial water of the streambed at a depth of 0.3 m in August 1998 for (a) PCE, (b) cDCE, and (c) VC. (d) Surface-water PCE concentrations measured just above streambed (composite of all sampling dates). Note: some locations in (d) were sampled multiple dates and some downstream locations are not shown.

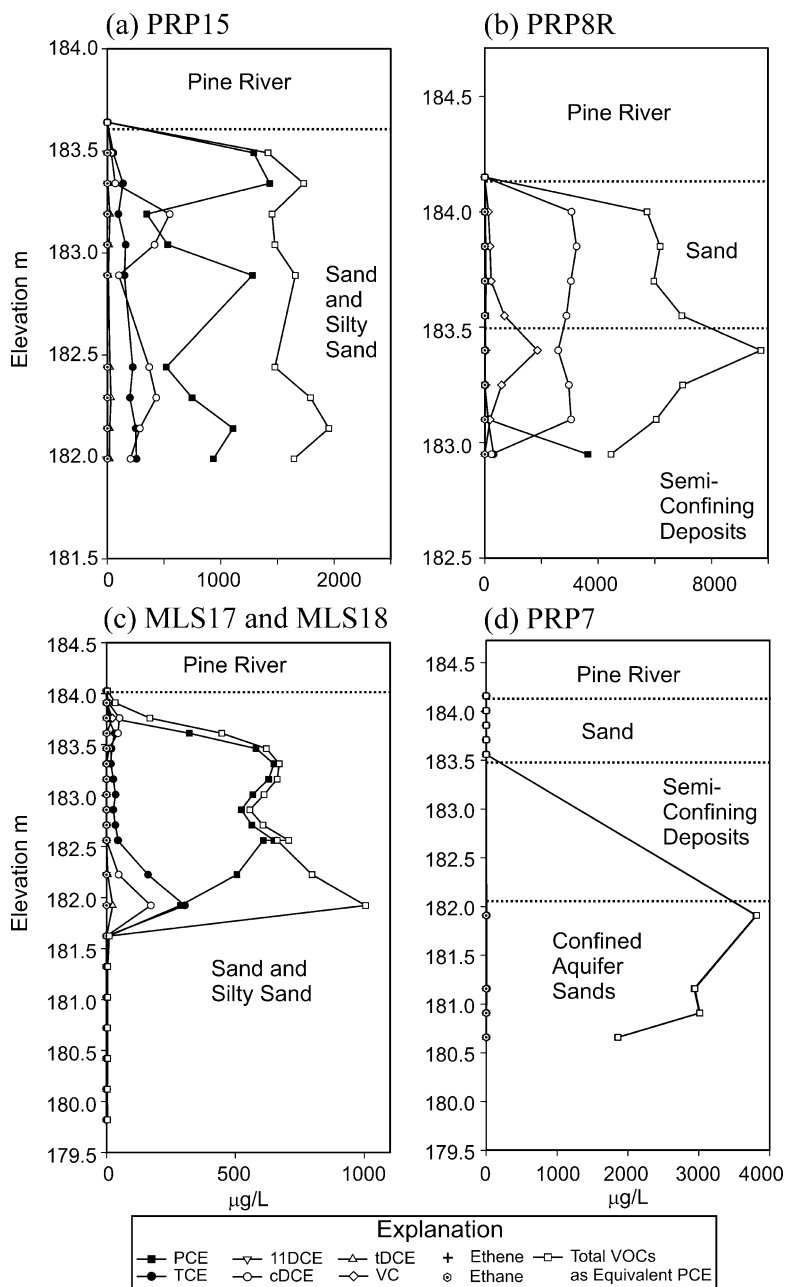


Fig. 9. Vertical profiles of VOC concentrations in interstitial water beneath and in the streambed at (a) PRP15 in October 1997, (b) PRP8R in August 1997, (c) MLS17 and MLS18 in November 1998, and (d) PRP7 in November 1996. Note: results for all eight VOCs were plotted in each figure but some lines overlap such as the PCE and total VOCs lines in (d).

