

# Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation

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[1] At an industrial site on a sand aquifer overlying a clayey silt aquitard in Connecticut, a zone of trichloroethylene dense nonaqueous phase liquid (DNAPL) at the aquifer bottom was isolated in late 1994 by installation of a steel sheet piling enclosure. In response to this DNAPL isolation, three aquifer monitoring wells located approximately 330 m downgradient exhibited strong TCE declines over the next 2–3 years, from trichloroethylene (TCE) concentrations between 5000 and 30,000  $\mu\text{g/L}$  to values leveling off between 200 and 2000  $\mu\text{g/L}$ . TCE concentrations from analysis of vertical cores from the aquitard below the plume and also from depth-discrete multilevel systems in the aquifer sampled in 2000 were represented in a numerical model. This shows that vertical back diffusion from the aquitard combined with horizontal advection and vertical transverse dispersion account for the TCE distribution in the aquifer and that the aquifer TCE will remain much above the MCL for centuries.

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## 1. Introduction

[2] It has long been recognized that DNAPL zones in aquifers cause persistent plumes composed of dissolved phase contaminants [Schwille, 1988; Mackay and Cherry, 1989]. Decades of experience indicates pump and treat fails to achieve permanent aquifer restoration due to the presence of DNAPL [U.S. Environmental Protection Agency (USEPA), 1999] and there is now strong regulatory and public pressure to fully remediate subsurface DNAPL zones, with the expectation that their plumes will then soon cease to exist due to natural flushing and attenuation [e.g., Interstate Technology and Regulatory Council, 2002; Stoo et al., 2003]. All types of DNAPL zone remediation techniques, such as DNAPL enclosure or in situ mass destruction by chemical treatment or degradation, have the same effect on the plume as long as complete prevention of contaminant mass flux from the source zone is achieved. Once all contaminant mass flux from the source zone ceases, in an ideal case, natural groundwater flow causes separation of the plume from the former source zone resulting in down-gradient migration of the entire plume. However, with the exception of hydraulic containment or isolation, controversy surrounds the efficacy of sufficient source mass reduction to achieve aquifer restoration [e.g., USEPA, 2003]. Wilson [1997] used modeling to show that aquifers subjected to pump-and-treat remediation in the absence of DNAPL can continue to have relatively high contaminant concentrations for a long time due to slow diffusion out of low-permeability zones within the aquifer. By extension, this reverse diffusion effect is also expected in plumes being flushed by natural flow after DNAPL

source removal or isolation if low-permeability zones are present within the aquifer, or at the top and/or bottom of the aquifer.

[3] A common situation at contaminated sites is the presence of a DNAPL accumulation zone at the bottom of unconfined sand or gravel aquifers underlain by clayey aquitards [Feenstra et al., 1996]. In this situation, dissolved mass from the DNAPL diffuses vertically into the aquitard, and other dissolved mass is transported horizontally creating a plume migrating along the bottom of the aquifer, below which downward diffusion from the aquifer into the aquitard occurs. This paper documents a field study at an industrial facility in Connecticut, where a large TCE DNAPL zone at the bottom of a sand aquifer was enclosed by steel sheet piling in 1994. Back diffusion from the underlying clayey-silt aquitard to the aquifer was assessed and quantified by detailed monitoring 6 years later in both the aquitard and overlying sand aquifer down gradient from the DNAPL enclosure. The sand aquifer is nearly homogeneous and the contact between the aquifer and underlying aquitard is sharp so that geologic complexity is minimal, thereby facilitating data interpretation and modeling. The aquitard is lacustrine in origin, which is a common aquitard type around the world.

[4] Although back diffusion has long been recognized conceptually as a potential impediment to restoration of aquifers to drinking water use, the only previous field verification of back diffusion was provided by Ball et al. [1997] and Liu and Ball [2002], who used core sampling inside a sheet piling enclosure at a remediation experiment site in a tetrachloroethylene (PCE) and TCE plume at Dover Air Force Base, Delaware. In this study, the aquitard PCE and TCE concentration profiles were the basis for one-dimensional diffusion modeling to make inferences regard-

ing historical concentration conditions in the overlying aquifer and to predict the long timescale for back diffusion. The field results from the Connecticut site presented in this paper are the first concerning full-scale DNAPL zone isolation, with downgradient monitoring of effects in both the plume and the aquitard under natural flow conditions.

[5] Field studies of back diffusion in aquitards are rare, however, field documentation of inward diffusion of contaminants in aquitards are more common. *Goodall and Quigley* [1977] were the first to use core analyses to demonstrate diffusion of contaminants from buried waste sources into natural clayey deposits, and *Johnson et al.* [1989] were first to report diffusion of a chlorinated solvent (TCE) into a natural clayey aquitard. On the basis of laboratory and field experiments performed over times ranging from a few weeks to several years, *Parker* [1996] provided evidence for diffusion-controlled transport occurring from chlorinated solvent DNAPLs in contact with natural clays, and showed that diffusion transport parameters derived from fitting the measured concentration profiles were consistent with previously reported parameter values for dilute concentration organic sources for the same clayey deposit [*Johnson et al.*, 1989; *Myrand et al.*, 1992]. *Grathwohl* [1998] provides an overview of diffusion transport issues related to subsurface contamination, and summarizes many of the available diffusion coefficient values for low-permeability geologic media.

## 2. Site Description

[6] The study area is located at a large industrial facility in Connecticut, where metal product manufacturing occurred from 1952 to 2001. TCE occurs in the surficial sand aquifer of glaciofluvial origin, which has minimal solid phase organic carbon and no silty or clayey lenses. The aquifer is underlain by a thick glaciolacustrine aquitard, composed of varved silts and clayey silts, lying on a lower sandy aquifer on bedrock. Prior to 2001, the lower aquifer was heavily pumped to supply water to the facility, which caused a strong, long-term downward hydraulic gradient ( $\sim 0.4$ ) across the aquitard [*Parker et al.*, 2004]. TCE was the primary solvent used for metals degreasing until the early 1970s, stored in underground tanks at the east side of the facility, where releases that likely started shortly after the facility began operation caused formation of a persistent DNAPL source zone at the bottom of the aquifer. This DNAPL zone was enclosed in November 1994 by a sheet piling barrier keyed into the aquitard. A small area of DNAPL, with less than 1% of the total DNAPL mass, remains outside the enclosure (Figure 1). Detailed investigations of the nature of the DNAPL accumulation zone by *Parker et al.* [2003], in which this site is referred to as "Connecticut A," showed that the DNAPL occurs within the bottom meter or less of the aquifer, in most cases as a thin (2–5 cm) layer of free product and/or residual DNAPL resting directly on the aquifer-aquitard interface, and was laterally discontinuous throughout the source zone. *Parker et al.* [2004] showed the 20 m thick aquitard provides long-term protection of the deeper aquifer and that, even with the strong downward hydraulic gradient, contaminant migration in the aquitard is dominated by diffusion.

[7] The study area is situated on an upper terrace, with a steep embankment west of the building transitioning to a

lower terrace (Figure 1) where the aquifer is much thinner. Groundwater flow in the aquifer is generally to the west toward a river, with an average hydraulic gradient of about 0.01 along the upper terrace. East of the building where the DNAPL zone exists, the aquifer is 9 m thick with the water table at 3 to 4 m below ground surface. Immediately west of the building where the TCE plume occurs, the saturated aquifer thickness ranges from  $<0.5$  to 5 m due to variation in the elevation of the aquitard surface. A site-wide network of conventional monitoring wells, monitored by the site owner since the early 1990s, provided uninterrupted monitoring data before and after installation of the sheet piling enclosure.

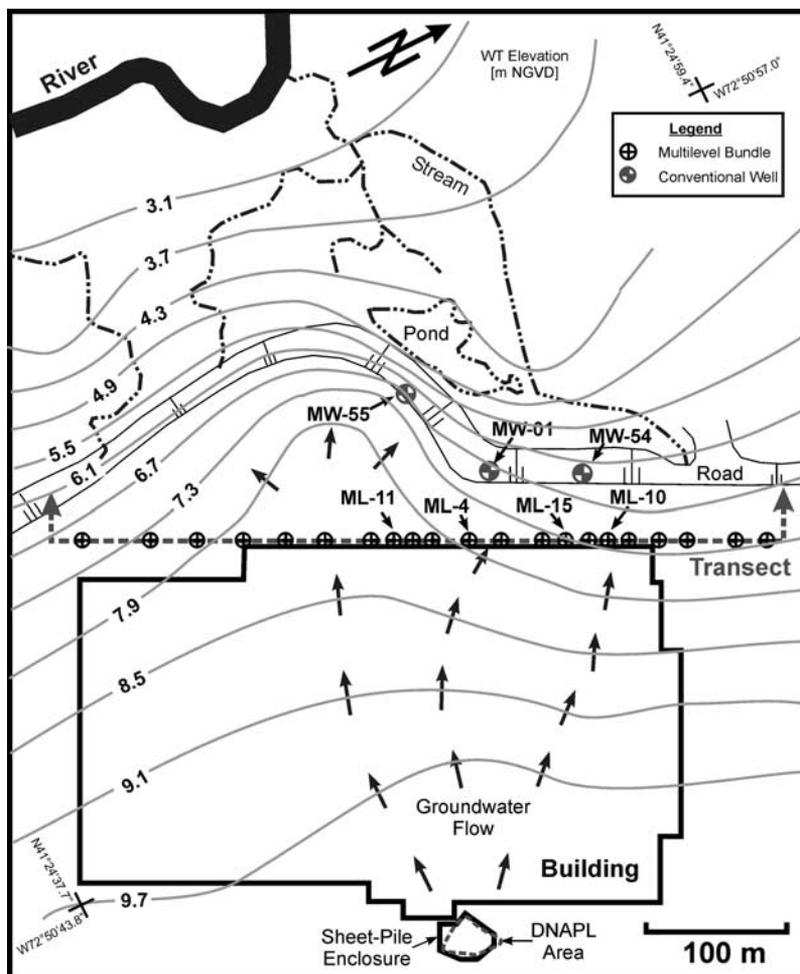
## 3. Methods

### 3.1. Groundwater Plume Sampling

[8] The field investigations were conducted during episodes in July 1999 and August 2000. Contaminant distribution in the aquifer was determined by depth-discrete groundwater sampling along a cross section perpendicular to groundwater flow (i.e., transect) along the west side of the building 280 m downgradient of the DNAPL source, using the type of multilevel samplers described by *Cherry et al.* [1983]. Each multilevel system has 4 to 8 sampling tubes, composed of 12.7 mm OD polyethylene tubing with 10 cm long intakes wrapped with Nitex™ fabric. These tubes are strapped around a 19 mm OD Schedule 80 PVC pipe, with the lower 15 cm screened to serve as the bottommost sampling point. Prior to installation, cores were collected at each location, as described later, to accurately determine the aquitard depth. The bottom sampling point in each multilevel was positioned at the base of the aquifer and top point near the water table. The vertical spacing of intermediate sampling points ranges from 0.3 to 1.0 m, with tighter spacing at the bottom of the aquifer. The multilevel systems were installed through 89 mm OD casing, driven to the target depth with an aluminum knock-out plug using a truck-mounted Enviro-Core direct push rig. Following insertion, the casing was withdrawn and aquifer sand collapsed, except above the water table where a bentonite seal was placed to ground surface.

