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Effect of source variability and transport processes on carbon isotope ratios of TCE and PCE in two sandy aquifers

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Abstract

Chlorinated ethenes often migrate over extended distances in aquifers and may originate from different sources. The aim of this study was to determine whether stable carbon isotope ratios remain constant during dissolution and transport of chlorinated ethenes and whether the ratios can be used to link plumes to their sources. Detailed depth-discrete delineation of the carbon isotope ratio in a tetrachloroethene (PCE) plume and in a trichloroethene (TCE) plume was done along cross-sections orthogonal to groundwater flow in two sandy aquifers in the Province of Ontario, Canada. At the TCE site, TCE concentrations up to solubility were measured in one high concentration zone close to the bottom of the aquifer from where dense non-aqueous phase liquid (DNAPL) was collected. A laboratory experiment using the DNAPL indicated that only very small carbon isotope fractionation occurs during dissolution of TCE (0.26‰), which is consistent with field observations. At most sampling points, the $\delta^{13}C$ of dissolved TCE was similar to that of the DNAPL except for a few sampling points at the bottom of the aquifer close to the underlying aquitard. At these points, a ^{13}C enrichment of up to 2.4‰ was observed, which was likely due to biodegradation and possibly preferential diffusion of TCE with ^{12}C into the aquitard. In contrast to the TCE site, several distinct zones of high concentration were observed at the PCE site and from zones to zone, the $\delta^{13}C$ values varied substantially from -24.3‰ to -33.6‰. Comparison of the $\delta^{13}C$ values in the high concentration zones made it possible to divide the plume in the three different domains, each probably representing a different episode and location of DNAPL release. The three different zones could still be distinguished 220 m from the DNAPL sources. This demonstrates that carbon isotope ratios can be used to differentiate between different zones in chlorinated ethene plumes and to link plume zones to their sources. In addition, subtle variations in $\delta^{13}C$ at plume fringes provided insight into mechanisms of plume spreading in transverse vertical direction. These variations were identified because of the high-resolution provided by the monitoring network.

Keywords: Chlorinated solvents; Groundwater; Stable isotopes; CSIA

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1. Introduction

Tetrachloroethene (PCE) and trichloroethene (TCE) are among the most common groundwater contaminants of industrial origin (Squillace et al., 1999). This type of contamination is persistent and is caused by subsurface accumulations of dense non-aqueous phase liquids (DNAPLs), which, in most cases, formed decades ago (Mackay and Cherry, 1989).

The contamination is commonly widespread because plumes of dissolved-phase contamination emanate from the DNAPL source zones. The plumes are not strongly restricted by sorption and substantial biodegradation generally occurs only under anaerobic conditions (Wiedemeier et al., 1999). The common occurrence of PCE and TCE in many aquifers, combined with their propensity to migrate long distances, can make it difficult to relate PCE and TCE in plumes to their specific DNAPL source areas.

Analysis of stable isotope ratios of PCE and TCE has been proposed as a method to distinguish between different subsurface DNAPL sources and to associate plumes with their particular sources (Van Warmerdam et al., 1995). This approach relies on the observation that PCE and TCE DNAPL from different manufacturers, and to a lesser degree different production batches, have different carbon, chlorine and/or hydrogen isotope ratios (Jendrzejewski et al., 2001; Shouakar-Stash et al., 2000; Van Warmerdam et al., 1995). Also, the stable isotope ratios of carbon in the PCE and TCE are used to provide insight into the influence of reductive dechlorination within PCE and TCE plumes (Bloom et al., 2000; Hunkeler et al., 1999; Slater et al., 2001). The substantial isotopic fractionation of carbon associated with anaerobic biodegradation of PCE and TCE limits the use of carbon isotope ratios for identification of different subsurface DNAPL sources to sites where little or no biodegradation occurs. However, many sites fall in this category.

Processes other than biodegradation can potentially also fractionate isotopes in the subsurface, particularly phase transfer processes and diffusion (Clark and Fritz, 1997). For chlorinated ethenes in the groundwater zone, two-phase transfers are relevant: DNAPL dissolution and sorption. Laboratory studies demonstrated that no significant carbon isotope fractionation occurs during sorption of chlorinated ethenes on activated carbon, graphite or polydimethylsiloxane (Hunkeler and Aravena, 2000; Slater et al., 2000). However, isotope fractionation during DNAPL dissolution has not been investigated, nor have the effects of diffusion on isotope ratios during solute transport been determined.

The goals of this study were to determine the effect of DNAPL dissolution and transport of PCE and TCE on their isotopic composition under field conditions in sandy aquifers and to acquire field evidence pertaining to the use of carbon isotopes to link plumes to DNAPL source zones in aquifers where degradation is minor. This study focuses on carbon isotopes because less mass is required for analysis compared to other isotopes, which allows for much lower detection limits. While laboratory studies make it possible to evaluate the effect of isolated processes on isotope ratios, they simplify the complexity of the field situation and generally omit effects arising from simultaneously occurring processes. Two field sites on sandy aquifers were selected, one in Kitchener, Ontario, where TCE contamination was caused by manufacturing operations occuring decades ago and the other in the town of Angus, Ontario, where PCE contamination originated in the 1970s and 1980s due to dry cleaning. At both sites, comprehensive networks of depth-discrete, multilevel groundwater samplers had been previously installed and previous studies indicated a lack of substantial degradation. These monitoring systems were essential to the study because they allowed for an exceptionally detailed delineation of the spatial distribution of the chlorinated ethene plumes detail, which enabled intensive sampling for carbon isotopes in the various zones of the contaminated systems. At the former manufacturing site, a pool of free-product TCE near the base of the aquifer provided DNAPL samples, which allowed determination of the isotope ratio of the DNAPL for comparison with the dissolved TCE in the downgradient plume. Also, the DNAPL was used in a laboratory experiment to examine carbon isotopic fractionation related to DNAPL dissolution. At the dry cleaning site, the PCE plume was known to exhibit three distinct segments immediately downgradient of the source area, which provided a field framework for examining whether these segments resulted from different DNAPL sources. Previous monitoring at the two sites established that the DNAPL sources have only one chemical component, PCE or TCE.

2. Site description

2.1. Kitchener site

This site is located in the City of Kitchener, Ontario, Canada, about 100 km southwest of Toronto. The TCE contamination was caused by former manufacturing operations at the site about which little is known. Sparse historical records indicate that the property was used by various businesses since 1928 and that TCE releases probably occurred several decades ago and may have continued into the 1980s or later. The TCE contamination, which was first detected in 1992, occurs in a surficial sandy deposit. The general geology in the source area consists of about 4 m of fine sand, overlying a 1 m thick transition zone that abruptly changes to a uniform clayey silt till aquitard. The transition zone exhibits much more textural variability, with thin layers or lenses of silty and clayey material separating distinct sandy layers. In the source zone, the TCE DNAPL occurs entirely in the transition zone within two thin vertically discrete sandy layers separated by silty or clayey beds (Parker et al., 2003). No DNAPL was found in the aquifer overlying the transition zone, suggesting there has been sufficient time for any DNAPL within the aquifer to dissolve away. Groundwater flow in the aquifer and transition zone is horizontal. The average linear groundwater velocity was estimated based on porosities and hydraulic conductivities measured in cores and hydraulic gradients. It amounts to 6–18 m/year in the aquifer and 3.5 m/year in the transition zone.

