

# Mass and Flux Distributions from DNAPL Zones in Sandy Aquifers

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## Abstract

At three industrial sites in Ontario, New Hampshire, and Florida, tetrachloroethylene (PCE) and trichloroethylene (TCE), released decades ago as dense nonaqueous phase liquids (DNAPLs), now form persistent source zones for dissolved contaminant plumes. These zones are suspended below the water table and above the bottoms of their respective, moderately homogeneous, unconfined sandy aquifers. Exceptionally detailed, depth-discrete, ground water sampling was performed using a direct-push sampler along cross sections of the dissolved-phase plumes, immediately downgradient of these DNAPL source zones. The total plume PCE or TCE mass-discharge through each cross section ranged between 15 and 31 kg/year. Vertical ground water sample spacing as small as 15 cm and lateral spacing typically between 1 and 3 m revealed small zones where maximum concentrations were between 1% and 61% of solubility. These local maxima are surrounded by much lower concentration zones. A spacing no larger than 15 to 30 cm was needed at some locations to identify high concentration zones, and aqueous VOC concentrations varied as much as four orders of magnitude across 30 cm vertical intervals. High-resolution sampling at these sites showed that three-quarters of the mass-discharge occurs within 5% to 10% of the plume cross sectional areas. The extreme spatial variability of the mass-discharge occurs even though the sand aquifers are nearly hydraulically homogeneous. Depth-discrete field techniques such as those used in this study are essential for finding the small zones producing most of the mass-discharge, which is important for assessing natural attenuation and designing remedial options.

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## Introduction

Chlorinated solvents are the most prevalent organic contaminants found in ground water (Stroo et al. 2003), and in the dissolved phase they are typically mobile and recalcitrant, particularly trichloroethylene (TCE) and tetrachloroethylene (PCE). Schwille (1984, 1988) was the first to recognize that chlorinated solvent plumes (i.e., zones of dissolved phase contaminants) are caused by immobile dense nonaqueous phase liquid (DNAPL) zones within the ground water. Ground water flowing through the DNAPL zones causes DNAPL dissolution, generating plumes that commonly achieve exceptionally large sizes relative to

plumes comprised of other types of organic contaminants (Mackay and Cherry 1989). Although the processes governing subsurface DNAPL and plume behavior are known (Cohen and Mercer 1993; Pankow and Cherry 1996) and numerous solvent contaminated sites have been investigated, DNAPL masses at field sites are not often quantified. (Feenstra 2003). Heterogeneity imposes severe limits for measuring DNAPL mass; however, determining the rate of dissolved-phase mass lost from DNAPL zones due to dissolution and ground water transport is a much more feasible endeavor.

In recent years, determining the discharge of the dissolved-phase mass emanating from DNAPL and other types of source zones has become important (Ptak et al. 1998; Einarson and Mackay 2001). Feenstra et al. (1996) defined the plume discharge as the amount of contaminant mass migrating through cross sections of the aquifer orthogonal to ground water flow per unit of time. The plume discharge measured on an orthogonal cross section (i.e., vertical control plane) positioned immediately downgradient of the source area is an important quantity for assessing plume impacts on water supply wells (Einarson

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and Mackay 2001) and several studies used plume mass-discharge measurements to estimate the mass of contaminant lost due to natural attenuation (Semprini et al. 1995; Borden et al. 1997; King et al. 1999; Wilson et al. 2000; Kao and Wang 2001). However, of the few plume discharge measurements for contaminated industrial sites reported in the literature, only one pertains to chlorinated solvents in natural sand aquifers (Semprini et al. 1995).

In most studies of plume mass-discharge, multilevel wells or screened auger holes are situated on a cross section perpendicular to the plume. For cases where the goal was quantification of natural attenuation, multiple cross sections were implemented at increasing distances from the source zone (Kao and Wang 2001; Wilson et al. 2000). In this method, the cross section is divided into many subareas, or elements, commensurate with the spatial array of monitoring points, and the mass-discharge through each element is calculated using the concentration values and the ground water discharge obtained from Darcy's law. The mass-discharges for all of the elements in a cross section are then summed to obtain the plume discharge. This cross sectional approach is subject to some uncertainty. The large spatial and temporal variations often associated with contaminant concentrations and aquifer properties result in greater uncertainty for a particular monitoring array (Béland-Pelletier et al. in review). Therefore, the spacing of monitoring points on the cross section is a critical aspect of this approach.

This paper reports on investigations of contaminant mass-discharge conducted at three sites where persistent TCE or PCE plumes occur in unconfined aquifers. The goal is to measure the mass-discharges by intensive monitoring along vertical cross sections positioned immediately downgradient of the DNAPL source zones and develop insight about the spatial scale necessary to reliably quantify contaminant mass-discharge. Ground water sampling along the cross sections was done at a spatial scale guided by the premise that chlorinated solvent plumes in sandy aquifers are typically formed by horizontal ground water flow through DNAPL source zones comprised of thin horizontal DNAPL layers. This conceptualization of DNAPL sources in sandy aquifers was first hypothesized by Anderson et al. (1992a, 1992b) who stated that plumes emanating from these source zones should possess considerably more internal spatial variability with respect to concentration than idealized plumes from homogeneous residual sources. The expectation that chlorinated solvent DNAPL source zones in unconfined sandy aquifers are comprised of multiple layers was later supported by the PCE-DNAPL release experiments conducted by Kueper et al. (1993) and Brewster et al. (1995) inside steel sheet pile enclosures in the undisturbed sand aquifer at the Borden field site. These enclosures precluded ground water flow. Also at the Borden site, Broholm et al. (1999) observed multiple high-concentration zones positioned downgradient of an infiltrated chlorinated solvent source zone in an enclosure in which horizontal flow was artificially imposed. Sale and McWhorter (2001) adopted the concept of multiple, thin, horizontal DNAPL layers to represent idealized source zones for the purpose of mathematical analysis of factors controlling mass transfer and source mass depletion. Although the experiments indi-

cated earlier provide expectations about the nature of plumes downgradient of chlorinated solvent DNAPL source zones, the actual spatial scale of plume concentration variability must be determined at field sites by detailed monitoring.