[9] Groundwater samples were collected using a peristaltic pump and dedicated 6.4 mm OD Teflon™ sampling tubes. After purging at least two tubing volumes, the pump was shut off (maintaining the vacuum at surface), the sample tube withdrawn from the multilevel point, the pump reversed or suction released and groundwater in the sample tube pumped or drained into a 25 mL VOA vial, allowing overflow to minimize sample contact with air prior to capping. The sample tube was decontaminated between points by flushing with methanol and distilled water.

[10] Groundwater samples were analyzed for VOCs in an on-site mobile lab (temperature controlled trailer) on a SRI8610 portable gas chromatograph (GC) equipped with a photo ionization detector (PID) and flame ionization detector (FID). Analyses were conducted using a solid phase microextraction (SPME) headspace technique described by *Pawliszyn* [1997] and *Górecki and Pawliszyn* [1997]. Concentrations were quantified using calibration curves generated daily using eight standards; lab blanks, duplicates and standard checks were routinely analyzed. Method detection limits (MDLs) for 1999 samples were



**Figure 1.** Site map showing locations of DNAPL area and sheet pile enclosure installed in 1994, plume multilevel monitoring transect, selected conventional monitoring wells west of the building, aquitard profile locations adjacent to multilevel wells, and representative water level contours for the surficial aquifer (September 1999) showing diverging flow down gradient of the sheet pile enclosure responsible for strong plume widening downgradient.

10  $\mu\text{g/L}$  for TCE, PCE and the dichloroethylene (DCE) isomers and 90  $\mu\text{g/L}$  for VC; the method was subsequently improved and samples from 2000 had detection limits of 1  $\mu\text{g/L}$  for TCE, PCE and the DCE isomers and 50  $\mu\text{g/L}$  for VC. Equipment blanks indicated negligible carryover except after points with very high concentrations. Maximum equipment blank TCE concentrations were 80  $\mu\text{g/L}$ , collected after sampling points with TCE concentrations of 17,000 and 25,500  $\mu\text{g/L}$ . Samples were collected from the top to bottom point on each multilevel (lowest to highest concentrations) to minimize carryover effects, in addition to using dedicated sampling tubes for each multilevel.

### 3.2. Acquisition and Analysis of Aquitard Cores

[11] Contaminant distribution in the aquitard below the plume was determined by sampling cores collected across the interface and into the upper portion of the aquitard, as described by Parker *et al.* [2004]. Cores were collected using the piston coring system [Zapico *et al.*, 1987] and Enviro-Core method of direct push driving of casing [Einarson, 1995; Einarson *et al.*, 1998] which provided minimally disturbed samples in aluminum tubes (1.52 m

long, 51 mm OD) with recoveries typically ranging from 90 to 100%. Within a few hours of collection, each core was split longitudinally in the field and half immediately wrapped in aluminum foil to minimize volatile losses. Small cylindrical subsamples were then collected at closely spaced intervals (typically 5 to 10 cm) using 15 mm ID stainless steel tubes and extruded into 25 mL glass vials containing 15 mL of HPLC grade methanol. Vials were weighed in the field empty, with methanol and then with the soil sample so the mass of soil and methanol were accurately known prior to shipping to the lab for analysis. On arrival at the lab, samples were reweighed, shaken on a vortex mixer to break up the soil and stored at 4°C for at least two weeks to allow adequate time for extraction. Samples were then centrifuged to separate the soil and methanol in the vial, and an aliquot of the methanol diluted into pentane and analyzed by direct injection on a HP6890 GC equipped with a micro-ECD detector. Concentrations were quantified using eight point calibration curves; lab blanks, duplicates and standard checks were routinely analyzed. MDLs were  $\sim 0.5$   $\mu\text{g/g}$  wet soil for TCE and PCE and 20  $\mu\text{g/g}$  for the DCE isomers, depending on the soil mass to methanol ratio. The pentane

dilution step was omitted for 2000 samples using direct injection of methanol onto the column, providing lower MDLs of  $\sim 0.01 \mu\text{g/g}$  for TCE, PCE and the DCE isomers. Hewitt [1998] indicates the robustness of methanol extraction for providing complete VOC recovery in various types of soils, and section 4.3 provides site-specific evidence for complete extraction in these samples.

[12] The laboratory analysis provides the total analyte mass per unit mass of wet soil, and does not distinguish between mass in the dissolved, sorbed or DNAPL (if present) phases. These total soil concentrations ( $C_t$ ) were converted to aqueous concentrations ( $C_w$ ) using

$$C_w = c_t \frac{\rho_{\text{bwet}}}{R\phi} \quad (1)$$

where  $\rho_{\text{bwet}}$  is the soil wet bulk density and  $\phi$  is the aquitard porosity. Retardation factors ( $R$ ) were estimated assuming linear sorption dominated by organic carbon in the aquitard using

$$R = 1 + \left[ \frac{\rho_{\text{bdry}}}{\phi} \right] K_d \quad (2)$$

where  $K_d$  is the distribution coefficient and  $\rho_{\text{bdry}}$  is the soil dry bulk density. Average site values for porosity ( $\phi = 0.43$ ) and bulk density ( $\rho_{\text{bwet}} = 1.95 \text{ g/cm}^3$ ,  $\rho_{\text{bdry}} = 1.50 \text{ g/cm}^3$ ) from Parker *et al.* [2004] were applied. The distribution coefficient was estimated using measured fraction of organic carbon ( $f_{\text{oc}}$ ) with  $K_d = K_{\text{oc}} f_{\text{oc}}$  where  $K_{\text{oc}}$  is the water/organic carbon partition coefficient ( $126 \text{ cm}^3/\text{g}$  for TCE [Pankow and Cherry, 1996]). Measurements of  $f_{\text{oc}}$  using the method of Churcher and Dickhout [1987] on subsamples at 0.3 m spacing from the upper 5 m of the aquitard ranged from 0.024 to 0.104% with an average of 0.054%, providing an average  $R$  value for TCE of 1.2 with a range from 1.1 to 1.5. Sorption is generally nonlinear for hydrophobic organic compounds like TCE in clay-rich aquitards [Allen-King *et al.*, 1996] and therefore application of a linear isotherm may underestimate sorption at the low end of the concentration range. However, sorption and retardation at higher concentrations typically approach values obtained by  $K_{\text{oc}} f_{\text{oc}}$  estimates [Allen-King *et al.*, 2002]. Our assumption of linear sorption is not a significant source of uncertainty in data interpretation because high TCE concentrations are dominant, and sorption is minimal in this predominately silt, low  $f_{\text{oc}}$  aquitard. Support for this method is provided by the good agreement between calculated pore water TCE concentrations in the aquitard in the DNAPL zone just below the aquifer-aquitard interface and literature TCE solubility values [Parker *et al.*, 2004]. Section 4.3 provides additional support for this approach. On the basis of the laboratory MDLs for TCE of 0.5 and  $0.01 \mu\text{g/g}$  for 1999 and 2000 samples, Equation 1 indicates pore water TCE detection limits of 2000 and  $40 \mu\text{g/L}$ , respectively.

## 4. Results and Discussion

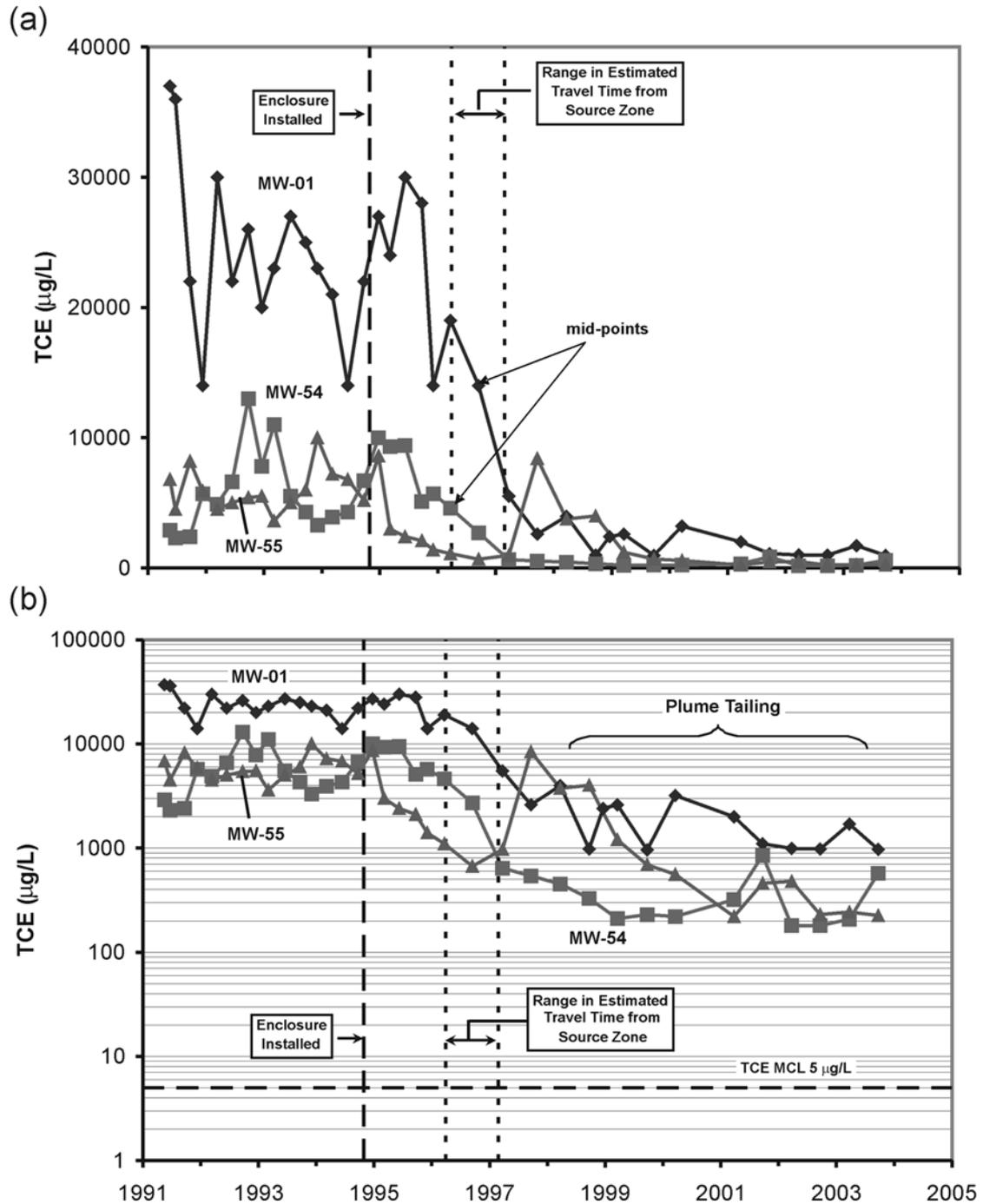
### 4.1. Plume TCE History From Conventional Wells