Groundwater conditions and the contaminant distribution are monitored using a network of conventional monitoring wells and depth-discrete multilevel samplers that were installed in previous studies. Fig. 1 shows the sampling instrumentation used in this study and the extent of the dissolved-phase plume. The conditions observed at the time of this study had not been disturbed significantly by any remedial activities.

The multilevel samplers were constructed to provide for acquisition of depth-discrete groundwater samples from different depths at each monitoring location. The multilevel samplers consist of 1/2-in. polyethylene (PE) tubes centered around a single 3/4-in. diameter PVC center stock (Cherry et al., 1983). Spacing between adjacent sampling points was 30 cm for most points. For identification of the sampling points, they were numbered starting with 1 from the top towards the bottom. Groundwater samples were taken using a peristaltic pump with a 1/4-in. teflon (PTFE) tube that was lowered into the PE tubes. The sampling points were purged to replace at least one tube volume before sampling. At sampling points in zones of low-permeability, samples were taken following

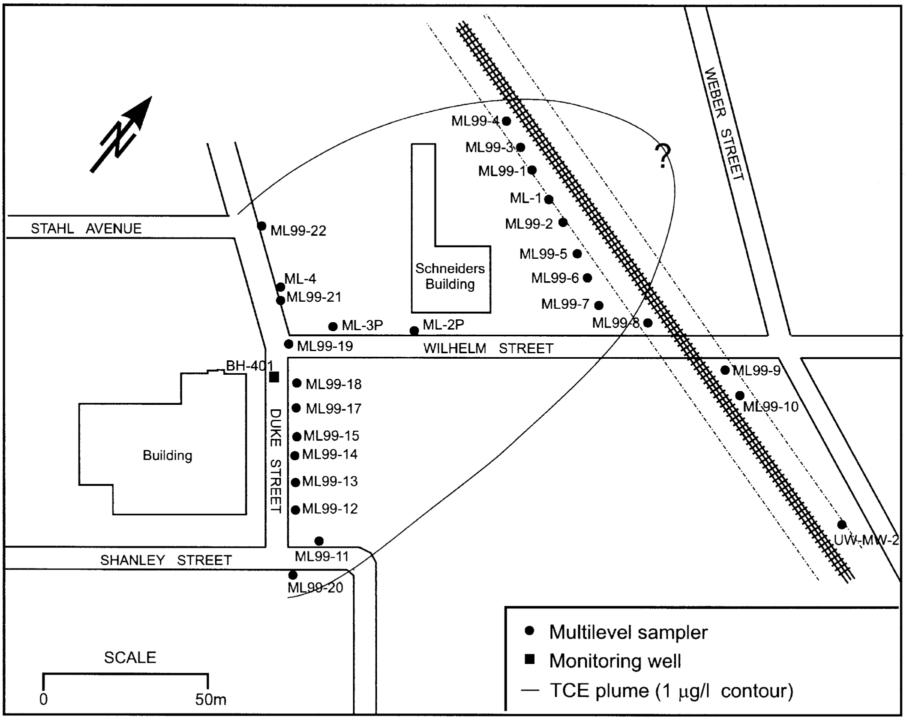


Fig. 1. Map of Kitchener field site with locations of multilevel samplers (circles) and monitoring well used for DNAPL sampling (BH-401). Due to lack of monitoring locations downgradient of the CN-transect, the current extent of the plume is not known.

a water level recovery, after completely emptying the sampling tubes. Aqueous samples were dispensed into 20 ml volatile organic compounds (VOC) vials for concentration analysis and 40 ml vials for isotope analysis. At selected sampling points, additional samples were taken in VOC vials for analysis of degradation products and in high-density polyethylene (HDPE) bottles for analysis of anions and cations. The pH, redox potential and temperature were directly measured in the field. DNAPL TCE was sampled from a conventional monitoring well, BH-401, which was screened at the bottom of the aquifer (Fig. 1). Sediments in the well prevented using a bailer to collect DNAPL. Therefore, sampling was carried out with a stainless steel tube with the bottom 30 cm screened and wrapped with a metal mesh. The tip of the tube was pushed into the sediments at the bottom of the well and DNAPL was sampled using a peristaltic pump.

2.2. *Angus site*

This site is located 80 km northwest of Toronto and 5 km northeast of the Borden hydrogeological research site operated by the University of Waterloo. Fig. 2 shows that a PCE plume in the sandy aquifer extends horizontally from the dry cleaning facility to a discharge zone in the bottom of a river (Conant, 2004; Conant et al., submitted for publication). Dry cleaning operations using PCE began in the early 1970s and PCE use

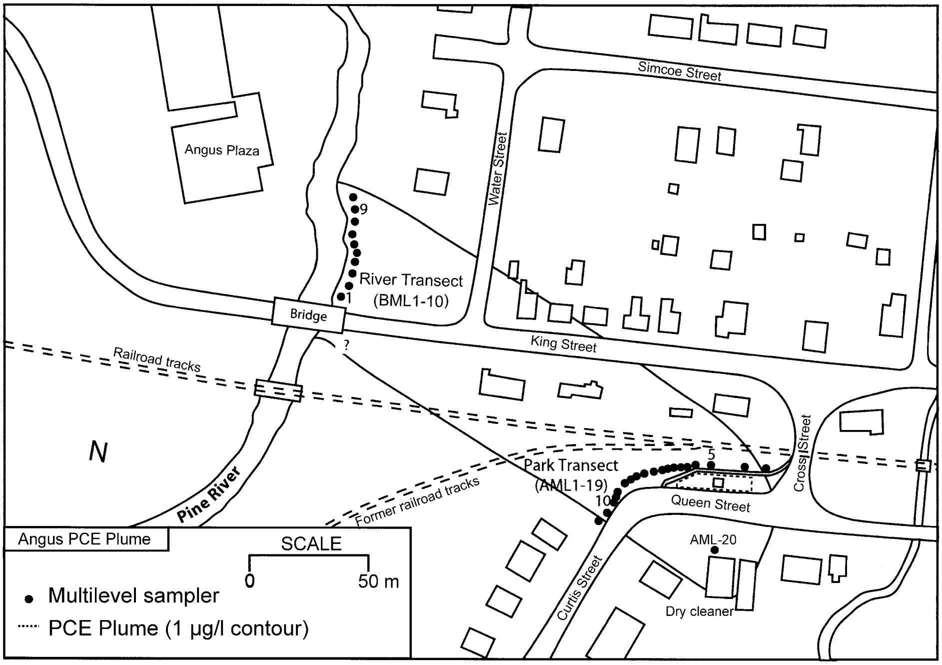


Fig. 2. Map of Angus field site with locations of multilevel samplers (circles) at park and river transects. The southern margin of the plume in the vicinity of the river is not known due to the absence of sampling locations outside of the plume.

continued until 1992, when the PCE contamination was discovered. Other PCE users may have existed in previous decades in the vicinity of the dry cleaner. The monitoring of the PCE plume began in 1992 with various expansions of the network since then. DNAPL has not been sampled at this site because the DNAPL zones occur beneath the dry cleaning building, which recently expanded in area, and beneath an adjacent building constructed a few years ago. The conclusion that DNAPL zones persist in the sand aquifer beneath the buildings is based on various lines of evidence including detailed dissolved-phase concentration profiles immediately downgradient of the buildings (Guilbeault et al., submitted for publication). The evidence indicates that the DNAPL occurs as thin layers suspended in the sand aquifer.