The approach taken in this study was to use multilevel ground water monitoring to characterize the TCE and PCE distributions in exceptional detail. Multilevel sampling systems were utilized along cross sections orthogonal to ground water flow and directly downgradient of each of the three DNAPL source zones. In the multilevel monitoring, each sample was drawn from a small volume of aquifer so that the resulting concentration distributions are depth-specific, rather than blended. Figure 1 shows a conceptual representation of this approach. Numerous vertical profiles comprised of these depth-discrete sampling points produced a relatively fine sampling grid. This detailed spatial coverage allowed for the delineation of individual high-concentration zones created from dissolution of the multiple DNAPL layers comprising the source area. They also provided sufficient detail for assessing the effect of vertical sample spacing.

## Site Characteristics

All three sites have the same type of DNAPL source zones comprised of single-component DNAPL, either PCE or TCE, suspended in unconfined sand aquifers. Table 1 indicates the geologic origins and industrial uses of the sites. The aquifer at the Ontario site, located beneath a small dry cleaning establishment, originated in a braided to meandering, glacially fed river flowing across a broad plain. The New Hampshire site's aquifer, situated at a former tool and die manufacturing plant, was deposited in a glacial melt water river flowing in a bedrock valley. The third aquifer, located at a metal fabricating and cleaning plant for the space industry near Cape Canaveral, Florida, was formed in a marine beach environment. Each of these sand aquifer types is common in their geographical region. Although the sites are in different areas and have different origins, each provides a desirable degree of simplicity due to a combination of factors, including aquifer materials suitable for direct-push monitoring, shallow water tables, and moderately homogeneous hydraulic conductivity within their respective sand aquifers.

Each of the three sites has a distinct plume emanating from a known DNAPL source zone, PCE at the Ontario and New Hampshire sites and TCE at the Florida site. The locations of the DNAPL source zones were delineated sufficiently for the mass-discharge cross section at each site to be positioned immediately downgradient of the source zone. Figure 2 shows the geologic settings and the positions of the source zones and their plumes. Prior to and during the site investigations, no disturbances to the source zones or the plumes in the vicinity of the cross sections had been caused by any engineering controls or remedial activities. Since the completion of our studies, major remedial measures were implemented in the source zones of the New Hampshire and Florida sites. Information provided by the site owners and regulatory agencies indicates that use of TCE or PCE DNAPL began in 1957 at the New Hampshire

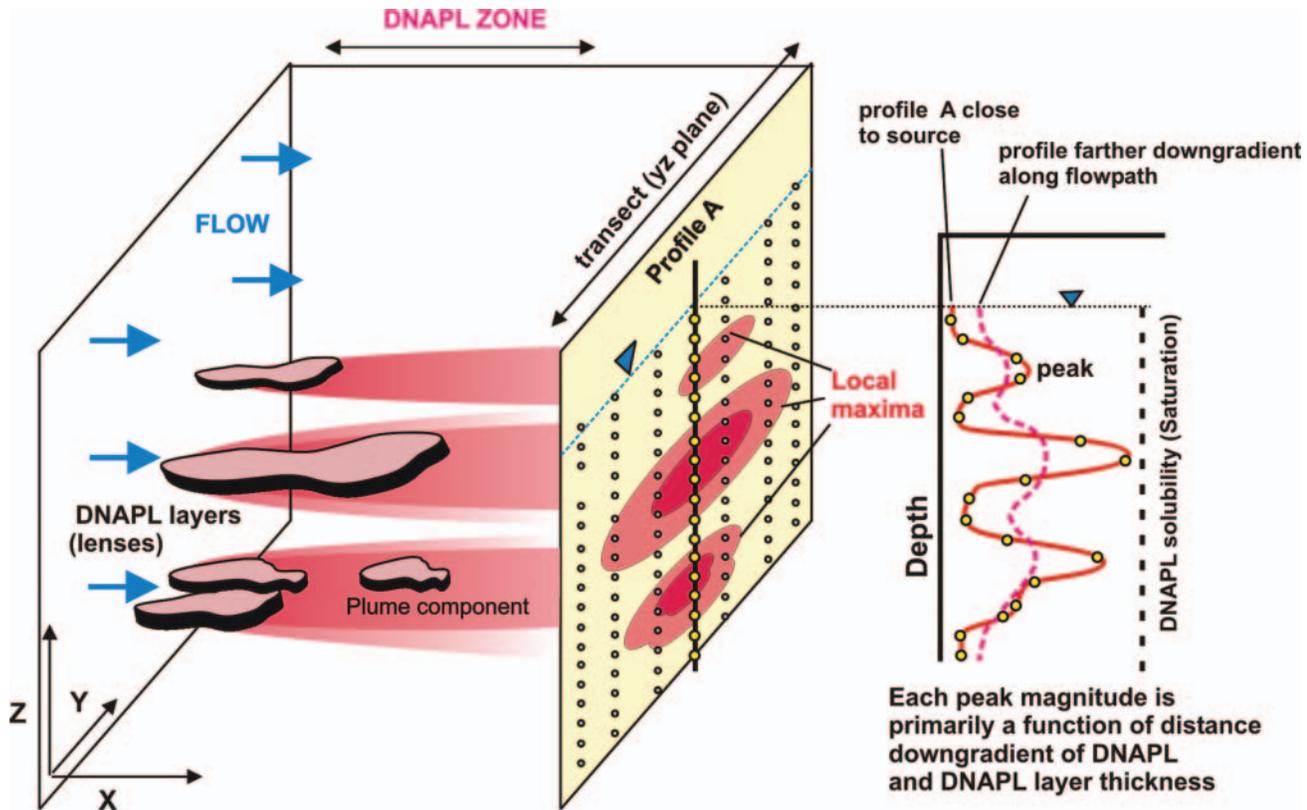


Figure 1. Schematic illustration of the contaminant distribution along the transverse cross section immediately downgradient of a DNAPL source zone comprised of separate DNAPL layers. The contaminant distribution on the cross section is determined from numerous depth-discrete sampling profiles.

site, in 1964 at the Florida site, and in the early 1970s at the Ontario site. DNAPL use ceased in the late 1970s at the Florida site and New Hampshire sites and in the early 1990s at the Ontario site. Solvent contamination was first discovered at these sites decades ago (Table 1). Water level measurements in the monitoring wells show that ground water flow is horizontal through each source zone at aver-

age linear ground water velocities in the range of 10 to 65 cm/d, and that ground water transports the contaminants towards surface water bodies (Figure 2).