[13] Two conventional monitoring wells (MW-01 and MW-54; Figure 1) situated approximately 330 m directly down gradient of the sheet pile enclosure showed large

declines in TCE concentrations beginning about seven to ten months after installation of the enclosure (Figure 2a). A third well (MW-55), excluded from further analysis, also showed declines but also exhibited more postenclosure variability, likely due to its location near the periphery of the plume. The midpoints ( $C/C_0 = 0.5$ ) of the strong decline segments of TCE concentration versus time for MW-01 and MW-54 occur at 1.8 and 1.5 years after installation of the enclosure (Figure 2a). TCE concentrations level off within the 200 to  $3000 \mu\text{g/L}$  range at about 2.5 years after the enclosure was installed (Figure 2b). This asymptotic nature of the graph is referred to as plume tailing. The midpoints of the strong decline segments (1.8 and 1.5 years) are considered representative of travel times for clean groundwater traveling at the average linear groundwater velocity over the 330 m distance between the enclosure and the wells. Just as with solute arrival breakthrough curves, the spread about the midpoint ranging over 1.8 to 2.0 years from the tops to the bottoms of these graphical segments is attributed primarily to longitudinal dispersion.

[14] The midpoint times for MW-01 and MW-54 are consistent with calculated groundwater travel time from the enclosure to these wells using the average linear groundwater velocity obtained by dividing the Darcy flux by aquifer porosity. Darcy flux values were obtained from measurements of the hydraulic gradient in the aquifer between the enclosure and wells and hydraulic conductivity values from two types of measurements: (1) slug tests in 37 monitoring wells (1.5–3.0 m long screens) provided a range from  $5 \times 10^{-4}$  to  $>10^{-1} \text{ cm/s}$  with a geometric mean of  $2.4 \times 10^{-2} \text{ cm/s}$  and (2) falling head permeameter tests conducted using the method described by Sudicky [1986] on 13 repacked core samples from several depths at two locations (including one along the transect) provided a range from  $2.1 \times 10^{-3}$  to  $4.1 \times 10^{-2} \text{ cm/s}$  with a geometric mean of  $1.5 \times 10^{-2} \text{ cm/s}$ . Applying the mean hydraulic conductivities from slug tests and permeameter tests, hydraulic gradient of 0.01 and aquifer porosity of 0.35 provides average linear groundwater velocities of 0.59 and 0.37 m/d, respectively, and travel times over the 330 m distance from the enclosure to the wells of 1.5 and 2.4 years. These times are in good agreement with those obtained from midpoints of the strong concentration decline graph segments from the monitoring wells.

[15] Travel times were also obtained independently from borehole dilution tests, which provide a direct point measurement of horizontal groundwater velocity. Freeze and Cherry [1979] provide an overview of borehole dilution and Halevy *et al.* [1967] and Drost *et al.* [1968] describe the theory and methods for borehole dilution. Measurements were made at 3 to 4 depths over the saturated aquifer thickness at two locations along the lower terrace, using a drive point well screen (3.8 cm OD, 18 cm long) coupled to steel casing. The test zone in the well screen was isolated with an inflatable packer. A peristaltic pump was used to circulate water within the screen to maintain well-mixed conditions and an in-line probe was used to monitor decline in electrical conductivity following addition of a spike of sodium chloride solution (i.e., borehole dilution curve). Each test was run for approximately one hour and the drive point was developed between depths by purging. Borehole dilution tests provided a range in groundwater velocity from



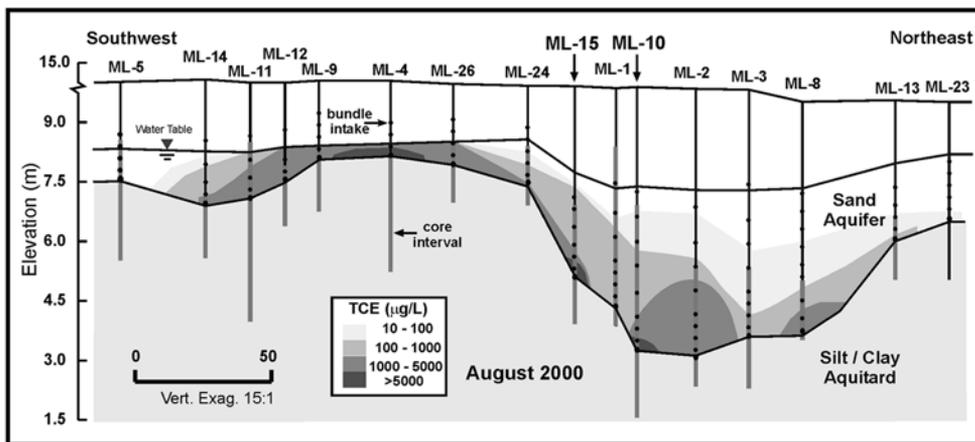
**Figure 2.** TCE concentrations in selected conventional wells west of the building: (a) linear and (b) log concentration scale. Monitoring covers the period from 1991 to 2004, nearly 4 years before to 10 years after the sheet piling enclosure was installed. The groundwater travel time window for the estimated groundwater velocity range of 0.37–0.59 m/d is consistent with the midpoints of the strong decline segments at the wells (i.e., arrival of clean groundwater from outside the enclosure).

0.15 to 1.43 m/d with an average of 0.66 m/d. The estimated travel time from the enclosure to the wells using the average borehole dilution value is 1.4 years, close to the range obtained using the Darcy method.

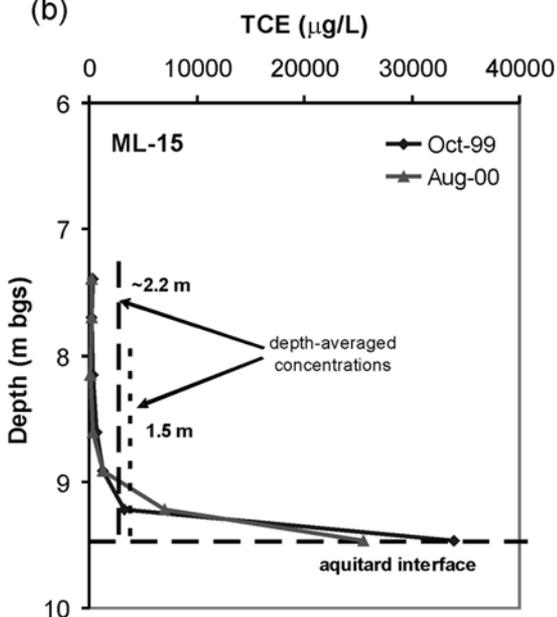
[16] The close agreement between the timing of the strong decline in TCE concentrations following installation of the sheet piling enclosure and the calculated travel times based on the Darcy approach and borehole dilution confirms

that the decline was caused by the sheet piling isolation of the DNAPL zone. In the travel time comparison, TCE retardation was assumed negligible given the low organic carbon content of the aquifer sand. Measurements of  $f_{oc}$  on aquifer core samples from seven depths at one location provided a range from 0.020 to 0.069% with an average of 0.038%. Assuming an aquifer porosity of 0.35 and dry bulk density of 1.70 g/cm<sup>3</sup> (average from repacked permeameter

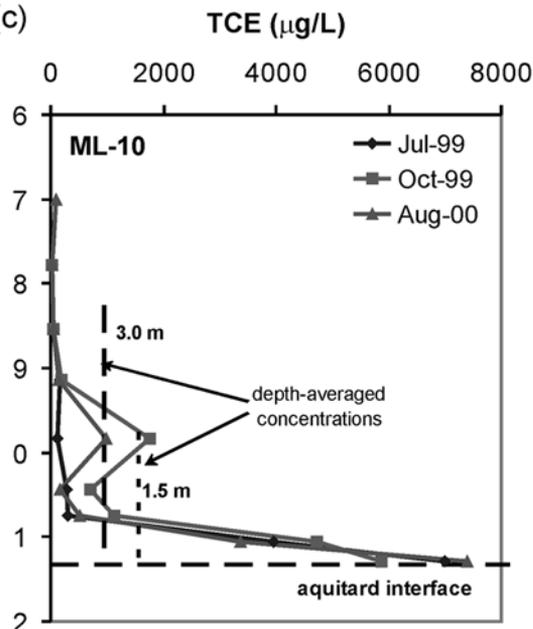
(a)



(b)



(c)



**Figure 3.** (a) Cross section showing depth-discrete TCE concentrations and plume contours along the transect 280 m down gradient of the source zone in August 2000 obtained using multilevel monitoring systems, 6 years after the source zone was isolated, and example aquifer TCE profiles along the transects at (b) ML-10 and (c) ML-15. Calculated depth-averaged concentrations (2000 data) are shown, representing concentrations in hypothetical monitoring wells screened over the specified intervals. See color version of this figure at back of this issue.

tests), equation (2) provides a range in R for TCE from 1.1 to 1.4 with an average of 1.2.

[17] Following the strong decline period, the low but persistent TCE concentrations in the two monitoring wells (MW-01 and MW-54; Figure 2b) continuing a decade after DNAPL zone isolation must be caused by input of TCE to the plume from sources outside of the sheet piling enclosure. Three hypotheses exist for such “sources”: (1) back diffusion from the aquitard in the area beneath the former high-concentration plume, (2) the small area of DNAPL found outside the enclosure (Figure 1), and/or (3) other unknown DNAPL zones. The assessment presented below indicates that back diffusion fully accounts for the plume

tailing and that, although other contributors of TCE mass may exist to some degree, they are not needed for explanation of the observed plume concentrations in the vicinity of the monitoring wells.

**4.2. Detailed Plume Characteristics Along the Transect**

[18] Detailed sampling of the plume in 2000 along a transect 280 m down gradient from the isolated DNAPL zone shows a wide plume with highest TCE concentrations along the bottom of the aquifer (Figure 3a). Results from 1999 sampling were similar, and therefore the 2000 results are taken as representative of the TCE distribution several years after DNAPL zone isolation. TCE degradation

assessed by analysis for degradation products (cis-1,2-dichloroethene (cDCE), trans-1,2-dichloroethene (tDCE) and vinyl chloride (VC)) and compound-specific carbon isotopes following the approach of *Hunkeler et al.* [2004] indicated negligible TCE degradation in the area between the DNAPL zone and transect. Therefore the TCE distributions indicated by the transect (Figure 3a) and monitoring wells (Figure 2) are the product of transport by advection and dispersion in the aquifer and the nature of the TCE “sources” contributing mass to the plume.