4.5. Interstitial water concentrations in the streambed versus groundwater discharge

An examination of streambed concentrations (Fig. 6a) versus groundwater discharge locations (Fig. 3b) and preferred flow pathways showed that the highest VOC concentrations did not occur where groundwater discharges were highest, but instead occurred where discharge was rather low. High-concentration ($>1000 \mu\text{g/l}$) portions of the plume in cross section (Fig. 7a and b) were not found along preferential groundwater flow pathways (geologic windows) but instead are present in low hydraulic-conductivity semi-confining deposits. Results of sediment analyses from cores RC1 and RC2 (Fig. 10a) confirmed that high concentrations of PCE, TCE, and cDCE were present within the low hydraulic-conductivity deposits. These high concentrations are likely highly retarded or slowly advecting remnants from an earlier time when overall plume concentrations were much higher (n.b., the time required for groundwater to travel from the dry cleaner to the river is about 1.1 to 3.9 years). Since the 1970s, the semi-confining deposits in the streambed were likely exposed to relatively high concentrations of PCE ($>10,000 \mu\text{g/l}$) that had ample time to penetrate the deposits and expand the

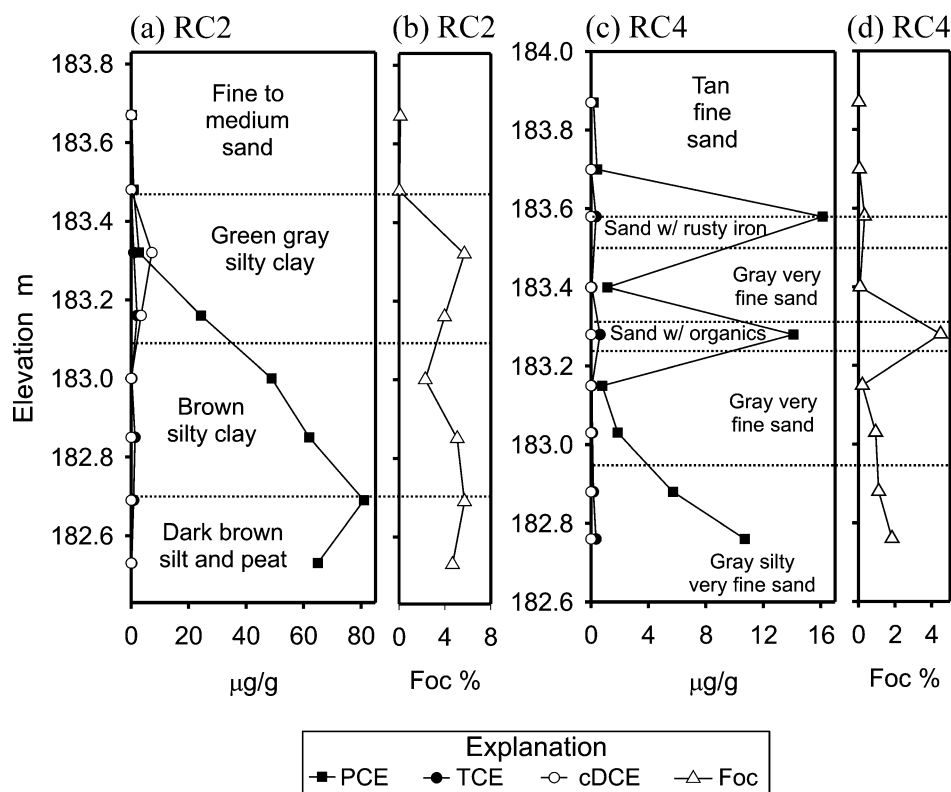


Fig. 10. Vertical profiles of sediment VOC concentrations at (a) RC2 and (c) RC4. Vertical profiles of fraction of organic carbon (f_{oc}) as a percentage at (b) RC2 and (d) RC4.

volume of contaminated deposits beyond the top of the confined aquifer and past the edges of the geological windows (shown in Fig. 7a and b). A slow release of contaminants from these deposits could explain why an equivalent PCE concentration of 10,323 $\mu\text{g/l}$ was detected at 16–16W 7.0 m but equally high concentrations were not detected in the upgradient sand aquifer beneath the riverbank during this study (Figs. 6b,c and 7b). An alternate explanation for why the high-concentrations areas in the streambed do not correlate with high groundwater-discharge locations is that the two types of locations simply do not line up (i.e., do not fall along the same groundwater flow paths). The high-concentration plume cores represent a very small portion of the total groundwater flow traveling from the east and so do not necessarily have to connect directly with the geological windows and high-discharge areas in the streambed.