## Field and Laboratory Methods

### Approach

Before sampling began at each site, the sample spacing needed for accurate delineation of the PCE or TCE distribution along the cross section was unknown, and therefore a strategy for selection of this spacing needed to be developed. The two sampling devices used in this study, specifically the Waterloo profiler described by Pitkin et al. (1999) and a modified version of the bundle wells described by Cherry et al. (1983), provide ground water samples drawn from an exceptionally small volume of aquifer relative to conventional monitoring methods. However, the aquifer volume providing each sample is sufficiently large to require consideration in the context of sample scale and spacing. The volume of aquifer from which each sample was drawn depends on both the purge volume taken prior to sampling and the sample volume. The purge volumes were dictated by the inside diameter of the tubing and sampling depth. At these three sites, ~ 300 mL were purged followed by collection of either a 25 or 40 mL sample. Assuming an aquifer porosity of 0.35 and isotropy with respect to aquifer hydraulic conductivity, the purge volume represents a spherical zone in the aquifer with a radius of 6 cm centered about the middle of the profiler tip or bundle well intake (Figure 3). Therefore, the sample, which is drawn from the aquifer zone just beyond this purge zone,

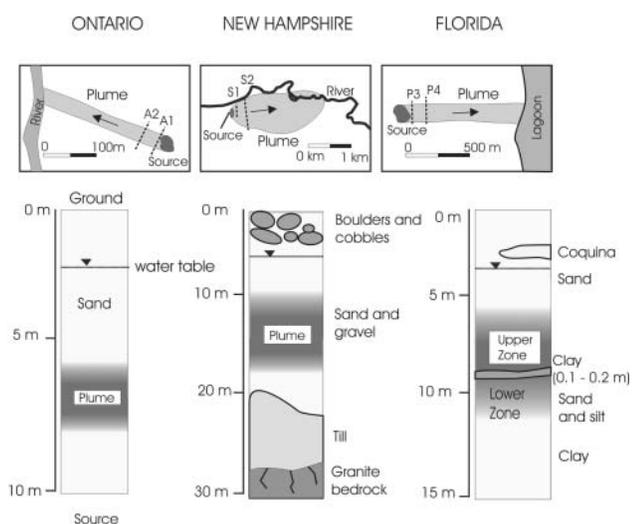


Figure 2. Schematic illustration of the plumes and geology of the three study sites. Each study site has a primary monitoring cross section a short distance downgradient of the DNAPL source area and a secondary cross section farther downgradient.

**Table 1**  
**Site Use and Characteristics**

	<b>Angus, Ontario</b>	<b>Milford, New Hampshire</b>	<b>Cocoa, Florida</b>
Type of facility	Dry cleaner	Tool and dye	Metals cleaning and fabricating
Years of operation	1970 to present	Late 1940s to early 1980s	1964 to present
Plume discovery	1992	1983	1966
Period of TCE or PCE use	Early 1970s to early 1990s	1957 to 1983	1964 to 1977; major use ceased in 1971
Contaminant (single-component solvent)	Tetrachloroethene (PCE) (C <sub>2</sub> Cl <sub>4</sub> )	Tetrachloroethene (PCE) (C <sub>2</sub> Cl <sub>4</sub> )	Trichloroethylene (TCE) (C <sub>2</sub> HCl <sub>3</sub> )
VOCs detected	PCE, TCE	PCE, TCE, c-DCE, t-DCE, 11-DCE, VC	TCE, c-DCE, t-DCE, VC, cfc-113
Degradation	None	None	TCE to c-DCE
Type of releases and release periods	Spill in 1970s from above ground (200 gallon) tank and smaller releases	Septic system discharges, septic tank, spills around loading dock, use spillages and above ground storage tank leak into floor drain	Two 55 US gal drums spilled in 1966, hose burst in 1977, routine spillages from cleaning operations from 1964 to 1977
Aquifer depositional environment	Braided to braided meandering transition alluvial channel (Writt 1996)	Glacio-fluvial deposition into a granite bedrock valley	Coastal, beach environment, shallow marine
Bedding characteristics	Very fine-grained to medium-grained unconsolidated sand, inclined and horizontal laminated	Stratified sand and gravel with some basal till overlain in some places with alluvium	Beach sand with discontinuous clay layers and some bioclasts (shells)
Aquifer saturated thickness	> 12 m	0 to 20 m	> 25 m
Depth to water table	3 m	3 m	4.5 m
Aquifer bottom	Unknown, deepest core (11 m bgs) indicated fine sand	Silty till at 20 m bgs	Clay and silty clay at 20 m bgs
Regulatory framework	Ontario MOE; aquifer use discontinued	U.S. EPA: CERCLA; source zone isolation: 1999	Florida DEP: U.S. EPA, RCRA; pump-and-treat; 2002