[19] TCE concentrations in the monitoring wells since 1999 (Figure 2) in the range of 200 to 3,000  $\mu\text{g/L}$  are much lower than the maximum along the transect in 2000 of 25,000  $\mu\text{g/L}$ . Two representative vertical TCE profiles from the transect (Figures 3b and 3c) show that the high concentrations in the aquifer occur at the aquifer/aquitard interface, and much lower concentrations occur at levels tens of centimeters above the interface. Numerical modeling, presented later, indicates that this profile shape is expected from a back diffusion generated plume. Figures 3b and 3c also display depth-averaged TCE concentrations for vertical intervals relevant to the lengths of the monitoring well screens. Screen lengths for the conventional wells are 1.5 m for MW-01 and MW-55 and 3.0 m for MW-54 with the screen bottoms at or slightly below the aquifer-aquitard interface. Depth-averaged concentrations were calculated assuming uniform hydraulic conductivity and applying each measured concentration value over an interval representing half the vertical distance between adjacent points. These calculated depth-averaged concentrations are substantially lower than the observed maximum point concentrations, and therefore it is reasonable to expect that depth-integrated concentrations provided by the monitoring wells are also much lower than the maximum concentrations in the aquifer at these locations. The highest TCE concentrations observed prior to installation of the enclosure occurred at the centermost well MW-01 ranging between 14,000 and 37,000  $\mu\text{g/L}$  (Figure 2a), much below TCE solubility range (1,100,000 to 1,400,000  $\mu\text{g/L}$ ) reported by *Pankow and Cherry* [1996] and *Broholm and Feenstra* [1995]. However, because of screen length considerations discussed above, the actual maximum TCE concentrations at the bottom of the aquifer were likely much above the observed values in the monitoring wells. Therefore, during the period of inward diffusion prior to the aquifer concentration decline due to DNAPL zone isolation, the rate of diffusion into the aquitard was much greater than would be the case if the monitoring well concentrations represented the maximum values.

[20] The plume width along the transect is about 300 m (to the 10  $\mu\text{g/L}$  contour), much larger than the width of the DNAPL zone ( $\sim 50$  m). This difference can be accounted for by strong divergence of groundwater flow lines in the aquifer combined with minor effects of transverse horizontal dispersion. Figure 1 shows water table contours based on a snapshot in September 1999 using the network of conventional wells (37 were used for this snapshot) screened in the aquifer. The contoured surface is representative of results from long-term water level monitoring. Figure 1 also shows flow directions orthogonal to the water level contours. This flow divergence is consistent with the topography of the aquitard surface. Figure 3a shows a hump

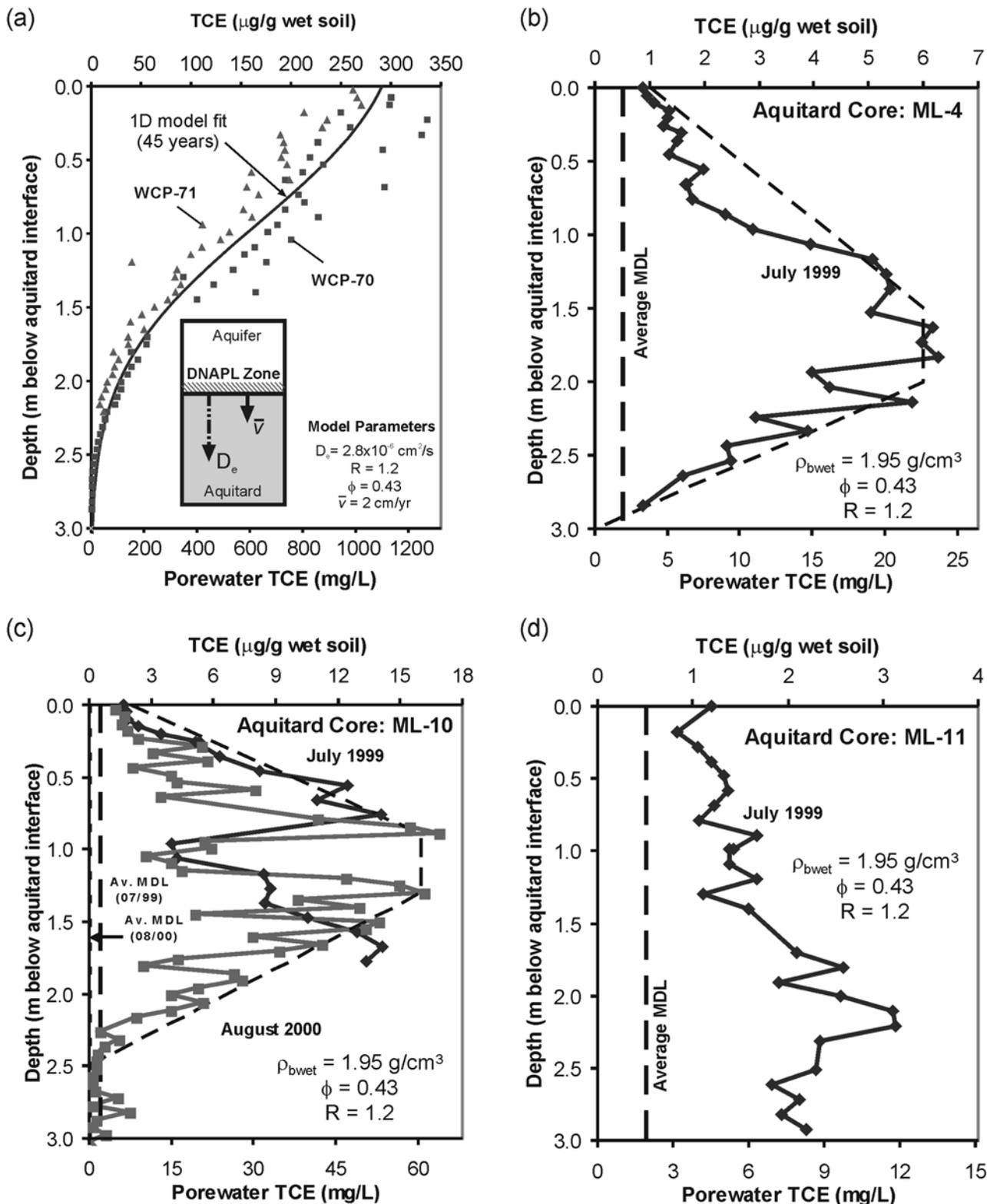
in the southwest half of the transect and a trough in the northeast half. The aquifer is much thicker in the trough, which draws flow lines toward the northeast. The three monitoring wells (MW-01, MW-54 and MW-55) span a distance of nearly 200 m orthogonal to flow, and all showed a strong decline in TCE concentration at the expected groundwater travel time following enclosure installation. This supports the conclusion that divergent flow results in a wide plume at the transect and monitoring wells.

[21] Transverse horizontal dispersion also causes plume spreading orthogonal to flow. To assess its possible magnitude, an analytical solution [*Domenico and Robbins*, 1985] was used to simulate the steady state width of a plume originating from a 50 m wide constant source with a height of 0.2 m ( $\sim$ maximum DNAPL thickness) within a uniform (nondivergent) flow field and constrained to one-directional vertical spreading, since DNAPL is situated at the base of the aquifer. Using a range in transverse horizontal dispersivity from 0.01 to 0.10 m reported for natural flow tracer tests and intensely monitored plumes in flat lying sandy aquifers [e.g., *Rivett et al.*, 1994, 2001; *van der Kamp et al.*, 1994] and a transverse vertical dispersivity of 0.002 m, plume widths (to  $C/C_0 = 1 \times 10^{-5}$ , the range between TCE solubility and 10  $\mu\text{g/L}$ ) at 280 m distance range from 68 to 106 m. Therefore transverse horizontal dispersion causes additional widening of the diverging plume, resulting in the observed plume width along the transect.

#### 4.3. TCE Mass Distribution in Aquitard Below Plume

[22] The distribution of TCE in the aquitard below the plume (Figures 4b–4d) was determined at three locations next to multilevels along the transect (Figure 1) in July 1999 to depths of 2.4 to 3.0 m into the aquitard. One location (ML-10) was repeated in August 2000 to 5.5 m. The profiles at ML-4 and ML-10 went deep enough to cover all or most of the zone of detectable TCE. The shapes of all three profiles are consistent with occurrence of back diffusion from the aquitard, with profiles at ML-4 (Figure 4b) and ML-10 (Figure 4c) providing the strongest evidence of back diffusion. Although back diffusion is evident at ML-11 (Figure 4d), the maximum TCE concentration remaining in the aquitard is dampened relative to the other profiles, likely due to historical variation in TCE concentration in the aquifer due to its proximity to the edge of the plume. This profile was excluded from further analysis because the boundary condition is least certain. At the other locations, the highest TCE concentrations were observed between 1 to 2 m below the interface, with much lower concentrations above and below this “bulge”, showing a TCE concentration gradient up to the aquifer as well as deeper into the aquitard. A reasonable explanation is that back diffusion was initiated by declines in concentrations at the aquifer-aquitard interface following isolation of the DNAPL zone. However, it is likely that plume concentrations began to decline prior to source zone containment, due to DNAPL mass depletion over decades by natural groundwater flow. For comparison, two profiles from *Parker et al.* [2004] from inside the enclosure below DNAPL are also provided (Figure 4a), indicating no back diffusion shape.