The hydrogeological conditions were determined in previous investigations (Guilbeault et al., submitted for publication) based on aquifer coring to determine geology and hydraulic conductivity. The sand aquifer, which is nearly homogeneous, is formed of medium sand deposited in a glacial meltwater river. A linear groundwater velocity of 0.5–1 m/day was obtained from hydraulic conductivities determined by permeameter measurements on eight core samples, the hydraulic gradient, and an estimated porosity.

In the vicinity of the dry cleaning facility, the sand deposit extends to ground surface. Therefore, the downward flow path of the DNAPL had no low-permeability obstructions. However, beginning a short distance downgradient, a thin silty clay and peat layer occurs at a depth of 5 m below ground surface. The PCE plume is positioned beneath this layer, which is continuous to near the river. The trail of residual DNAPL at shallow depth has been removed by groundwater dissolution over decades and therefore no plume occurs above the silty clay and peat layer.

The plume has been delineated in detail all the way from the front of the dry cleaning building to the river (Conant, 2004; Conant et al., submitted for publication; Guilbeault et al., in press). This delineation was accomplished using transects of depth-discrete multilevel samplers and/or the Waterloo groundwater profiler, as described by Pitkin et al. (1999). Our study made use of two transects of multilevel samplers, located in Fig. 2. One of the transects is situated 40–50 m downgradient of the dry cleaning facility and the second one is farther downgradient close to the river. The multilevel samplers are similar in general design to those used at the Kitchener site, but the dimensions of some of the tubing are different with 1/4-in. instead of 1/2-in. PE tubes. Spacing between adjacent sampling points was 15 cm for most points. Groundwater samples from multilevel sampler with 1/2-in. tubes were taken as described above for the Kitchener site. For those with 1/4-in. tubes, a 1/4-in. HDPE tube was directly connected to the tubes of the samplers. At the river transect, it was possible to take samples using syringes directly attached to the tubes of the samplers due to the shallow location of the aquifer. At selected sampling points, additional samples were taken in VOC vials for analysis of degradation products.

3. Laboratory experiment

A laboratory experiment was performed to evaluate isotope fractionation during dissolution of TCE and to determine the expected δ^{13}C of dissolved TCE at the Kitchener field site. The experiment was performed using TCE DNAPL recovered from the site. The $\delta^{13}C$ of TCE was determined after complete dissolution of a small quantity of DNAPL to obtain a 50 mg TCE/l aqueous solution, followed by isotope analysis as described below for field samples.

Carbon isotope fractionation during dissolution of TCE was evaluated by adding a drop of TCE DNAPL to a 40 ml VOC vial containing distilled water. The amount of DNAPL was chosen such that $<15\%$ of DNAPL would dissolve when TCE solubility was reached to simulate DNAPL dissolution at field sites. Stirring with a magnetic stirrer was not done to avoid dispersion of the drop into smaller droplets, which would have made it difficult to identify potential isotope fractionation because some of the small droplets would completely dissolve. Therefore, dissolution of the TCE was promoted by placing the vial on a tilting shaker. During tilting, the drop rolled along the wall of the vial without disintegration. The vial was placed on the shaker for 24 h, which was sufficient to reach solubility as indicated by preliminary experiments. After 24 h, aqueous samples were taken and analyzed in the same manner as field samples (see below). For comparison, the laboratory experiment also included simultaneous analysis of the two samples from the Kitchener field site with the highest groundwater TCE concentrations.

4. Analytical methods

4.1. Concentration analysis

Concentrations of chlorinated ethenes were determined using a Hewlett-Packard 6890 (Agilent, Palo Alto, USA) gas chromatograph equipped with a HP-624 column (30 m × 0.32 mm, 1.8 μm film thickness, Agilent) and an electron capture detector. Aqueous samples were extracted with pentane containing 1,2-dibromoethane as internal standard. One microliter pentane was injected in splitless mode at 225 °C and at 3 ml/min carrier gas flow. The following temperature programme was used: 4 min at 35 °C, then to 60 °C at 10 °C/min, then to 105 °C at 30 °C/min, and 2.5 min at 105 °C. Concentrations were quantified using external standards. The detection limit was 1 μg/l for PCE and TCE, and 100 μg/l for the DCE isomers. Selected samples were also analyzed for degradation products using a headspace method with a detection limit of 1 μg/l for DCE isomers and vinyl chloride. The headspace samples were analyzed with a Hewlett-Packard 5890 (Agilent) gas chromatograph equipped with a HP-7694 autosampler and an electron capture detector. Concentrations of nitrate (MDL 0.05 mg/l) and total dissolved Fe (MDL 0.02 mg/l) were determined using an automated colorimetric analyzer and ICP−AES, respectively. The redox potential was measured directly in the field with a potentiometric electrode (Fisher).

4.2. Stable isotope analysis

Carbon isotope ratios were determined using a gas chromatograph (Hewlett-Packard 6890, Agilent) equipped with a RTX-5 column (60 m × 0.25 mm, 1.0 μm film thickness, Restek, Bellefonte, PA) and connected via a combustion interface to a Micromass Isochrom isotope-ratio mass spectrometer (Micromass, Manchester, UK). Water samples were extracted with solid phase microextraction (SPME) using polydimethylsiloxane–carboxen fibers. To reach a high accuracy and precision of the measurement despite concentration variations over five orders of magnitude, all samples with concentrations >50 μg/l were diluted to 50 μg/l before analysis using Nanopure water. Samples with concentrations < 50 μg/l were diluted to 20 μg/l and 25% weight NaCl was added. After dilution in 40 ml VOC vials, 5 ml of aqueous phase was replaced by air and the SPME fiber was exposed to the headspace for 15 min, while the aqueous phase was stirred with a magnetic stirrer at 1100 rpm. The fiber was desorbed at 300 °C for 5 min. The carrier gas flow was 1.2 ml/min. The oven temperature was held at 80 °C for 1 min and then heated to 210 °C at 15 °C/min. The $\delta^{13}C$ values were calculated relative to external CO_2 reference gas and corrected for the small isotope fractionation during extraction using reference TCE and PCE that were analyzed analogous to the samples at corresponding concentrations. The detection limit was 10 μg/l for TCE and 5 μg/l for PCE. Except for the few samples with concentrations < 50 μg/l, the analytical procedure led to similar peak shapes and peak sizes independent of the concentration thus avoiding potential amount-dependent isotope fractionation. Each sample was analyzed twice and the standard deviation for the entire set of samples was calculated, which was 0.23‰ for TCE and 0.12‰ for PCE. All results are reported in the δ-notation relative to the international VPDB standard.