4.6. Sediment concentrations and contaminant partitioning

Analyses of sediment samples from river cores RC1 to RC4 indicated that the VOC plume contaminated both the fine-grained semi-confining deposits and the streambed sands. Samples of semi-confining deposits from RC1 and RC2 contained maximum concentrations of PCE, TCE and cDCE of 81.02, 2.07, and 7.19 $\mu\text{g/g}$, respectively (Fig. 10a). Streambed sand samples had concentrations up to 16.14 $\mu\text{g/g}$ for PCE and up to 0.63 $\mu\text{g/g}$ for TCE but no cDCE was detected in the samples (Fig. 10c). Samples collected where the plume passes through the sands of the confined aquifer at SC12 were less contaminated and contained a maximum PCE concentration of only 1.33 $\mu\text{g/g}$ for PCE but no TCE was detected and the samples were not analyzed for cDCE.

Contamination of sediments is a function of the interstitial water concentration that they are exposed to and sorption factors (Luthy et al., 1997) that affect the distribution coefficient (K_d) of the material. For materials containing greater than 0.1% f_{oc} , K_d can be approximated by the product of the f_{oc} of the material and the organic-carbon/water partitioning coefficient (K_{oc}) for the contaminant (Schwarzenbach and Westall, 1981; Chiou et al., 1983), which is 364 ml/g for PCE (Mabey et al., 1982). When K_d values were calculated using the f_{oc} data for sands in core RC4, it closely matched the in situ K_d values obtained by core sampling with simultaneous sampling of the water and soil. This match suggests that the K_{oc} – f_{oc} relationship was valid and that the deposits were in chemical equilibrium with PCE. The f_{oc} values for streambed sand samples ranged from 0.027% to 4.5% with a mean of 0.15% (Fig. 10d) and samples of the semi-confining deposits beneath the river ranged from 1.7% to 7.2% with a mean of 4.9% (Fig. 10b). The f_{oc} values were much lower for samples of sand from the confined aquifer, ranging between 0.007% and 0.04%. Based on the f_{oc} values, PCE will tend to adsorb much more to the semi-confining deposits than to the streambed sands or aquifer sands. Calculations of retardation (R) using K_d values (Freeze and Cherry, 1979) indicated that the transport of PCE through the streambed sands will be retarded by a factor of between 1.4 and 67 (with a mean value of 3.2). R values for PCE in the semi-confining deposits beneath the river were between 22 and 88 (with a mean value of 60), and was approximately 1.2 to 1.8 for the aquifer sands. Since the K_{oc} values for TCE (126 ml/g), the three DCE isomers (48 to 65 ml/g) and VC are lower than

that for PCE, K_d and R values for the other VOCs were also smaller. In general, the plume would move relatively quickly and unretarded through the confined aquifer but then move quite slowly beneath the streambed where large amounts of sorption would occur.

Since the plume has been migrating to the river for decades, the semi-confining deposits have likely accumulated (adsorbed) many kilograms of VOC contamination. Even if the upgradient source of PCE at the dry cleaner is remediated, the low vertical groundwater flow velocities (0.016 to 5.1×10^{-5} m/day) and high R factors in the semi-confining deposits could cause the plume to take decades to hundreds of years to flush completely clean under natural conditions. Travel time calculations indicate that, on average, it would take about 4.7 years for PCE to travel through 2 m of silty sand deposits and about 390 years to travel through 2 m of silty clay deposits of the semi-confining deposits. Another concern is that this mass of contaminated sediment can be eroded and carried downstream. While sediments are being transported, they may not have sufficient time to desorb their contaminants prior to being redeposited and buried (Cheng et al., 1995; Rathbun, 1998) and may be detectable further downstream. Even if contaminated sediments are eroded away and transported downstream, the clean materials that are redeposited in their place will be subsequently contaminated by the continued discharge of the groundwater plume.

4.7. Surface-water concentrations

The first two surface-water sampling events in June and October 1996 (consisting of 23 samples) resulted in non-detectable levels for all VOCs except for three samples containing less than $1.6 \mu\text{g/l}$ PCE. Additional sampling over the next few years confirmed these findings with only 5 of 48 samples containing PCE and 5 containing TCE. The highest PCE concentration was $23.2 \mu\text{g/l}$ observed at PRP12, which was immediately downstream of an underwater spring that was discharging groundwater containing up to $806 \mu\text{g/l}$ of PCE and $3.8 \mu\text{g/l}$ of TCE. The other surface-water samples that detected PCE and TCE had concentrations that were less than 3.1 and $3.2 \mu\text{g/l}$, respectively. However, the TCE is likely an artifact of incomplete decontamination of the mini-profiler used for those five samples. None of the 71 surface-water analyses detected 11DCE, cDCE, tDCE, VC, ethene or ethane. The lack of cDCE in the surface water is somewhat surprising since the cDCE plume was larger and had higher concentrations than the PCE plume (Fig. 8a and b, respectively). Possible explanations are that either the cDCE plume mass fluxes are low even though the streambed concentrations are high or that the cDCE aerobically biodegrades (Bradley and Chapelle, 1998) in the top 0.3 m of the streambed prior to reaching the surface water.