[23] Calculated aqueous TCE concentrations in the aquitard from the core results just below the interface were consistent with measured groundwater concentrations in the



**Figure 4.** TCE distribution in the upper portion of the aquitard: source area (a) below DNAPL from Parker et al. [2004] (reprinted with permission from Elsevier) and below the plume next to selected multilevels along the transect at (b) ML-4, (c) ML-10, and (d) ML-11. Both total TCE concentrations (obtained directly from the laboratory analysis) and calculated aqueous concentrations are shown. The dashed lines (in Figures 4b and 4c) indicate areas assumed for aquitard mass estimates below the plume.

aquifer just above the interface in the bottom multilevel points; specifically ML-4 showed 3.5 mg/L in the aquitard versus 3.0 mg/L in the aquifer and ML-10 showed 6.0 mg/L in the aquitard versus 7.4 mg/L in the aquifer. This comparison provides independent support for the methanol extraction procedure and sorption parameter values used to estimate aqueous concentrations. Similarly, *Parker et al.* [2004] showed agreement between calculated aqueous TCE concentrations in the aquitard just below DNAPL and literature solubility values. At ML-4 (Figure 4b), the zone of highest TCE concentration occurs 1 to 2 m below the interface with a peak of 25 mg/L, much higher than observed in the overlying aquifer. The maximum depth of detectable TCE penetration was extrapolated just beyond the base of the profile to 3.0 m. At ML-10 (Figure 4c), the highest TCE concentrations occur 0.8 to 1.8 m below the interface with some samples exceeding 60 mg/L, an order of magnitude higher than groundwater at the bottom of the aquifer. The maximum depth of detectable penetration occurs at about 2.5 m. Profiles at ML-10 from 1999 and 2000 (Figure 4c) are similar, with slightly lower concentrations in the upper portion of the profile in 2000, consistent with continued back diffusion. Tighter sample spacing used for the 2000 profile likely contributes to higher observed concentration variability. *Parker et al.* [2004] indicate that the varved nature of the deposit causes variability of concentrations at the cm or less scale of the varve layers, due to variation in parameters controlling mass distribution not represented in average values used to calculate the aqueous concentrations. Both ML-10 profiles indicate a strong dip in TCE concentration at 1.0 m below the interface, which we believe occurs due to an adjacent corehole and well (1 m away) drilled in 1994, which allows groundwater from the aquifer to cross connect and flow along coarser varved layers in the aquitard at this depth, creating a thin zone where TCE concentrations are lower and similar to that at the base of the aquifer. This zone may also have larger differences in properties controlling mass distribution.

[24] The occurrence of much higher concentrations below the aquitard interface compared to those close to the interface and in the overlying aquifer in this diffusion controlled environment provides clear evidence that historical concentrations in the aquifer were much higher than those observed at the time of this study. Back projection of the lower portion of the ML-4 and ML-10 aquitard profiles assuming diffusion controlled transport suggests maximum TCE concentrations at the interface may have been in the range of a few hundred mg/L. Such high historical plume concentrations likely occurred shortly after the DNAPL accumulation zone formed, prior to gradual reductions in concentration due to removal of DNAPL mass by natural groundwater dissolution and, later on, more abruptly by isolation of the DNAPL source.

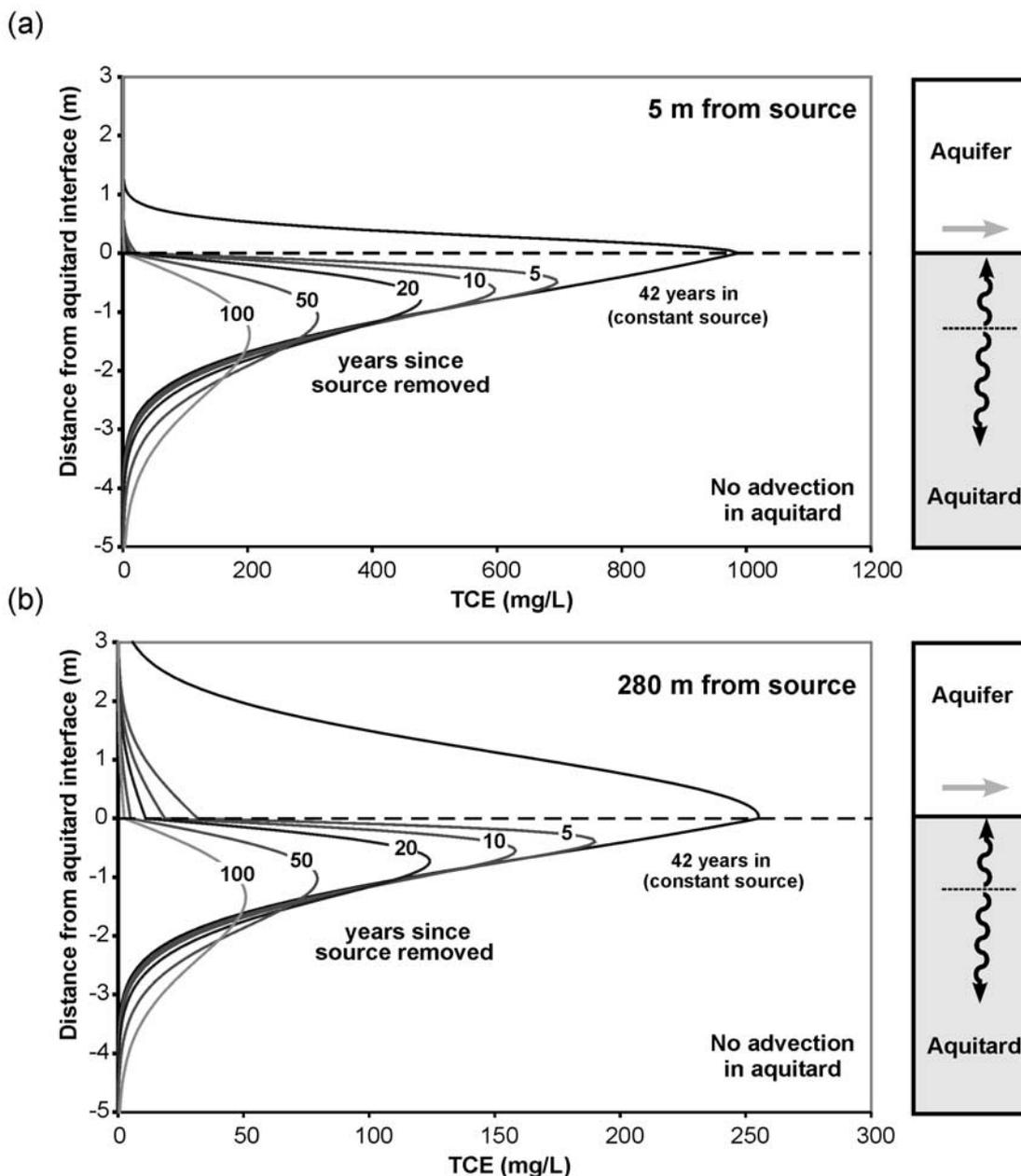
#### 4.4. Numerical Simulation of Back Diffusion Effects

[25] The present and future impacts of back diffusion on the aquifer were examined using a numerical model developed by *Therrien and Sudicky* [1996]. Simulations represent TCE transport by advection and dispersion in the aquifer and diffusion dominated TCE migration in the underlying aquitard. The simulations were done for a cross-sectional

plane with a unit thickness perpendicular to flow extending along the groundwater flow direction from the DNAPL zone to a distance of 300 m down gradient. The domain is 15 m high with a 5 m thick aquifer overlying a 10 m thick aquitard. The aquitard thickness in the field is greater than 20 m; however, 10 m is sufficient to avoid boundary effects over the relevant timescales. The domain was discretized with 120,000 finite element hexahedral blocks, with a total of 241,602 nodes ( $NX = 601$ ,  $NY = 2$ ,  $NZ = 201$ ) and tighter vertical nodal spacing near the aquifer/aquitard interface. Constant head boundaries were assigned to both ends of the domain within the aquifer zone creating a horizontal hydraulic gradient of 0.01 in the aquifer, and along the sides and bottom of the aquitard to cause a downward gradient of 0.4 in the aquitard. The horizontal aquifer gradient represents the field measured gradient from the water table contour map (Figure 1), and the downward gradient was measured by *Parker et al.* [2004] using an aquitard piezometer nest. The aquifer was assigned a hydraulic conductivity ( $K$ ) of  $2 \times 10^{-2}$  cm/s, which is the average of the geometric means obtained from slug tests and laboratory permeameter tests. This average  $K$  value, along with a porosity of 0.35 and gradient of 0.01 provides an average linear groundwater velocity of 0.5 m/d and travel time of 1.6 years, consistent with that observed for the arrival of the postenclosure groundwater at the monitoring wells. TCE retardation in the aquifer was negligible, which is appropriate considering the very low aquifer  $f_{oc}$ . Longitudinal and transverse vertical dispersivities for the aquifer were set to 1.0 m and 0.002 m, respectively, consistent with literature values for sandy aquifers [e.g., *Rivett et al.*, 1994, 2001; *Klenk and Grathwohl*, 2002]. The low transverse vertical dispersivity results in strong concentration gradients at the base of the aquifer, consistent with aquifer profile shapes along the transect (Figures 3b and 3c).

[26] Parameter values for the aquitard were determined by *Parker et al.* [2004] on the basis of the study of TCE transport beneath DNAPL accumulations inside the enclosure. Figure 4a shows an example of a 1-D model fit to two aquitard TCE profiles, indicating reasonableness of the parameters. Inclusion of a small downward velocity provides a slightly better fit than the diffusion-only case. The aquitard was assigned  $K = 5 \times 10^{-8}$  cm/s and an effective porosity of 0.43, which gives a downward velocity of 1.5 cm/year with the gradient of 0.4, within the range obtained in sensitivity analyses by *Parker et al.* [2004]. The assigned aquitard retardation factor was 1.2, calculated using measured  $f_{oc}$  values and consistent with *Parker et al.* [2004].

[27] The numerical model simulations were conducted in two stages. In the first stage, a constant TCE source at the aqueous solubility (1100 mg/L) with dimensions of 20 m length and 0.1 m height was applied at the up-gradient end at the aquifer bottom. This first stage had a duration of 42 years, representing the period between the beginning of major TCE use at the site and installation of the sheet piling enclosure in 1994. During this time, TCE mass flux occurs into the aquitard beneath both the source the plume that forms downgradient. Then, in the second stage, the source is removed and clean water flushes the TCE from the aquifer to cause back diffusion from the aquitard that impacts the aquifer. Two scenarios were examined, one in which the