5. Results and discussion

5.1. Kitchener field site

Fig. 3 illustrates the distribution of TCE at the Kitchener field site along two transects (Fig. 1) roughly perpendicular to groundwater flow in July 2001. One of the transects is located immediately downgradient of the source (source transect), the other lies about 120 m downgradient of the source (CN-transect). In the source transect, one zone with high TCE concentrations (>100 mg/l) can be observed extending from ML99-17 to ML99-19 (Fig. 3A). The highest TCE concentrations occur in the transition zone where DNAPL was detected in previous studies (Nowak, 2000; Parker et al., 2003). The highest TCE concentration (1422 mg/l) is close to TCE solubility, which is 1400 mg/l at 23–24 °C (Broholm and Feenstra, 1995). The plume of dissolved TCE has a width of over 100 m, reflecting the DNAPL distribution in the source area and a water table mound immediately upgradient of the source area that causes diverging groundwater flow across the source area. In the CN-transect, much lower TCE concentrations were detected with concentrations of up to 2.33 mg/l. Comparison of the measured concentrations with values obtained 2 years earlier indicate that the plume is still expanding.

To evaluate carbon isotope fractionation during DNAPL dissolution, the $\delta^{13}C$ of DNAPL from the site was compared to the $\delta^{13}C$ of the laboratory dissolution experiment and to the $\delta^{13}C$ of sampling points #6 and #7 in ML99-18, which show TCE concentrations close to solubility (Table 1). The comparison of the $\delta^{13}C$ for TCE from complete and partial (< 15%) DNAPL dissolution indicates that a statistically significant

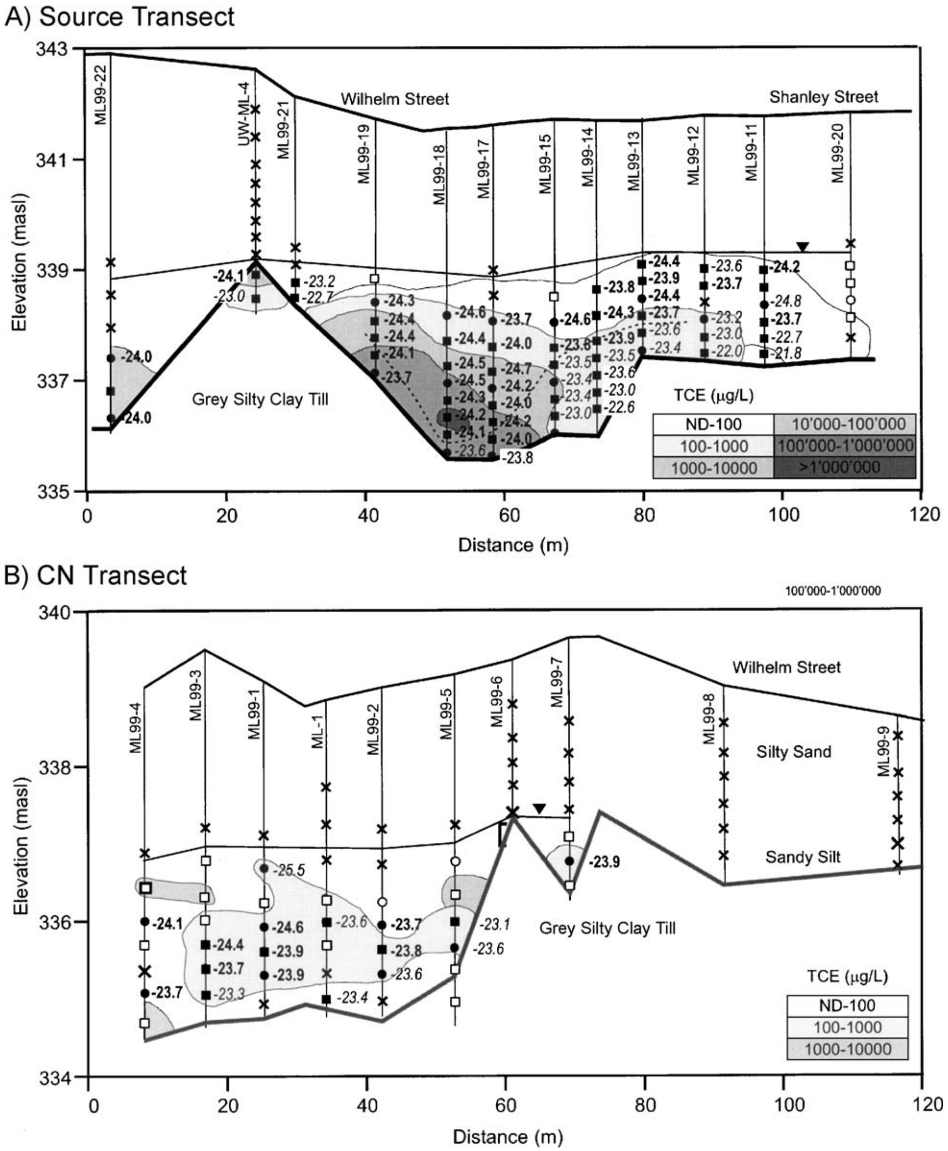


Fig. 3. Kitchener site: TCE concentration contours and $\delta^{13}C$ values of TCE for transect close to source (A, source transect) and along the railway line (B, CN-transect). Values in italics indicate $\delta^{13}C$ deviates by more than 2σ from $\delta^{13}C$ of source. Open symbols, sampling locations where TCE concentrations were measured; filled symbols, sampling locations where concentrations and $\delta^{13}C$ of TCE were measured; circle, locations where in addition nitrate, total iron and degradation products (dichloroethene isomers, vinyl chloride) were measured; cross, no measurements made because of location above water table or because sampling point was clogged. Dotted line in source transect, boundary below which redox potential was <100 mV.

Table 1
$\delta^{13}C$ values of TCE from Kitchener field site with 95% confidence interval

Sample	$\delta^{13}C$ (‰ VPDB)
TCE DNAPL (complete dissolution of small DNAPL quantity)	-24.45 ± 0.01 ($n=3$)
Dissolved TCE equilibrated with DNAPL drop (partial dissolution of DNAPL $<15\%$)	-24.19 ± 0.06 ($n=3$)
ML99-18 #6 (1432 mg/l TCE)	-24.19 ± 0.02 ($n=3$)
ML99-18 #7 (978 mg/l TCE)	-24.11 ± 0.20 ($n=3$)

though very small carbon isotope fractionation occurs during DNAPL dissolution under equilibrium conditions (Table 1). Dissolved TCE is slightly enriched in ^{13}C compared to DNAPL TCE. The $\delta^{13}C$ for partially dissolved TCE in the laboratory experiment (-24.19 ± 0.06‰) is in excellent agreement with the $\delta^{13}C$ of the two field samples (ML99-18-#6/7, Table 1). Thus, the partial dissolution experiment adequately agrees with the $\delta^{13}C$ of dissolved TCE close to the DNAPL at the field site. Therefore, the $\delta^{13}C$ values of TCE at the field site are compared to the $\delta^{13}C$ of partially dissolved TCE (denoted below as $\delta^{13}C$ of the source) to identify isotope fractionation due to processes other than dissolution.