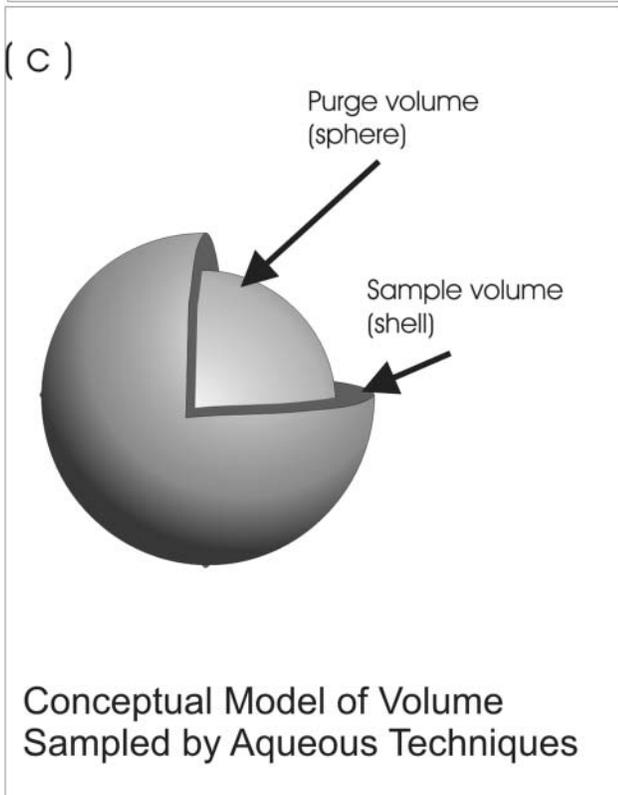
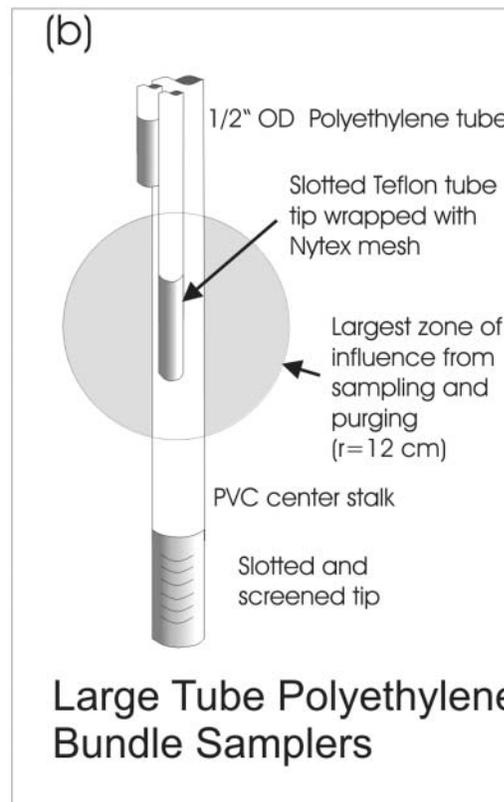
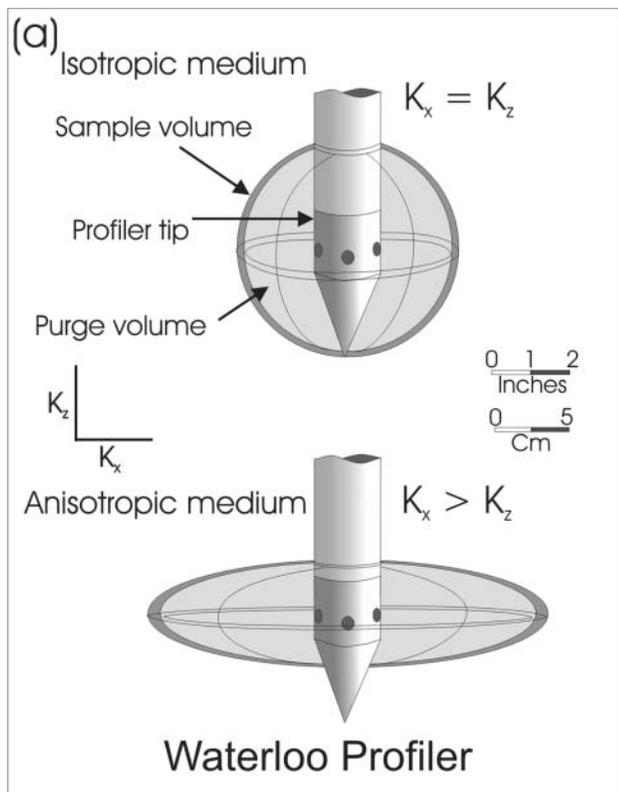
represents a thin spheroid with a diameter slightly > 12 cm. If the sampling zone is anisotropic with permeability greater in the horizontal than the vertical direction, the sampling zone would be elongated (Figure 3). The selection of 15 cm as the smallest vertical sampling interval when using the Waterloo profiler therefore should be appropriate for minimizing overlap effects. The smallest sampling intervals used on the bundle wells was also 15 cm because the scale of purging and sampling produced results similar to profiler results.

Much of the VOC sampling was accompanied by rapid on-site analyses (Górecki and Pawliszyn 1997) so that the characteristics of the PCE or TCE concentration versus depth profiles were determined as the sampling was in progress. This allowed the sample spacing to be adjusted for smaller sample spacing in zones showing abrupt changes in concentration. Also, the acquisition of data by the rapid on-site analyses allowed better positioning of sampling locations along the cross sections because the results were plotted as the field work proceeded.

#### Monitoring Methods

The Waterloo profiler produced nearly all of the ground water samples on which this paper is based. The Waterloo profiler was developed to obtain very small volume ground

water samples from multiple depths at the same location without having to remove the sampling tool for decontamination between samples (Pitkin et al. 1999). The profiler consists of a 4.4 cm diameter stainless steel tip with four or six circular screened ports (4 mm diameter) through which ground water enters stainless steel tubing and is carried to the surface. A peristaltic pump attached in-line after a stainless steel sampling manifold was used to collect water at the surface in 40 or 25 mL glass vials with plastic open screw top caps lined with Teflon™/silicon septa. This setup prevents air bubbles and other possibilities for loss of VOCs by volatilization during sampling. The Waterloo profiler was driven using a vibratory hammer or a direct-push rig. At each sampling location, the profiler tip, attached to a drill rod, was driven to the shallowest sampling depth below the water table. Driving ceased while this first sample was collected. The rod was then driven downward to the depth desired for the second sample while the line was purged slowly outward with distilled water. This outward purging ceased just before the sampling depth was reached and then inward purging was done followed immediately by sample collection. This sequence of driving, purging, and sampling was repeated at many depths until the bottom of the sampling interval was reached. Pitkin et al. (1999) provide details of the sampling procedure.