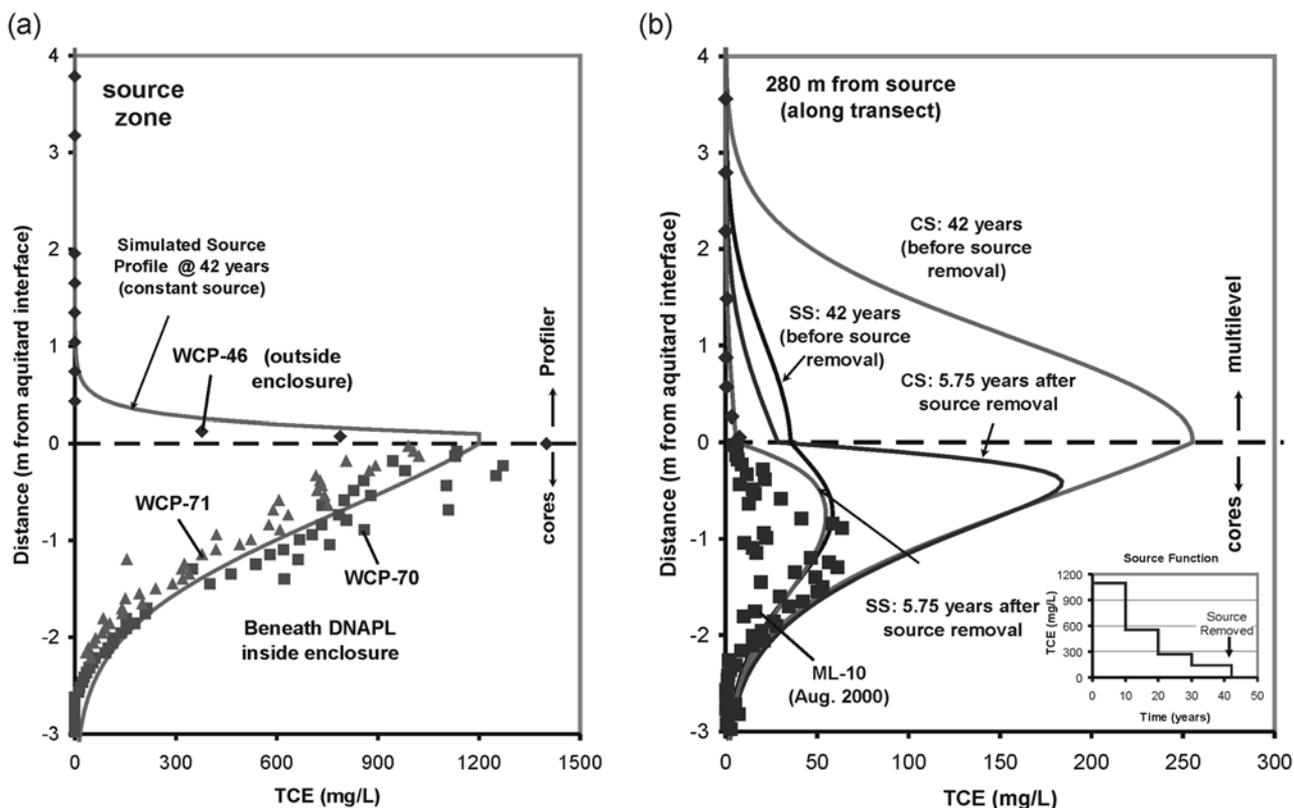
**Figure 5.** Results of 2-D cross-section simulation showing aquifer and aquitard TCE profiles, assuming advection in the aquitard dissipates after DNAPL source isolation, at (a) 5 m and (b) 280 m down gradient of the source. Profiles are shown at the end of the 42 year constant source period and at 5, 10, 20, 50, and 100 years after source isolation.

small advective velocity exists for both stages, and one in which no advection in the aquitard persists beyond 42 years. This second scenario is the only one presented here because it best represents site conditions, given that pumping from the lower aquifer was discontinued when operations ceased in 2001, and scaled back even before this time. The two scenarios produce results that are only minimally different.

[28] Figure 5 shows simulated vertical TCE profiles in the aquifer and aquitard close to the source and at 280 m down gradient from the source. The peak TCE concentration at the interface at the down-gradient location (Figure 5b) just prior to source removal at 42 years is 250 mg/L, and diffusion

caused penetration of the 5  $\mu\text{g/L}$  TCE front to 4.7 m below the interface. After source removal, concentrations at the interface decline and the peak concentration bulge moves slowly deeper into the aquitard. This concentration decline occurs more rapidly near the former source (Figure 5a) compared to the down-gradient location (Figure 5b). At the down-gradient location at 100 years after source removal, the bulge occurs at about 1.2 m below the interface and the 5  $\mu\text{g/L}$  TCE front occurs at 7 m below the interface.

[29] Figure 6 compares complete field measured aquifer and aquitard TCE profiles with simulated profiles. Figure 6a



**Figure 6.** Comparison of simulated and field profiles: (a) source zone and (b) plume 280 m down gradient of the source. The source zone aquifer profile (WCP-46) was collected in 1997 just outside the enclosure using the Waterloo profiler and aquitard profiles (WCP-70 and WCP-71) were obtained from subsampling of cores collected inside the enclosure in 1997 below DNAPL. The plume aquifer profile (ML-10) was obtained from multilevel sampling and aquitard profile from core subsampling in 2000. Simulated downgradient profiles are shown at the end of the 42 year constant source (CS) period and at 5.75 years after source removal for comparison to the field profile. Also shown in Figure 6b are simulated profiles assuming a stepped declining source (SS) (see inset) at 42 years and at 5.75 years after source removal, which provides a better match to the field profiles.

shows a composite profile with aquitard data from two cores taken inside the enclosure (WCP-70, WCP-71) and aquifer data obtained using the Waterloo Profiler at a location just outside the northeast side of the enclosure (WCP-46) in the active groundwater flow field, where a thin DNAPL layer occurs at the interface. The field and simulated profiles near the source are similar, displaying a sharp decrease in TCE concentrations in the aquifer just above the interface. The maximum aquifer concentration from the Profiler (1400 mg/L) is slightly above the maximum calculated aquitard value just below the interface from the core analyses (1300 mg/L), but both are in the range of literature values for TCE solubility. The match between model and field results for the 280 m distance at 5.75 years after DNAPL zone isolation (Figure 6b) is weak; however, they show similar general shape and maximum depth of TCE penetration into the aquitard. The simulated profile shows a much higher peak concentration in the aquitard of 180 mg/L, compared to the field peak of 60 mg/L. Also, the field peak (bulge) occurs deeper in the aquitard than the simulated peak.

[30] This discrepancy between the field and simulated TCE concentrations at the down-gradient location (Figure 6b) is

likely due to decline over time in the TCE mass discharge emanating from the DNAPL zone due to dissolution by natural groundwater flow through this zone prior to the sheet piling enclosure, resulting in reduced down-gradient concentrations at the interface. The period of major TCE use at the site occurred between the mid-1950s and early 1970s, and it is expected that the majority of the DNAPL was released in the 1950s and 1960s when use was highest and regulatory concerns for leaks and environmental awareness were minimal. Thus three to four decades of DNAPL zone mass depletion occurred prior to installation of the sheet pile enclosure. The total mass depletion is estimated to be nearly 40,000 liters of DNAPL (justification presented in section 4.5). Such large mass depletion presumably caused decline in thickness and aerial shrinkage of DNAPL zones within the source area, resulting in a gradual decline in concentrations at the transect location prior to source isolation. TCE concentration profiles from the aquitard inside the enclosure also provide evidence for DNAPL mass depletion. *Parker et al.* [2004] indicate that some profiles show no back diffusion evidence (e.g., Figure 4a), whereas others display characteristic back diffusion shapes indicating complete dissolution of DNAPL locally followed

by a period of reverse diffusion due to decline in TCE concentration at the aquifer-aquitard interface.

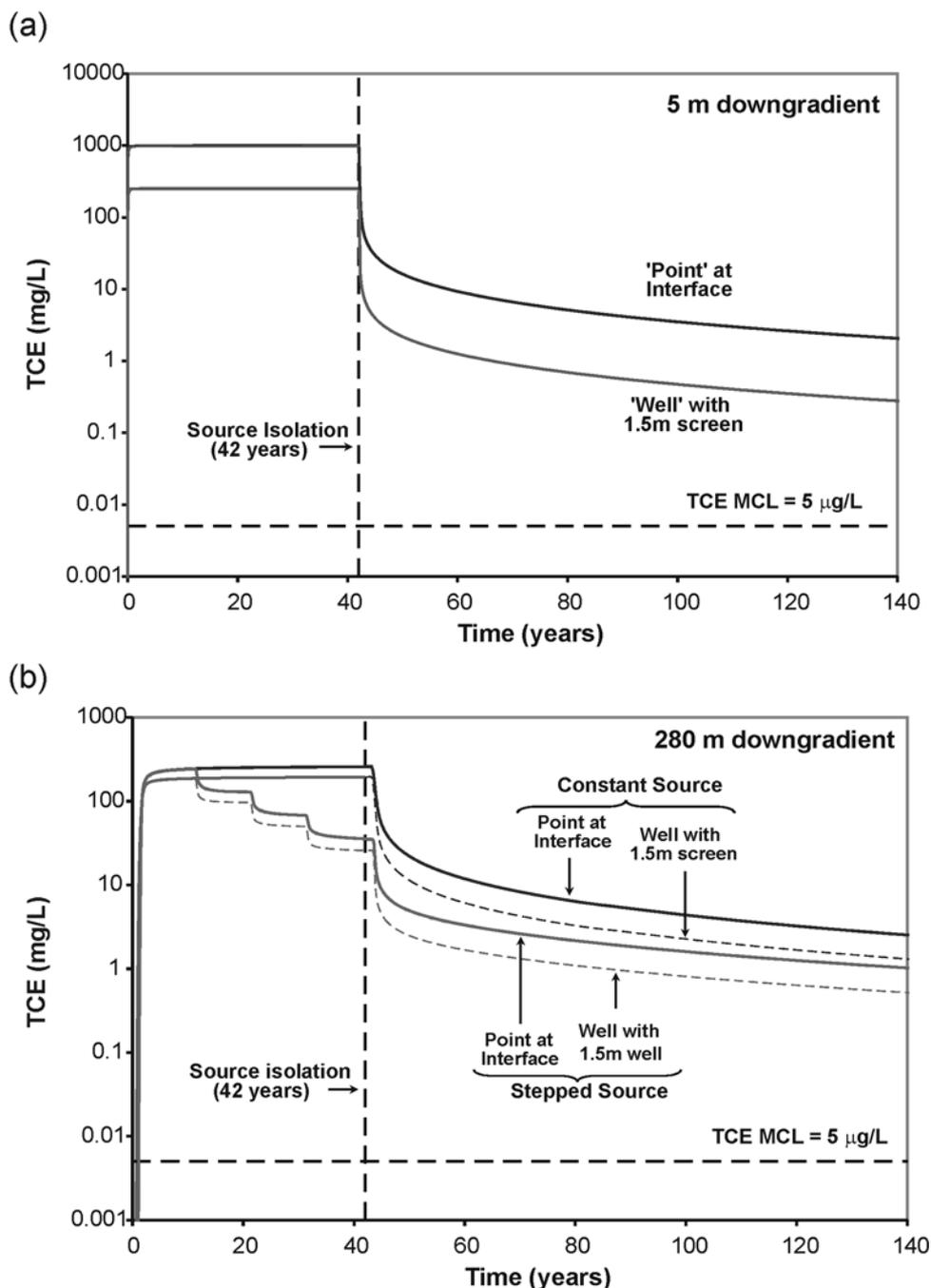
[31] We examined the effects of DNAPL mass depletion by applying a stepped declining source concentration (see Figure 6b, inset) during the period prior to source isolation, representing average concentrations emanating from the source zone. Application of a 2-D vertical cross-section model does not allow inclusion of transverse horizontal dispersion. Such dispersion only has a minor effect on the overall plume width, as explored earlier, and the field profile was collected along the plume centerline where effects of such dispersion should be minimal. However, the effect of transverse horizontal dispersion on internal plume concentrations may be much stronger. At the time of source isolation much of the original DNAPL mass was depleted, however, high concentrations (i.e., approaching or at solubility) would still be emanating from the small, discontinuous DNAPL zones remaining in the source area. These high concentration zones would be reduced by transverse horizontal dispersion down gradient within the plume, causing mixing of these small high concentration zones with groundwater containing much lower concentrations from zones where the DNAPL was depleted. As shown in Figure 6b, the stepped source representing such lower average concentrations produces a simulated profile more closely matching the upper portion of the field profile, while maintaining a good fit to the lower portion.