In the source transect (Fig. 3A), the $\delta^{13}C$ values vary between -21.8‰ and -24.8‰. To evaluate the spatial distribution of $\delta^{13}C$ variations, all values that deviate by more than two times the standard deviation of the measurement from the $\delta^{13}C$ of the source (± 0.5‰) are given in italics in Fig. 3A. Most of the $\delta^{13}C$ values in the high concentration zone are close to -24.2‰, the isotope composition of the TCE source. The slightly ^{13}C enriched values compared to the source mainly occur at deeper sampling points within a multilevel sampler, which suggest that the enrichment in ^{13}C could originate from some biodegradation or from preferential diffusion of TCE with ^{12}C from the transition zone into the aquitard. Diffusion of TCE into the aquitard was shown to occur at the site (Nowak, 2000). Concentration of redox sensitive species (nitrate, iron), redox potential, and occurrence of degradation products provide information about biodegradation. Note that concentrations of nitrate, iron, and degradation products were only determined for selected sampling points illustrated by circles in Fig. 3. Redox conditions tended to be more reducing towards the bottom of the aquifer as illustrated by the dotted line below which the redox potential was <100 mV (Fig. 3A). The occurrence of more reducing conditions near the aquitard is also demonstrated by low nitrate concentrations (<0.3 mg/l) and presence of dissolved Fe (0.09–0.33 mg/l) in sampling points below the dotted line. In contrast, in sampling points above the dotted line, no dissolved iron was detected (<0.02 mg/l) and nitrate was present at concentrations of up to 36 mg/l. Furthermore, in the lowest sampling point of AML-15, 17, 18, 19 and 22, total concentrations of DCE and VC were >100 μg/l while at sampling points further away from the aquitard, DCE and VC were absent or total concentrations were <100 μg/l. The maximum total concentration of degradation products corresponds to 1.2% of the TCE concentration, except for ML99-22 where higher fractions of degradation products (up to 8%) were found. The presence of degradation products closer to the aquitard support the hypothesis that enrichment of ^{13}C is due to some biodegradation closer to the aquitard, which maybe caused by the presence of more organic carbon in this part of the aquifer. In ML99-18 and ML99-17, only the lowest point shows a shift in δ^{13}C in contrast to ML99-15 and ML99-14. At ML99-18 and ML99-17, biodegradation may have been impeded by the very high TCE concentration at depths above the lowest point.

The hypothesis that the shift in δ^{13}C is due to biodegradation can further be tested by calculating the amount of biodegradation necessary to explain the observed shift in δ^{13}C, which amounts to 1‰ in the average. Using the average enrichment factor for TCE dechlorination from previous studies (− 5.4‰, Bloom et al., 2000; Sherwood Lollar et al., 1999), a shift of 1‰ corresponds to 17% biodegradation of TCE. This is larger than expected based on concentrations of degradation products. The discrepancy could be due to some contribution of diffusion of TCE from the transition zone into the aquitard to the shift in δ^{13}C, or because the degradation products (cDCE and VC) were degraded as well.

In the downgradient CN-transect, 10 out of 17 sampling locations have δ^{13}C values similar to the δ^{13}C of the source (Fig. 3B). Most of the other points show shifts towards more enriched δ^{13}C values possibly due to some biodegradation. However, the deviations from the source δ^{13}C are generally less than 1‰ indicating that degradation is minimal in this plume. The conservative behavior of δ^{13}C values of TCE is also apparent in Fig. 4, which illustrates the δ^{13}C values for the sampling point with the highest TCE concentration in ML99-19, ML-3P, ML-2P and ML99-7. Despite the strong decrease of the TCE concentration with increasing distance from the source, the δ^{13}C of TCE in the high concentration core of the plume is not significantly different from the δ^{13}C of the source.

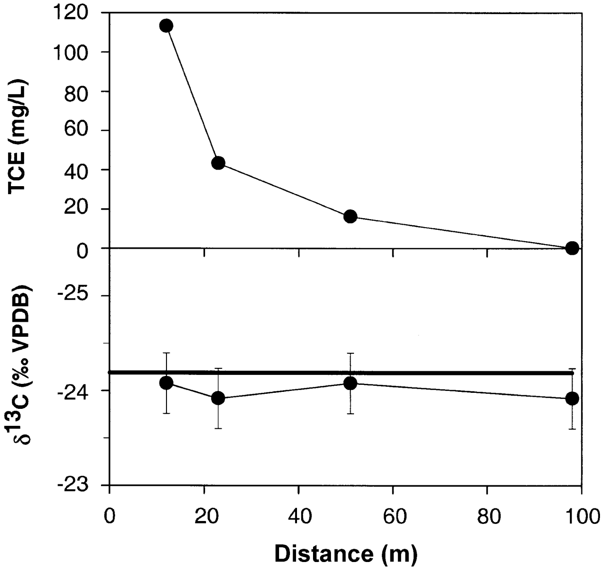


Fig. 4. TCE concentration and δ^{13}C of TCE for sampling point with highest TCE concentration in ML99-19, ML-3P, ML-2P and ML99-7 as a function of distance from source at Kitchener site. Line, δ^{13}C of TCE of the source.