**Figure 3. Aqueous sampling techniques including the (a) Waterloo profiler, (b) polyethylene tube samplers, and (c) conceptual model of sample zone of influence showing sample comes from thin shell.**

At the Ontario and Florida sites, a second method in addition to the Waterloo profiler was used to obtain VOC profiles. This method also uses a single direct-push hole to produce a profile; however, the sampling installation in the hole is permanent. This depth-discrete monitoring system, referred to as bundle wells, is comprised of numerous half-

inch or one-quarter O.D. polyethylene, Teflon, or stainless steel tubes strapped as a bundle around a three-quarter inch O.D. PVC pipe (Cherry et al. 1983). The PVC pipe provides the rigidity needed for installation and in some cases forms the deepest monitoring point. Each tube extends to a different depth with a 5 cm screen interval so that sampling all tubes and the PVC pipe provides a vertical concentration profile. Teflon and stainless steel tubing were used to minimize diffusion of contaminants through the tubing. Also, the standing water column was purged prior to sampling and the sample water was drawn rapidly to further reduce diffusion effects. Each bundle well was installed down the inside of temporary steel flush-joint casing driven using a direct-push rig. The aquifer material below the water table caved quickly around the bundle of tubes as the casing was removed and the open hole above the water table was sealed with bentonite. Bundle wells comprised of one-half inch O.D. tubes were also used for measurement of hydraulic head profiles at the Ontario and Florida sites.

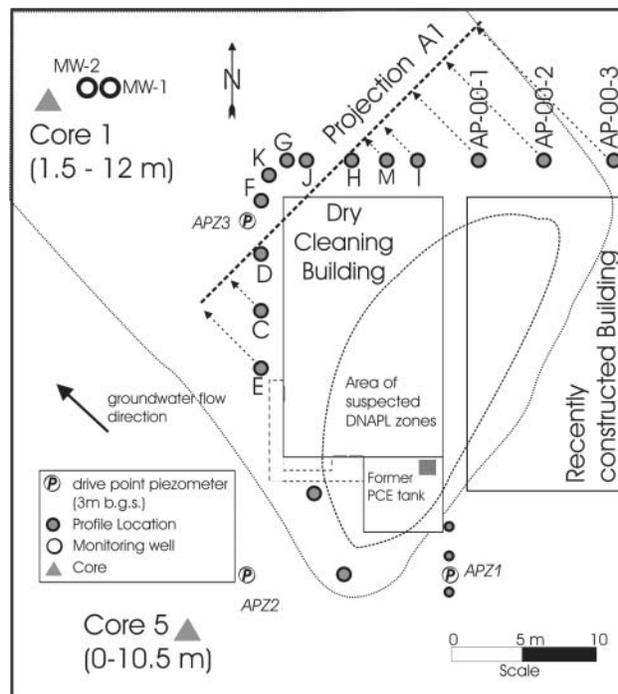
To provide values for the hydraulic gradient acting across each cross section, a network of monitoring wells was used at each site. The hydraulic head profiles from the bundle wells at the Ontario and Florida sites and nested wells at the New Hampshire site indicated no measurable vertical components of the hydraulic gradient in the aquifers, and therefore the horizontal hydraulic gradient associated with each cross section was obtained from head differences between wells associated with each cross section.

Continuous cores for geologic inspection and hydraulic conductivity measurements were obtained from the aquifer at each site using a piston coring system described by Zapico et al. (1987). The piston in the core barrel (1.52 m long) creates suction inside the core tube as the barrel is

removed from the ground. The suction created inside the tube prevents loss of sediment and pore water, and therefore core recovery is typically complete or nearly so. Although each core segment was five feet in length, repeated core acquisition from each hole resulted in continuous core sets through the relevant aquifer zones. Each core was cut in half lengthwise and one half was examined for sediment structure and texture. Samples were taken from the other half at specific depth intervals for hydraulic conductivity and grain size measurements in the laboratory. The hydraulic conductivity of segments of core material from each site was determined using two methods: the falling head permeameter method using repacked samples as described by Sudicky (1986) and the Hazen formula using grain-size analysis parameters (Freeze and Cherry 1979).

Ground water analyses for VOCs were conducted in a laboratory at the University of Waterloo or at the field sites using equipment from the university. At the field sites, the high-speed gas chromatograph used for quantifying VOC concentrations (Górecki and Pawliszyn 1995a, 1995b; 1997) was set up in a temperature controlled room or trailer. The on-site VOC analyses were performed using a high-speed gas chromatograph (SRI 8610C) equipped with a flame ionization detector (FID), photo ionization detector (PID), and dry electrolytic conductivity detectors (DELCD). The gas chromatograph was also equipped with a DB-ProSteel 624 column (5 m long, 0.53 mm I.D., 3 µm film thickness). The temperature program was started and held at 40°C for 0.5 min and then ramped at 20°C/min to 54°C and held for 0.3 min. The pressure program was started and held at 8 psi for 0.5 min, ramped at 20 psi/min to 25 psi and held for 0.15 min. The carrier gas was helium and the total run time per sample was 1.5 min. The samples were prepared by taking two aliquots, one diluted and one undiluted. The samples were quantified using the solid phase microextraction (SPME) headspace technique described by Pawliszyn (1997). 3 mL of sample were syringed into a 5 mL bottle equipped with a Teflon-lined septum. 15 µL of methanol and 15 µL of internal standard solution (cis-1,3-dichloropropene) were added through the septum. The solution was vortexed at high speed for 10 s. An SPME (solid phase microextraction) fiber (100 µm polydimethylsiloxane coating) was exposed to the headspace in the vial for 60 s. The analytes were thermally desorbed from the fiber in an SPME injector equipped with a capacitor for rapid heating and desorption. One of the three detectors was then used to quantify the amount of VOCs in the sample. In most cases, the PID was used because it yielded the most sensitive and accurate results. Mass was quantified using a seven-point polynomial calibration curve. The method detection limits varied for different field episodes and usually ranged from 5 to 10 µg/L for different contaminants.