[32] Back diffusion effects on plume tailing are illustrated with TCE breakthrough and elution curves immediately downgradient of the source zone and at 280 m downgradient (Figure 7). Concentrations decline rapidly within the first few years after source removal, with the decline beginning instantaneously close to the source (Figure 7a) and 2 years later at the down-gradient location (Figure 7b), with the lag representing the groundwater transit time. For this ideal case with complete and instantaneous source removal, the concentration decline is greater and more abrupt near the source. The tailing effect is larger downgradient due to the accumulated effect of back diffusion to the aquifer from the aquitard along the entire plume extent. Within the first decade after source removal, simulated concentrations decline by more than an order of magnitude at the 280 m distance, but strong long-term tailing persists thereafter, with monitoring well TCE concentrations exceeding 1000  $\mu\text{g/L}$  100 years after complete source removal. Continued downward advection in the aquitard marginally reduces the magnitude of plume tailing by opposing back diffusion (simulations not shown). The simulation using the stepped declining source indicates tailing at slightly lower concentrations compared to the case where the source was constant (Figure 7b), but nevertheless, at 100 years after source removal concentrations remain more than two orders of magnitude above MCLs. The simulations indicate that plume tailing observed in monitoring wells west of the building (Figure 2) and plume distribution along the transect 6 years after source isolation (Figure 3a) can be fully accounted for by back diffusion from the aquitard without need for other influences. Therefore the small area of DNAPL mass outside the enclosure, and other unknown but possible locations of DNAPL, are negligible in this context. The simulations indicate back diffusion causes TCE plume persistence in the aquifer for

more than a century at concentrations over two orders of magnitude above the TCE MCL.

[33] The only previous field evidence in the literature for aquitard back diffusion is that for Dover Air Force Base, Delaware, presented by *Ball et al.* [1997] and *Liu and Ball* [2002]. The Dover aquitard profiles exhibited a much different shape than the Connecticut profiles because the Dover aquitard has two layers with very different properties, particularly retardation factors, while the Connecticut aquitard shows no evidence of large-scale layering. At the Dover site, modeling suggests that the aquifer contaminants (PCE and TCE) arrived at the aquitard profile sites 10 to 15 years prior to the profile determinations, whereas at the Connecticut site arrival occurred four decades prior to profile determination. At the Dover site the deepest contaminant penetration (TCE) was 1 m, while the deepest TCE penetration at the Connecticut site was over 3 m. *Ball et al.* [1997] used one-dimensional modeling of back diffusion to predict, based on the imposition of zero concentration at the aquifer-aquitard interface, long-term back diffusion showing nearly 50% of TCE mass remaining in the aquitard after 100 years. The Connecticut site simulations indicate 45 and 58% of the TCE mass present in the aquitard at 42 years (time of source isolation) for the constant source and stepped source cases, respectively, remains after 100 years of back diffusion at the downgradient distance where aquitard profiles were collected. *Liu and Ball* [1999] and *Michalak and Kitandis* [2004] applied geostatistical inverse modeling to reassess inferences concerning the historical concentration conditions in the overlying aquifer at the Dover site. This modeling reduced the uncertainty in the inference of historical conditions for forensic purposes, based on the premise of the diffusion origin of the aquitard profiles. In the Connecticut study, characterization of contamination in both the aquifer and aquitard help to constrain the possible interpretations.

[34] Aquifer contamination caused by chlorinated solvent DNAPL at the bottom of sandy aquifers resting on clayey aquitards is common, and compounds other than TCE are often involved. The magnitude of plume tailing caused by back diffusion will be greater for compounds having the largest difference between solubility and their respective MCLs, which can vary widely. For example, the reported solubility ( $S_w$ ) of some common chlorinated solvents released as DNAPLs, dichloromethane (DCM), TCE and PCE are 20,000, 1100, and 200 mg/L, respectively [*Pankow and Cherry*, 1996, Table A1] while MCLs are 0.005 mg/L for each compound; with ratios of solubility to the respective MCLs ranging by more than four to six orders of magnitude. Other relevant differences include free solution diffusion coefficients and partitioning coefficients. Using reported  $K_{oc}$  values of 8.8, 126 and 364 mL/g for DCM, TCE and PCE, respectively [*Pankow and Cherry*, 1996] and the average study site aquitard  $f_{oc}$ , Equation 2 provides retardation factors of 1.0, 1.2 and 1.7 for DCM, TCE and PCE, respectively. However, at sites where the aquitard  $f_{oc}$  is higher, the magnitude of and differences in retardation factors could also be much higher. For example, *Johnson et al.* [1989], *Myrand et al.* [1992], and *Ball et al.* [1997] report retardation factors for TCE ranging from 1.4 to >65 for nonindurated aquitards. Higher sorption results in higher capacity for mass storage in the aquitard and



**Figure 7.** Simulated TCE breakthrough and elution curves following source removal showing plume tailing at (a) 5 m and (b) 280 m down gradient of the source. Both point concentrations at the aquitard interface and hypothetical well concentrations (depth averaged over a 1.5 m screened interval, assuming uniform hydraulic conductivity) are shown. Also shown in Figure 7b are simulated curves for a scenario with a stepped declining source (see Figure 6b, inset). In all cases the aquifer TCE concentrations persist at levels orders of magnitude above the MCL for more than a century.

longer persistence of steep concentration gradients near its surface, thus causing more extensive mass transfer by diffusion into low-permeability zones, and therefore eventually causing stronger tailing effects due to back diffusion. Back diffusion effects are not limited to chlorinated solvents or chemicals released as DNAPLs, but apply to many other contaminants (e.g., MTBE, perchlorate, etc.). For contaminants released as light nonaqueous phase liquids (LNAPLs)

or as dissolved solutes, the main prerequisite for back diffusion potential is contact of high concentration plumes with low-permeability layers or underlying aquitards, allowing diffusive mass transfer into and later back out of these zones. Timing also plays an important role; at sites where contaminant sources have existed for decades prior to source remediation or isolation and with large downgradient plumes, the potential for long-term back diffusion is much

greater than for sites with more recent contamination and limited plume extent.

#### 4.5. Aquitard Mass Storage and Plume Mass Discharge

[35] Field data collected during the study were used to provide estimates of mass stored in the aquitard relative to that in the aquifer and discharged beyond the transect. These estimates allow assessment of the consistency between the field data and simulation results, and provide another indication of the long-term nature of plume tailing due to back diffusion. The TCE mass stored in the aquitard between the DNAPL source and transect 6 years after source isolation was estimated by approximating the area of the TCE plume as a trapezoid with a length of  $h = 280$  m (distance from source to transect) and widths of  $a = 50$  m at the source zone (enclosure width) and  $b = 250$  m along the plume transect (zone with TCE  $>1$  mg/L), providing a plume footprint area of  $42,000$  m<sup>2</sup> ( $A = h/2(a + b)$ ). Along the transect, the aquitard TCE mass per unit surface area was estimated by multiplying the area under the ML-4 and ML-10 profiles (Figures 4b and 4c) by the aquitard wet bulk density of  $1.95$  g/cm<sup>3</sup>, providing values of  $20.5$  and  $45.2$  g TCE per m<sup>2</sup>, respectively, with an average of  $32.9$  g/m<sup>2</sup>. Simulation results for the stepped declining source case indicate that the aquitard mass per m<sup>2</sup> just downgradient from the source was about four times higher than along the transect at 6 years after source isolation. Therefore multiplying the average mass along the transect by four provides a source area aquitard mass of  $131.6$  g/m<sup>2</sup>. This is lower than the mass in the aquitard below DNAPL ( $630$  g/m<sup>2</sup>, Figure 4a) by a factor of five, reflecting an average value due to DNAPL depletion as described earlier. Assuming a linear mass decline in the aquitard over the  $280$  m distance ( $h$ ) between the source ( $M_s = 131.6$  g/m<sup>2</sup>) and transect ( $M_t = 32.9$  g/m<sup>2</sup>), the mass stored in the aquitard was calculated as the volume of an object with the trapezoid as its base and height varying from  $M_s$  at the narrow end ( $a$ ) and  $M_t$  at the wide end ( $b$ ). This volume was obtained by subdividing the object into a series of blocks varying in width from  $a$  to  $b$  and height from  $M_s$  to  $M_t$  along the length  $h$ , providing a total mass in the aquitard of  $3000$  kg ( $2050$  L as equivalent TCE DNAPL, assuming a density of  $1.46$  g/cm<sup>3</sup>).

[36] The TCE mass discharge in the aquifer across the transect was obtained from the depth-discrete multilevel concentrations using the approach for sand aquifers described by *Einarson and Mackay* [2001] and *Guilbeault et al.* [2005], with

$$M_d = \sum_{i=1}^n C_i A_i q_i \quad (3)$$

where  $M_d$  is the total contaminant mass discharge (mass/time),  $C_i$  is the concentration (mass/volume) assigned to transect area element  $A_i$  (area) with Darcy Flux  $q_i$  (volume/area/time). In this case,  $C_i$  is the TCE concentration at each monitoring point, applied uniformly over  $A_i$ , which is approximated as a rectangle with a width of half the distance to adjacent multilevels and a height of half the vertical interval between sampling points above and below, except for the bottommost point at the interface where only half the distance between the upper point was applied.

Using the geometric mean  $K$  from slug tests ( $2.4 \times 10^{-2}$  cm/s) and average hydraulic gradient ( $i$ ) of  $0.01$  provides a Darcy flux of  $0.2$  m/d. Relative to the hydraulic conductivity of this nearly homogeneous aquifer, the spatial variability in TCE concentration distribution is large, therefore the Darcy flux was applied as a single uniform value along the transect. This homogeneity assumption was also used by *Einarson and Mackay* [2001] and *Guilbeault et al.* [2005]. The estimated TCE mass discharge using the 2000 TCE results (Figure 3a) is  $36$  kg/yr ( $25$  L/yr as equivalent DNAPL), 6 years after DNAPL zone isolation. Therefore, if the plume TCE mass discharge remains constant, more than  $80$  years must pass for the estimated  $3,000$  kg of TCE in the aquitard to be removed by back diffusion. However, the timescale will increase substantially as the back diffusion flux declines.