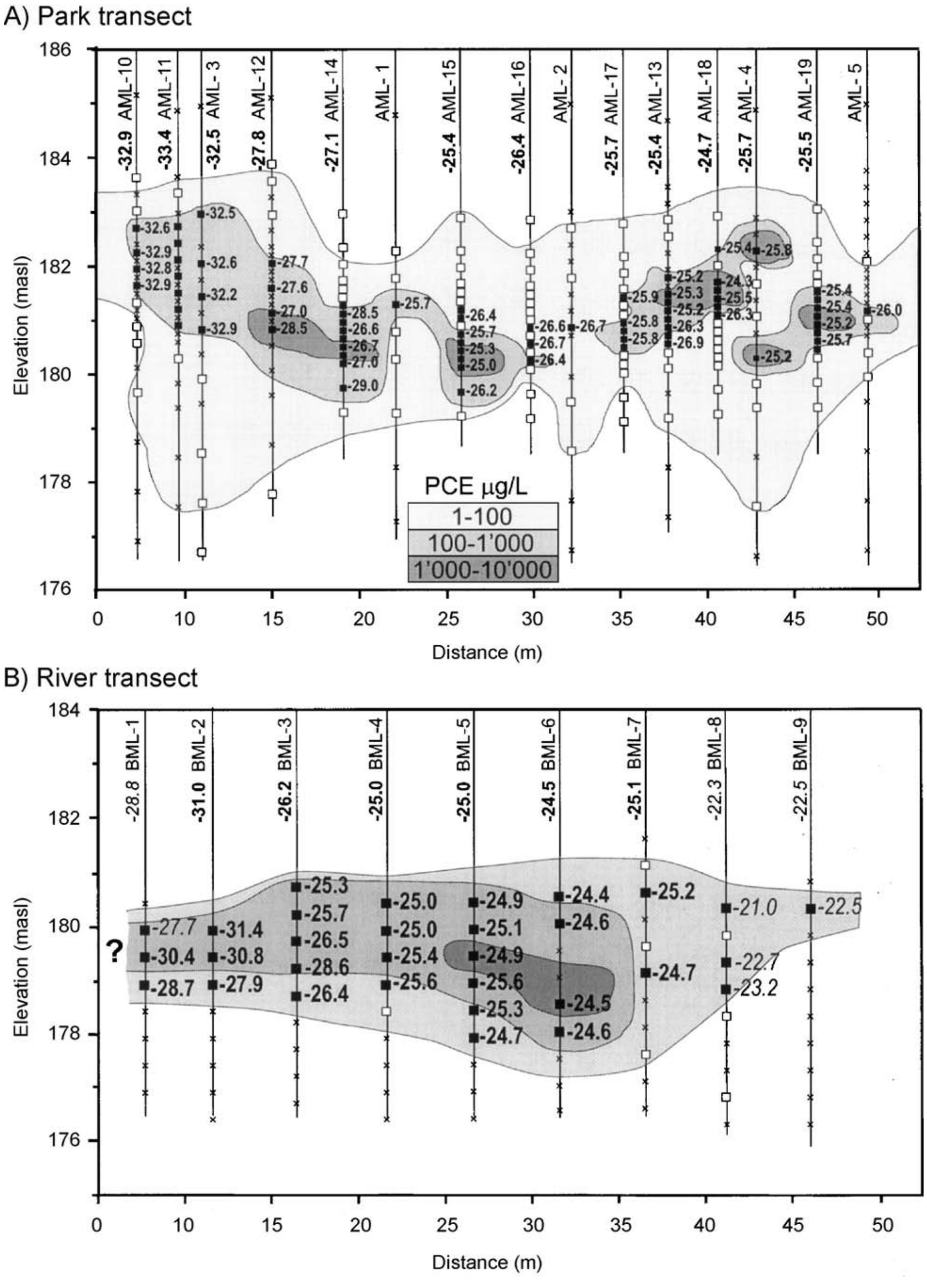
5.2. Angus site

Fig. 5 shows the PCE contours along the park and river transects located about 40–50 and 220 m downgradient of the suspected source area, respectively. The PCE plume consists of several hot spots (PCE concentrations >1000 μg/l) up to 30 m apart with peak concentrations of up to 6460 μg/l originating from DNAPL suspended in the aquifer separated by zones of lower concentrations. This raises the question whether the different hot spots in the plume originate from the same PCE release or whether release of different PCEs at different locations have occurred. Fig. 5A shows substantial variation of the carbon isotope ratio with $\delta^{13}C$ values from − 24.3‰ to − 32.9‰ in the park transect. Biodegradation is an unlikely cause for the observed variations of $\delta^{13}C$ given that the PCE degradation products, TCE and DCE, occur at very low concentrations (< 16 μg/l) or below the detection limits nearly everywhere and vinyl chloride was absent. Slightly elevated TCE concentrations (up to 45 μg/l) were only found in AML-19. Thus, the variations in $\delta^{13}C$ are likely due to variations in $\delta^{13}C$ of the source and/or physical processes. In multilevel samplers with steep concentration gradients, variations of the $\delta^{13}C$ within multilevel samplers tend to consist of more negative $\delta^{13}C$ values at the fringes of the hot spots compared to the core as illustrated for selected locations in Fig. 6. The depleted PCE $\delta^{13}C$ values at the plume fringes may be due to diffusion, which is expected to be slightly faster for molecules with ^{12}C compared to ^{13}C. Transverse vertical dispersion is typically very small in relatively homogeneous sand aquifers as demonstrated by tracer experiments (Freyberg, 1986) and landfill plumes studies (Frind and Hokkanen, 1987) conducted in the same sand aquifer at the Borden site located about 5 km from the Angus site. Low transverse vertical dispersion is also indicated by the abrupt changes in concentration displayed by the profiles observed in this study. To take an extreme example, in AML-18, the concentration drops over nearly three orders of magnitude from 6460 to 89 μg/l within 45 cm in vertical direction. Due to the small vertical transverse dispersion, the diffusive contribution to vertical transverse dispersion may be sufficient to cause carbon isotope fractionation in the vertical direction.

To facilitate the comparison between $\delta^{13}C$ values in different parts of the plume, the concentration-weighted average $\delta^{13}C$ value for each multilevel bundle was calculated (Fig. 5). The average $\delta^{13}C$ values agree well with the $\delta^{13}C$ at the hot spot (concentration >1000 μg/l) of the corresponding bundle. The close agreement of average and peak $\delta^{13}C$ can be explained by the relatively small mass of PCE that occurs in the fringes. In the park transect, the $\delta^{13}C$ of PCE varies between − 24.3‰ and − 33.4‰. This range is similar to the range of $\delta^{13}C$ for PCE from different manufacturers, which was − 24.10‰ to − 35.82‰ (Beneteau et al., 1999; Jendrzejewski et al., 2001; Van Warmerdam et al., 1995). Comparison of the average $\delta^{13}C$ values indicates that PCE in bundles AML-17 to

Fig. 5. Angus site: PCE concentration contours and $\delta^{13}C$ values of PCE for park transect (A) and river transect (B). The water table is located above the upper end of the figures. Open squares, sampling locations where PCE concentration were measured; filled squares, sampling locations where concentration and $\delta^{13}C$ of PCE were measured. The $\delta^{13}C$ value in front of the name of the sampling location corresponds to the concentration-weighted average $\delta^{13}C$ of the multilevel sampler. Only selected $\delta^{13}C$ values for PCE are shown due to space restriction. Selected profiles are illustrated in more detail in Fig. 6. The $\delta^{13}C$ in italics in (B) corresponds to sampling points that are likely affected by biodegradation as indicated by TCE concentrations >5% of PCE concentrations.

AML-5 likely originated from the same spill and that DNAPL had migrated laterally and to different depths. The hot spot at AML-15 has a $\delta^{13}C$ in the same range, while the $\delta^{13}C$ of PCE in the low concentration zone in between (AML-2, AML-16) is slightly