Ground water samples analyzed for VOCs at the University of Waterloo were first extracted with pentane containing 1,2-dibromoethane as an internal standard. The pentane extract was then analyzed using an HP 5890 gas chromatograph equipped with a 6890 autosampler, a 6890 integrator, a GC autosampler controller, a DB-624 column (60 m length, 0.53 mm I.D., 3.0 µm film thickness), and an electron capture detector (ECD). The carrier gas was



**Figure 4. Locations of the primary sampling cross section, wells, and core holes at the Ontario site.**

helium at 8 mL/min. Dilution was used to ensure that samples fell within the calibration range of the standards, which were made by injecting methanolic stock solutions into water, then extracting the water with pentane, as for the water samples. The calibration curve used to quantify mass in each sample was made up of 10 points. Method detection limits for PCE, TCE, c-DCE, t-DCE, 1,1-DCE, and VC are 10, 10, 6, 10, 6, and 10 µg/L, respectively. All methods and procedures were performed according to the standard U.S. EPA methods and guidelines (U.S. EPA 1997).

## Results and Discussion

### Concentration Distribution

The PCE distribution on the cross section at the Ontario site (Figure 4), determined using 13 profiles with 322 sampling points, shows large spatial variability, ranging from concentrations below detection to ~ 16% of solubility (Figure 5). PCE was the only contaminant detected at this site above 0.5 mg/L and therefore, in the context of this paper, only PCE is relevant. PCE solubility in water is 240 mg/L according to measurements at 23°C by Broholm and Feenstra (1995), which is the value used here. Somewhat higher and lower values have been reported in the literature, such as the low value of 150 mg/L at 25°C (Horvath 1982). Figure 5a shows four distinct, local, high concentration zones at different elevations on the cross section, each surrounded by lower concentration water. Each of these four zones has a closed contour surrounding a local maximum concentration. These zones are henceforth referred to as local maxima. Each of the four local maxima shows relatively high PCE concentrations (Figure 5b), in the range of 1% to 15% of PCE solubility. The concentration zones on