[37] The total TCE mass discharged across the transect prior to the sheet piling enclosure was estimated assuming that mass discharge just prior to source isolation was an order of magnitude higher than the 2000 estimate, consistent with the magnitude of concentration declines in the wells (Figure 2). Prior mass discharge was then assumed the same as the stepped source applied to fit the transect aquitard profile ML-10 (Figure 6b), i.e., assume preenclosure discharge applies over the 12-year period from 1982 to 1994, then increasing by a factor of two during each decade back to 1952. These assumptions provide a total dissolved TCE mass removed from the DNAPL zone and transported in the aquifer beyond the transect of  $54,700$  kg ( $\sim 37,500$  L as equivalent TCE DNAPL) prior to source isolation. Estimates of the DNAPL mass remaining inside the enclosure, based on the detailed sampling described by *Parker et al.* [2003, 2004], range from  $5000$  to  $20,000$  kg ( $\sim 3400$  to  $13,700$  L as equivalent DNAPL). This remaining mass is much smaller than that removed by dissolution, and either stored in the aquitard upgradient of the transect ( $\sim 3000$  kg) or discharged across the transect ( $\sim 54,700$  kg). This supports the premise used previously that depletion of much of the original DNAPL mass by groundwater dissolution occurred prior to DNAPL zone isolation, and the stepped source function used in the model.

[38] The simulation using a stepped source function indicates that, at the time of source isolation, about  $6.2\%$  of the total mass dissolved from the source during the 42 year period prior to source isolation remained stored in the aquitard, with the remainder consisting of mass in the aquifer ( $1.0\%$ ) and the mass discharged out of the domain ( $92.8\%$ ). Six years after source isolation, the  $6.2\%$  has diminished to  $5.8\%$  for the mass remaining in the aquitard, with  $<0.1\%$  in the aquifer and  $94.1\%$  discharged out of the domain. These simulation results show good comparison with the field estimates, where the mass remaining in the aquitard 6 years after source isolation ( $3000$  kg) represents  $5.2\%$  of the total removed from the source ( $57,700$  kg, with  $3000$  kg in the aquitard and  $54,700$  kg discharged beyond the transect, neglecting mass remaining in the aquifer). Simulations indicate that in the 6 years of back diffusion, only  $7.4\%$  of the mass accumulated in the aquitard after 42 years were removed. The simulated elution curves (Figure 7) show that the remaining mass will be released from the aquitard even more slowly. After 100 years of back diffusion, simulations indicate that only  $42\%$  of the

aquitard mass present at the time of source isolation will have been removed.

## 5. Conclusions

[39] Groundwater monitoring at the Connecticut study site shows a persistent TCE plume down gradient of the DNAPL zone 6 years after the DNAPL was isolated from groundwater flow by the sheet piling enclosure. Groundwater flow in this minimally heterogeneous sand aquifer should have flushed the aquifer TCE plume beyond the monitoring area during this period. However, the persistent aquifer TCE concentrations of hundreds to thousands of  $\mu\text{g/L}$  indicate one or more continuing TCE sources. Numerical simulations indicate that back diffusion from the aquitard can fully account for this plume tailing in the area down gradient of the DNAPL enclosure. While a small DNAPL zone outside the enclosure contributes some TCE mass to the plume, aquitard back diffusion fully accounts for the observed concentrations in the aquifer monitoring wells, and therefore DNAPL outside the enclosure has negligible impact in the focus area of this study. The interpretations of this study are strengthened by the hydrogeologic simplicity of the aquifer-aquitard system and quantification of both parts of the system; the aquifer and the aquitard. Numerical simulations of the back diffusion effects on the aquifer indicate that the largest concentration decline in the aquifer occurred within the first five to ten years following DNAPL zone isolation, which was confirmed by monitoring well results. Back diffusion will occur over a much longer time frame than the period of inward diffusion prior to DNAPL source isolation, which was about 40 years. Simulations using a stepped declining source concentration to account for DNAPL depletion prior to source isolation indicate that 6% of the total mass discharged from the source zone during the period prior to isolation remained stored in the aquitard. Six years of back diffusion and aquifer flushing removed about 7% of this stored mass and simulations indicate that after 100 years, 58% of this mass still remains, highlighting the slow rate of mass removal from the aquitard. In the general case at any site when DNAPL source removal or isolation is accomplished completely, back diffusion from an underlying aquitard can be the sole cause for strong plume tailing, and simulations indicate that centuries will pass before aquifer TCE concentrations reach the MCL ( $5 \mu\text{g/L}$ ).

[40] In this study, the strong back diffusion effects are caused only by the underlying aquitard in which large TCE mass was stored prior to source isolation, producing a plume with highest concentrations along the bottom of the aquifer. Conditions generally similar to these are common at many sites because chlorinated solvents as dense, low-viscosity liquids readily sink to bottoms of sandy aquifers underlain by aquitards. Even much thinner aquitards can provide sufficiently large mass storage to cause strong, persistent back diffusion. The aquifer at this site also has no silty or clayey layers or lenses within it, but many aquifers do. Such low-permeability zones would also store and then release contaminants over long time to further contribute to back diffusion strength. Long-term back diffusion causing MCL exceedences would also have been the case if other common chlorinated solvent chemicals such as PCE, 1,1,1-TCA and DCM were the site contaminant, because their respective aqueous solubility are also several

orders of magnitude greater than their MCLs. High sorption capacity aquitards can accentuate back diffusion effects and expand the list of relevant organic contaminants. However, back diffusion effects are not limited to chlorinated solvents or chemicals released as DNAPLs, because any high-concentration contaminant plume migrating past low-permeability layers within or at the bottom of the aquifer will result in back diffusion when plume concentrations decline.

[41] **Acknowledgments.** The field and laboratory analytical data reported on in this paper resulted from the skillful work of several University of Waterloo staff: in the field, Bob Ingleton, Jesse Ingleton, Paul Johnson, Hester Groenevelt, Daryl Bassett, Bryn Shurmer, Matt Nelson, Martin Guilbeault, Colin Meldrum, and David Thomson and, in the lab, Maria Gorecka, Daryl Bassett, and Hester Groenevelt. Lisa Akers, Erin MacDonald Sullivan, and Lauren Levine of United Technologies Corporation provided the essential on-site support for field activities. The authors are grateful to John Cherry for his careful review of the manuscript. The manuscript benefited greatly from the journal review process with comments from two anonymous reviewers and the Associate Editor. Funding for this research was provided by United Technologies Corporation and the University Consortium Solvents-in-Groundwater Research Program.

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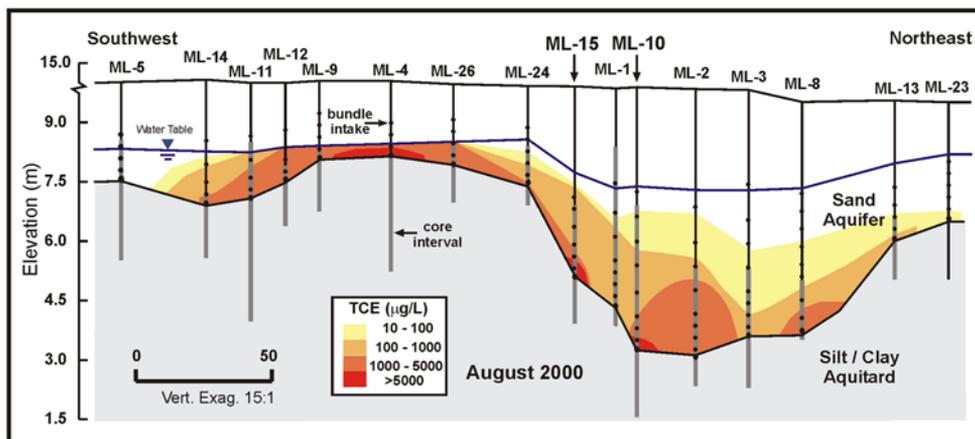
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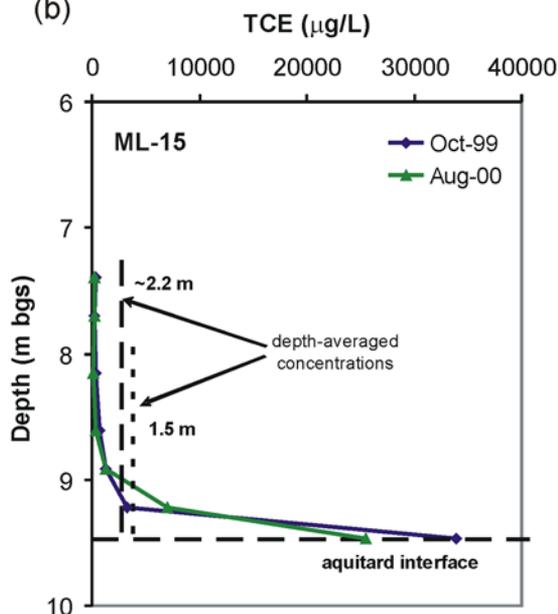
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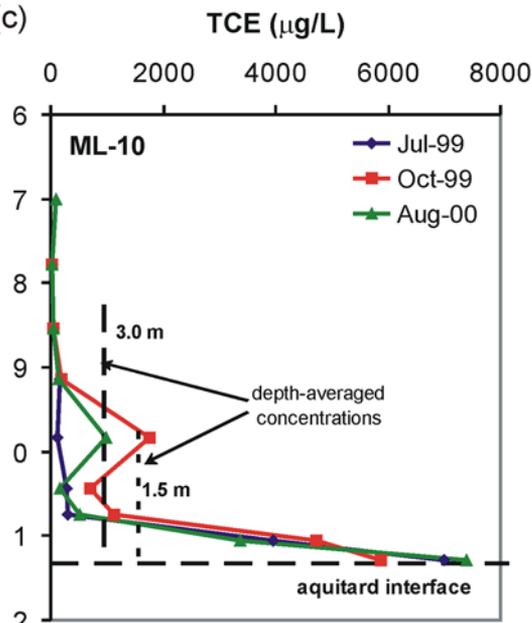
(a)



(b)



(c)



**Figure 3.** (a) Cross section showing depth-discrete TCE concentrations and plume contours along the transect 280 m down gradient of the source zone in August 2000 obtained using multilevel monitoring systems, 6 years after the source zone was isolated, and example aquifer TCE profiles along the transects (b) ML-10 and (c) ML-15. Calculated depth-averaged concentrations (2000 data) are shown, representing concentrations in hypothetical monitoring wells screened over the specified intervals.