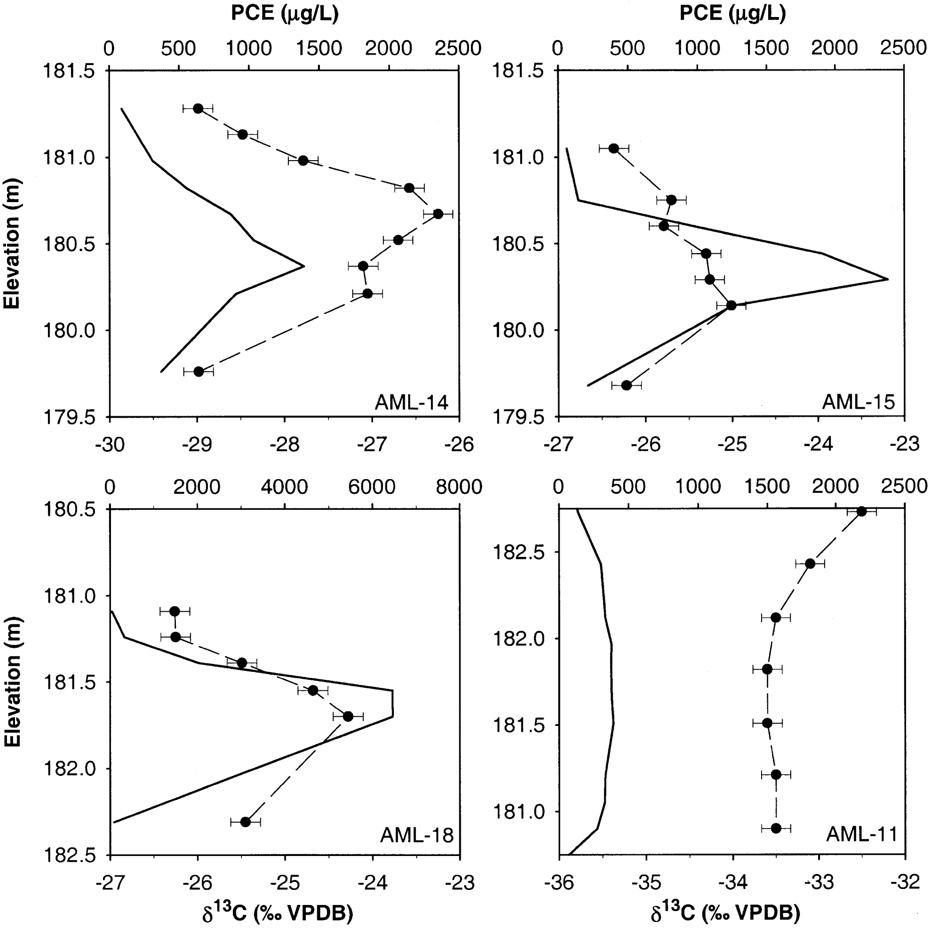


Fig. 6. Depth-profiles of PCE concentration (line), $\delta^{13}C$ of PCE (filled circles) for multilevel sampler AML-11, 14, 15 and 18 at Angus site.

depleted possibly due to diffusion in the horizontal direction. The $\delta^{13}C$ value of these hot spots is similar to the $\delta^{13}C$ of PCE at AML-20 immediately in front of the dry cleaner, which had a $\delta^{13}C$ of $-25.5‰$ for the point with the highest PCE concentration (5800 μg/l). The hot spot between AML-12 and AML-14, and especially the zone between AML-10 and AML-3 have $\delta^{13}C$ values that are significantly different from each other and from the other hot spots suggesting that these two zones originate from other spills. The zone between AML-10 and AML-3 is not only depleted in ^{13}C but has also a different vertical concentration distribution lacking a sharp peak (Fig. 6). The fact that the range in $\delta^{13}C$ values of the PCE is large and covers much of the range shown by PCE from different manufacturers is consistent with what is known generally about the history of the PCE use at the Angus site. Dry cleaning operation at the site was conducted by the first owner of the property beginning in the early 1970s to the mid-1980s, when the current owner purchased the property and continued dry cleaning with PCE until the mid-1990s. The PCE was supplied to the owner by chemical distribution companies, which obtained the PCE from the manufacturers. The PCE purchase records could not be obtained and the manufacturing companies are unknown. Therefore, the hot spots cannot be related to PCE use records. However, given the change in ownership and the long periods of PCE use, it is expected that PCE from different manufacturers was used at the site.

The plume is much wider than the width of the dry cleaning building, and its current property. A residential building was constructed immediately to the east of the dry cleaner (Fig. 2) in the mid-1990s. Formerly, this property was owned by the owner of the dry cleaning company and it is likely that PCE was disposed of in this area as well as on the current dry cleaner property. Although the details cannot be determined, it is likely that PCE as immiscible phase liquid was released to the ground at various locations during the 25-year PCE use period. These release locations included an outdoor storage tank, infiltration through the floor inside the building, and disposals on vacant land east of the building. When released, the free-phase PCE flowed downward to zones below the water table where it probably spread out laterally along bedding features in the aquifer. The major differences in $\delta^{13}C$ values between the hot spots suggest that the various release locations were active at different periods in the history of dry cleaning at the site.

In the downgradient river transect, a maximum PCE concentration of 5220 μg/l was measured (Fig. 5B). Compared to the other transect, less hot spots are visible which is partly due to peak concentrations slightly below the contouring interval of 1000 μg/l on the left side of the transect. The multilevel bundles with the highest PCE concentration (BML-5 and BML-6) have a similar average $\delta^{13}C$ value as the zone between AML-15 and AML-19 in the park transect and AML-20 in front of the dry cleaner. As in the park transect, more depleted $\delta^{13}C$ values are measured to the left of the high concentration zone (Fig. 5B). BML-3 could correspond to the zone between AML-12 and AML-14 in the part transect and BML-2 could correspond to the zone between AML-10 and AML-3. To the right of the high concentration zone, a zone with more ^{13}C enriched PCE appears. These values can be attributed to degradation as indicated by TCE concentrations >5% of PCE concentrations in BML-8 and BML-9. Similarly, the presence of TCE and enriched $\delta^{13}C$ values compared to the neighboring bundle can be observed at BML-1. Degradation in these zones is likely due to a higher content of organic material in the aquifer material close to the river (Conant, 2001). For the zone to the right, the extent of biodegradation was estimated based on the Rayleigh equation. Using an average enrichment factor of $-3.9‰$ for reductive dechlorination of PCE (Hunkeler et al., 1999; Slater et al., 2001) and a value of $-25.2‰$ as initial $\delta^{13}C$ value (average of hot spot $\delta^{13}C$ values of AML-4, 13, 18 and 19), up to 66% biodegradation of PCE is obtained. In zones with low biodegradation (BML-2 to BML-7), the three zones with different $\delta^{13}C$ values observed at the park transect are preserved, although the $\delta^{13}C$ values tend to be slightly enriched in ^{13}C in comparison to their corresponding locations in the park transect. This demonstrates that different sources can still be distinguished after 220 m of flow distance.

Since a large number of measurements were made, the minimal difference in $\delta^{13}C$ between two sources that is statistically significant can be estimated. The calculation requires a measure of the variability of the $\delta^{13}C$ values within a plume from a single source. For this purpose, the standard deviation of the average $\delta^{13}C$ values of bundles between AML-15 and AML-5, which are likely downgradient of the same source, was calculated. Average $\delta^{13}C$ values were used because in most applied field studies, wells are sampled which yield depth-averaged values. The calculated standard deviation (0.52‰) is larger than the standard deviation associated with the analytical method (0.12‰), which reflects processes in the plume that lead to small shifts in $\delta^{13}C$. The minimal $\Delta\delta^{13}C$ that is statistically significant was calculated using a *t*-test at a 95% significance level and assuming that in both plumes an equal number (n) of measurements are made. The following values were obtained: 2.3‰ ($n=2$); 1.2‰ ($n=3$); 0.9‰ ($n=4$); and 0.8‰ ($n=5$). Thus, if biodegradation is absent and sufficient measurements are made, it should be possible to distinguish sources with differences in $\delta^{13}C$ as little as 1‰.