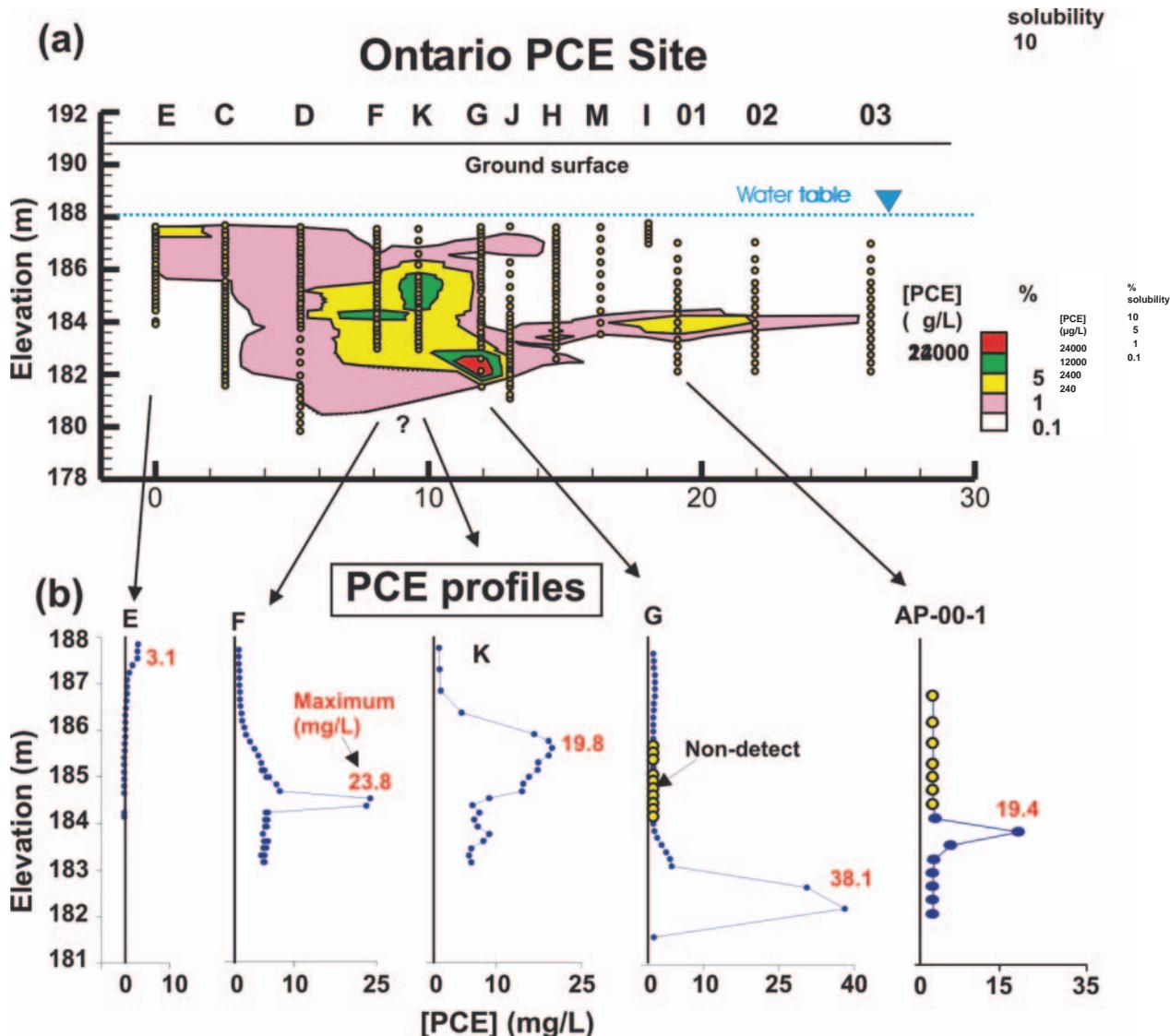


Figure 5. Results of ground water sampling along the cross section at the Ontario site. (a) PCE distribution expressed as percent PCE solubility (240 mg/L) projected onto the cross section (see Figure 3). (b) Major profiles of PCE concentration (mg/L) versus depth. Maximum concentrations of each profile are noted (mg/L).

the cross section (Figure 5a) were generated using the triangulation routine in TEC PLOTv.7.0. Other routines were used to draw contours; however, only minor differences were found with no change in the number or general shape of the local maxima. The PCE mass-discharge values reported later in this paper do not depend on concentration contouring.

The PCE concentration distribution shown in Figure 5a exhibits a large degree of variability; however, the aquifer is exceptionally uniform in texture and hence in hydraulic conductivity. Examination of cores shows some erosional interfaces between textural zones and crude upward-fining in sedimentary units, but no silty or clayey layers were found. The permeameter results from tests on core samples from the contaminated part of the aquifer show a narrow range, with nearly all values within half an order of magnitude, which is consistent with the lack of distinct visual variability of texture seen in the cores. Cores showed no distinct geological layering, and therefore the general position of the DNAPL layers in the aquifer has no distinct geologic control visible at this scale.

The cross section at the New Hampshire site, situated within 3 m downgradient of the DNAPL source zone (Figure 6), shows the PCE distribution based on 257 sampling points from 12 vertical profile locations (Figure 7a). TCE was found in some sampling points, but at concentrations below 100 µg/L. Therefore, TCE is negligible relative to PCE. There are 15 local PCE maxima with peak concentrations ranging from 1% to 62% of PCE solubility. In contrast to the Ontario and Florida sites, the local maxima are more irregular in shape and less elongated in the horizontal direction (Figure 7a). Some of the concentration profiles within the interior of the cross section display two prominent concentration peaks at different depth zones while others show only one (Figure 7b).

The cross section represented in Figure 7a is downgradient of an area where historical information indicates DNAPL leaked from an aboveground PCE storage tank into a floor drain and directly into underlying soil. The occurrence of DNAPL in the aquifer in this area was confirmed by coring in the location of the floor drain. However, there must be multiple DNAPL layers because there

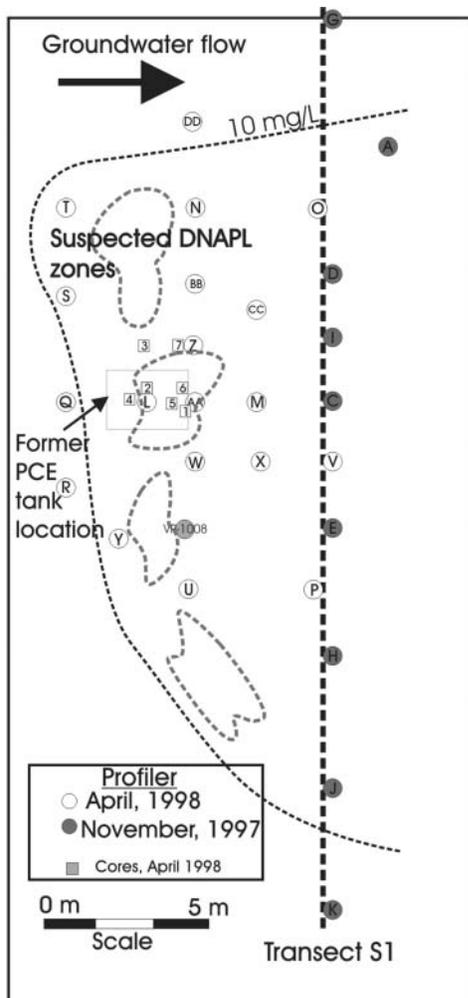


Figure 6. The primary sampling cross section at the New Hampshire site and locations of profile and core holes.

are several local maxima spread out along the cross section. The cross section shown in Figure 7a covers one particular cluster of DNAPL zones likely associated with the area of the former PCE storage tank. A much longer cross section done farther downgradient of this source area indicates that another DNAPL zone cluster must also be present beyond the extent of the first cross section. The DNAPL zone cluster causing the plume monitored on the first cross section (Figure 7a) is, in effect, a distinct DNAPL source area, and therefore the nature of the plume represented by this cross section is comparable to the plume at the Ontario and Florida sites, each of which have a distinct source area associated with DNAPL use or release locations.

Examination of cores collected from the vicinity of the former floor drain location (Figure 6) showed no visual, textural, or stratigraphic reason for the depth of the local maxima. Because ground water flow is horizontal, the elevation of the local maxima indicates the elevation of the upgradient DNAPL zones from which the local maxima are derived. Like the Ontario site, the present-day DNAPL is suspended above the bottom of the aquifer, and therefore we infer that their positions were governed by the volumes and rates of DNAPL release and subtle textural variations rather than any distinct silty or clayey layers. Over the many years since the DNAPL releases occurred, dissolu-

tion has removed considerable DNAPL mass, and in earlier times such mass may have existed shallower and deeper than the existing DNAPL zones.