Fig. 8d shows that the PCE detected in surface water is generally found either within or downstream of the places where PCE is discharging through the streambed (Fig. 8a). PCE contamination in the streambed seems to coincide with or is down gradient of high groundwater-discharge zones (Fig. 3b), which likely explains why the discharging PCE is detectable in the surface water and has not been diluted to non-detectable levels at those locations. A simple dilution calculation indicated the average surface-water concentration would be $0.16 \mu\text{g/l}$ and thus below detection limits even in this worse case scenario where

the entire mass of PCE migrating toward the river along transect 5 is instantaneously mixed with river water under low flow conditions ($1.39 \text{ m}^3/\text{s}$).

4.8. Potential adverse ecological effects of the discharging plume

In this study, potential adverse ecological effects on aquatic life were inferred by comparing observed water and sediment concentrations to published criteria and guidelines for protecting aquatic life. In the surface water, all the PCE and TCE concentrations detected were considerably lower than established freshwater aquatic life guidelines and would likely not trigger further regulatory actions. USEPA ambient water quality criteria for PCE in freshwater is set at $5280 \text{ }\mu\text{g/l}$ for acute toxicity and $840 \text{ }\mu\text{g/l}$ for chronic toxicity (USEPA, 1986) and the values for TCE are even higher. The interim Canadian water quality guidelines for the protection and maintenance of freshwater aquatic life (which are long-term no-effect levels) issued by the CCME (Canadian Council of Ministers of the Environment, 1993) are 110 and $20 \text{ }\mu\text{g/l}$ for PCE and TCE, respectively. However, surface water guidelines are also used to assess interstitial water quality of the streambed because the organisms there are believed to be equally sensitive to contaminants as those in the water column, even though there may be unique benthic and hyporheic-zone aquatic organisms in the streambed that have different sensitivities. Using this guideline approach, it appears the plume may be causing adverse ecological effects in the streambed; 9 out of 53 locations that detected VOC contamination during the 1998 mapping of the streambed contained PCE concentrations higher than CCME guidelines and the USEPA chronic toxicity guideline was exceeded at one of those locations. Three locations had TCE concentrations that exceeded the CCME guidelines. Assessing the potential impacts of the cDCE, tDCE, 11DCE, and VC found in the streambed is problematic since USEPA chronic toxicity and CCME guidance levels have not been established for them. Furthermore, the published criteria do not take into account the potentially synergistic effects of exposing aquatic life to multiple contaminants simultaneously.

Adverse ecological effects might also occur as a result of aquatic life coming into contact or ingesting contaminated streambed sediments. Even though VOCs are much more volatile and have far lower bioconcentration factors than more recalcitrant contaminants like PCB and polyaromatic hydrocarbons, chronic exposures to VOCs are still possible in the streambed because the dissolved-phase groundwater plume emanates from a relatively long-lived and continuous DNAPL source. Nonetheless, neither the USEPA or CCME have established freshwater guidelines for PCE or its degradation products in sediments. Furthermore, the set of screening quick reference tables (SQUIRTs) for contaminants in water, soil, and sediments compiled from several sources by the National Oceanic and Atmospheric Administration (Buchman, 1998) indicate there were no freshwater sediment guidelines for any of the 32 volatile aromatic and halogenated compounds they listed. However, the concentrations of some sediment samples were higher than ecological toxicity screening criteria (USEPA, 1996) and/or the U.S. Department of Energy (USDOE) preliminary remediation goals (Efroymson et al., 1997), and so would likely trigger further investigations (if these guidelines were applied). Given the complex nature of the exposures in the streambed,

direct in situ toxicity methods (Chappie and Burton, 2000; Greenberg et al., 2002) would likely be a more successful approach to accurately assess the adverse effects of this plume at discharge areas. There is a need for more ecotoxicological research to establish toxicity criteria for volatile organic compounds in freshwater environments and also to evaluate how the areas contaminated by groundwater plumes affect the overall health of the river.