6. Conclusions

Based on the two sites investigated, this study shows that the $\delta^{13}C$ signatures of the DNAPL source zones persist without significant modification in the high concentration zones of the plumes downgradient of the source zones. This persistence occurs because biodegradation is a minor process and the effect of dispersion including diffusion is not influential in the isotope composition of PCE and TCE. Laboratory and field evidence indicate that DNAPL dissolution also does not alter the $\delta^{13}C$ values of the dissolved-phase feeding the plumes. Thus, at sites where different zones of the DNAPL source area have different $\delta^{13}C$ values due to different DNAPL input history, these zones impart their distinct $\delta^{13}C$ signature to the plumes as long as the organic carbon content is low and thus biodegradation of PCE and TCE is likely insignificant.

The study of the two plumes showed small influences of biodegradation only in part of the lower concentration zones. Of the physical processes that act on the chlorinated solvent plumes, only diffusion seem to have a noticeable effect on the carbon isotope ratio. This effect is small and only was observed in the plume fringes where vertical concentration gradients were large. Isotope fractionation associated with diffusion can provide insight into the contribution of diffusion to plume spreading in transverse vertical direction. This insight could not have been gained if the contamination had been investigated using conventional monitoring wells rather than the numerous depth-discrete multilevel systems.

This study demonstrates, using both laboratory and field evidence, that $\delta^{13}C$ values in chlorinated ethene plumes are not significantly different from the $\delta^{13}C$ of the DNAPL causing the plume. The $\delta^{13}C$ values remain constant in the core of chlorinated ethene plumes, except for zones with biodegradation and variations in $\delta^{13}C$ associated with different events of DNAPL release can be tracked over extended distances. This demonstrates that $\delta^{13}C$ values are a valuable tool to distinguish between different plumes of chlorinated ethenes and to link plumes to their sources, provided they have a different isotopic composition.

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References

Beneteau, K.M., Aravena, R., Frape, S.K., 1999. Isotopic characterization of chlorinated solvents: laboratory and field results. Org. Geochem. 30, 739–753.

Bloom, Y., Aravena, R., Hunkeler, D., Edwards, E., Frape, S.K., 2000. Carbon isotope fractionation during microbial dechlorination of trichloroethene, *cis*-1,2-dichloroethene and vinyl chloride: implication for assessment of natural attenuation. Environ. Sci. Technol. 34, 2768–2772.

Broholm, K., Feenstra, S., 1995. Laboratory measurements of the aqueous solubility of mixtures of chlorinated solvent. Environ. Toxicol. Chem. 14 (1), 9–15.

Cherry, J.A., Gilham, R.W., Anderson, E.G., Johnson, P.E., 1983. Hydrogeological studies of a sand aquifer at an abandoned landfill: 2. Groundwater monitoring devices. J. Hydrol. 63, 31–49.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis, Boca Raton, FL. 328 pp.

Conant, B., 2001. A PCE plume discharging to a river: investigations of flux, geochemistry, and biodegradation in the streambed. PhD thesis, University of Waterloo, Waterloo.

Conant, B., 2004. Delineating and quantifying ground-water discharge zones using stream temperatures. Ground Water 42, 243–257.

Conant, B., Cherry, J.A., Gillham, R.W., 2004. A PCE groundwater plume discharging to a river: influence of the streambed and near-river zone on contaminant distributions. J. Contam. Hydrol. (submitted for publication).

Freyberg, D.L., 1986. A natural gradient experiment on solute transport in a sand aquifer: 2. Spatial moments and the advection and dispersion of nonreactive tracers. Water Resour. Res. 22, 2031–2046.

Frind, E.O., Hokkanen, G.E., 1987. Simulation of the Borden plume using alternating direction Galerkin technique. Water Resour. Res. 23, 918–930.

Guilbeault, M.A., Parker, B.L., Cherry, J.A., 2004. Mass and flux distributions from DNAPL zones in sandy aquifers. Ground Water, in press.

Hunkeler, D., Aravena, R., 2000. Determination of stable carbon isotope ratios of chlorinated methanes, ethanes and ethenes in aqueous samples. Environ. Sci. Technol. 34, 2839–2844.

Hunkeler, D., Aravena, R., Butler, B.J., 1999. Monitoring microbial dechlorination of tetrachloroethene (PCE) using compound-specific carbon isotope ratios: microcosms and field experiments. Environ. Sci. Technol. 33 (16), 2733–2738.

Jendrzejewski, N., Eggenkamp, H.G.M., Coleman, M.L., 2001. Characterisation of chlorinated hydrocarbons from chlorine and carbon isotopic compositions: scope of application to environmental problems. Appl. Geochem. 16, 1021–1031.

Mackay, D.M., Cherry, J.A., 1989. Groundwater contamination: pump-and-treat remediation. Environ. Sci. Technol. 23 (6), 630–636.

Nowak, W., 2000. Age determination of a TCE source zone using solute transport profiles in an underlying clayey aquitard. MSc thesis, University of Waterloo, Waterloo, 117 pp.

Parker, B.L., Cherry, J.A., Chapman, S.W., Guilbeault, M.A., 2003. Review and analysis of chlorinated solvent dense nonaqueous phase liquid distributions in five sandy aquifers. Vadose Zone J. 2, 116–137.

Pitkin, S.E., Cherry, J.A., Ingleton, R.A., Broholm, M.M., 1999. Field demonstration using the Waterloo Groundwater Profiler. Ground Water Monit. Remediat. 19 (2), 122–131.

Sherwood Lollar, B., Slater, G.F., Ahad, J., Sleep, B., Spivack, J., Brennan, M., MacKenzie, P., 1999. Contrasting carbon isotope fractionation during biodegradation of trichloroethylene and toluene: implications for intrinsic bioremediation. Org. Geochem. 30, 813–820.

Shouakar-Stash, O., Drimmie, R., Morrison, J., Frape, S.K., Hemmskerk, A.R., Mark, W.A., 2000. On-line D/H analysis of water, natural gas, and organic solvents by manganese reduction. Anal. Chem. 72, 2664–2666.

Slater, G.F., Ahad, J.M.E., Sherwood Lollar, B., Allen-King, R., Sleep, B., 2000. Carbon isotope effects resulting from equilibrium sorption of dissolved VOCs. Anal. Chem. 72, 5669–5672.

Slater, G.F., Sherwood Lollar, B., Sleep, B., Edwards, E., 2001. Variability in carbon isotopic fractionation during biodegradation of chlorinated ethenes: implications for field applications. Environ. Sci. Technol. 35, 901–907.

Squillace, P.J., Moran, M.J., Lapham, W.W., Clawges, R.M., Zogorski, J.S., 1999. Volatile organic compounds in untreated ambient groundwater of the United States, 1985–1995. Environ. Sci. Technol. 33 (23), 4176–4187.

Van Warmerdam, E.M., Frape, S.K., Aravena, R., Drimmie, R.J., Flatt, H., Cherry, J.A., 1995. Stable chlorine and carbon isotope measurements of selected organic solvents. Appl. Geochem. 10, 547–552.

Wiedemeier, T.H., Newell, C.J., Rifai, H.S., Wilson, J.T., 1999. Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. Wiley, New York. 617 pp.