5. Implications for monitoring the streambed and river

The results of this study clearly illustrate that monitoring and characterizing a discharging plume is a challenge because of the fine-scale heterogeneous nature of the plume, geology, and groundwater discharge. For example, the four vertical concentration profiles shown in Fig. 9 illustrate the high spatial variability in the plume vertically and laterally and begs the question of how many samples and at what depth should samples be collected to adequately characterize the site (n.b., profiles were done at different times but PRP15 and MLS17 are only 0.4 m apart while PRP7 and PRP8R are 2 m apart). Spatial variability in sediment concentrations were also seen (Fig. 10) and again raises the question of what depth should sampling be done to obtain “representative” samples. Even the selection of surface-water monitoring locations must be done with care, otherwise one may choose sampling locations that never detect contamination even when there are distinct areas where contamination of surface water continuously occurs. Although this plume is very well characterized, one could still argue that even more investigations would be necessary to resolve some unanswered questions such as what happened to the northern high-concentration plume core? Many VOC plumes at hazardous waste sites are much larger than the Angus plume and discharge to even larger rivers, so the idea of having to monitor a plume on an equally fine scale over a much larger area is daunting. However, if too few monitoring points are used, one may miss high-concentration “hot spots”, high-discharge, or high-biodegradation areas and potentially draw erroneous conclusions regarding the potential impact of the plume. To determine how much monitoring is enough one must first clearly define the questions that need answering and overall goals of the investigation. Hydrogeologists and ecologists need to coordinate their efforts (USEPA, 2000) to develop more effective monitoring strategies for ecological risk assessments. The key is to find quick and low cost ways to characterize the heterogeneity of both the hydrogeological systems (e.g., Conant, 2004; Vroblesky et al., 1996) and ecological systems and then target a subset of representative (or critical) problem areas for further in-depth studies. Since the variability of the hydrogeologic and ecological systems may be quite different, monitoring should be done on a fine enough scale to assure that significant areas of adverse ecological impacts are not missed.

6. Conclusions

This study provides the first comprehensive assessment of a PCE groundwater plume discharging into a river and shows that the near-stream zone substantially modifies the

distribution, concentration, and composition of the plume prior to its reaching the surface water. The complex concentration distribution observed in the streambed was caused by: (1) temporal and spatial variations in the dissolved phase contaminant plume that is emanating from a DNAPL source and is entering the near-stream zone; (2) low-hydraulic conductivity silty-clay semi-confining deposits beneath the river that affect groundwater discharge into the river; (3) extensive biodegradation within the top 2.5 m of the streambed that changes the composition of the plume; and (4) sorption of contaminants to high f_{oc} streambed deposits. Locating the plume in the aquifer upgradient of the river was useful in predicting the section of river where the plume would discharge and the potential range of concentrations headed toward the stream (e.g., plume cores with $>10,000 \mu\text{g/l}$ of PCE); however, it did not provide an accurate image of what the concentration distribution or composition of the plume would be in the streambed. Of the various factors affecting the plume, biodegradation occurring in the shallow streambed deposits had the greatest effect because it altered the composition and potentially changed the overall toxicity of the plume by producing cDCE and VC and, to a lesser extent, TCE, 11DCE, tDCE, ethene, and ethane. The degree of biodegradation in the streambed was not uniform and approximately 54% of the plan-view area of the VOC plume consisted solely of PCE degradation products. High-concentration areas in the streambed did not coincide with the groundwater discharge areas but were associated with low groundwater discharge areas and may represent adsorbed or retarded high-concentration remnants of the plume that have yet to travel all the way through the high f_{oc} semi-confining deposits. Despite the relatively large area of VOCs discharging through the streambed, rapid dilution by clean river water caused the VOCs to be rarely detected in surface water. The low concentrations of PCE that were detected (usually less than $3.2 \mu\text{g/l}$ but once as high as $23.2 \mu\text{g/l}$) were generally found at or downstream of high groundwater-discharge locations. Surface-water concentrations were well below Canadian “no-adverse-effect” levels and USEPA chronic toxicity guidelines for freshwater aquatic life; however, at several locations the high-VOC concentrations within the streambed were higher than those levels and so may represent a hazard to benthic and hyporheic aquatic life. In this study, testing of surface water samples gave no indication of the large amounts of cDCE or VC and other VOCs present in the streambed and; therefore, this study clearly demonstrates that to characterize the nature of a discharging plume one cannot rely on surface-water sampling and that one must investigate the interstitial water quality of the streambed.

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