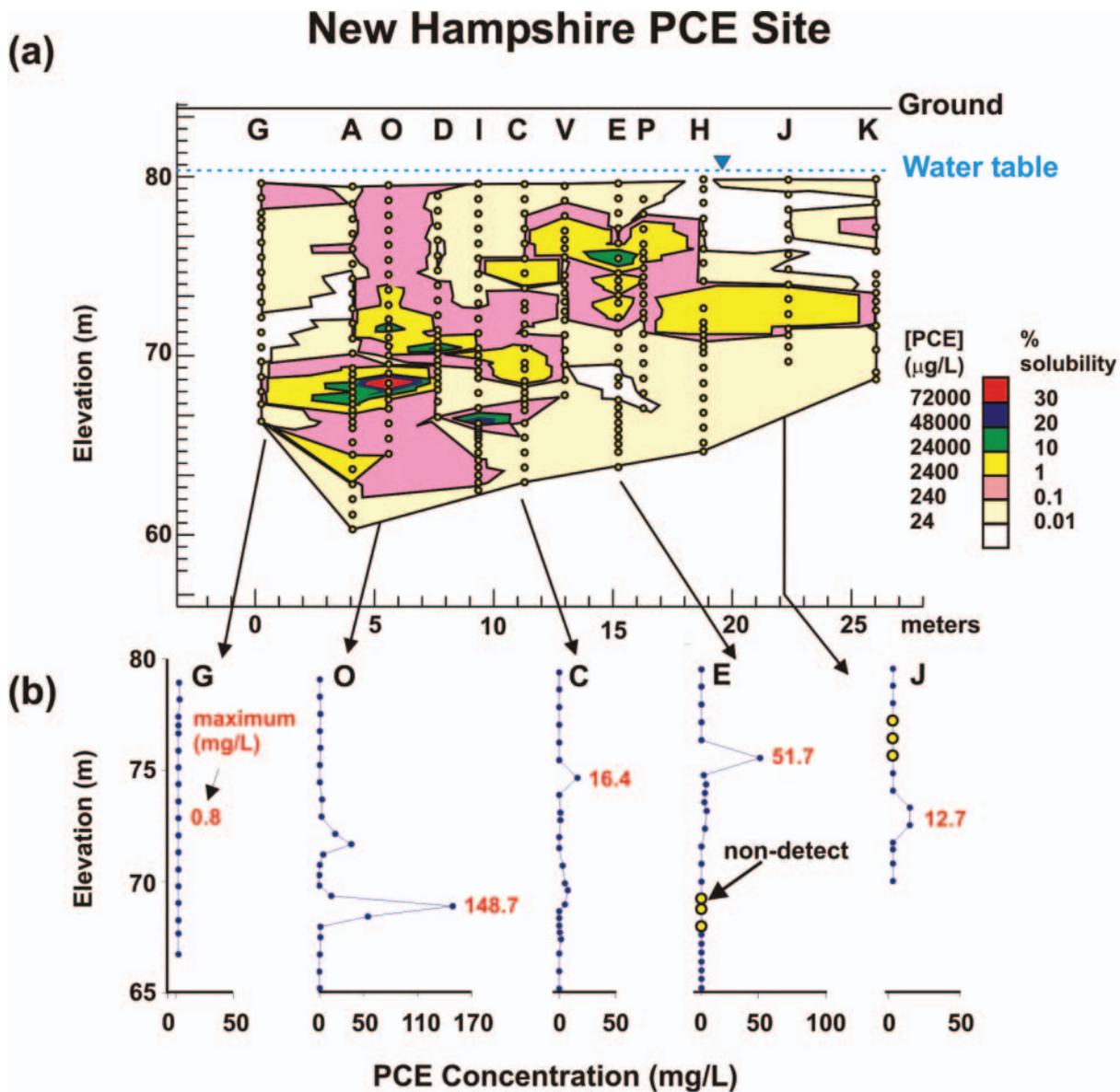
The concentration distribution along the cross section at the Florida site, which has 15 profiles with a total of 146 sampling points, located ~ 25 m downgradient of the DNAPL source area (Figure 8), shows three distinct local maxima (Figure 9a). The local maxima have peak concentrations between 4% and 15 % of TCE solubility (1200 mg/L). Records provided by the site owner show that TCE DNAPL is the cause of the VOC contamination at this site, but cis 1,2-DCE occurs at many sampling points due to transformation of TCE. Wiedemeier et al. (1999) indicate that production of cis 1,2-DCE from TCE by microbial reductive dechlorination has been observed in many aquifers. Absence of vinyl chloride along the cross section suggests that there is likely minimal degradation of cis 1,2-DCE in this area. Where TCE exceeded 100 mg/L, cis 1,2-DCE was generally less than 5 mg/L. At several sampling points, cis 1,2-DCE exceeded TCE but this occurred only where TCE was below 5 mg/L. Therefore, cis 1,2-DCE represents only a small percentage of the total VOC mass. However, to accurately reflect the fact that the cis 1,2-DCE mass is derived from the TCE source zone, the concentration distribution represented in Figure 9 is the total equivalent TCE, expressed as

$$[\text{TCE total}] = [\text{TCE}] + 1.35 [\text{DCE}]$$

where the brackets indicate concentration in mg/L, and the factor 1.35 represents the loss of the one chlorine atom from TCE during transformation to DCE.

A thin (10 to 20 cm) horizontal clay layer extends through the middle of the plume. For the three local maxima found at this site, the peak value is immediately above this clay layer in one and immediately below it in the other two. Cores taken in and near the source zone by Guilbeault (1999) indicate that the clay extends from the cross section into the source zone as a continuous, yet thin, distinct layer. The presence of abundant TCE considerably below this clay layer indicates that some DNAPL migrated through it, likely through fractures or other preferential pathways. There is a strong downward hydraulic gradient across the clay layer and some of the conventional monitoring wells installed during a previous investigation are screened across it, thereby allowing cross connection of TCE laden water from above the layer to below it. The lack of clay layers at the bottom of the contamination in the source zone indicates that the DNAPL is suspended in the aquifer without an apparent geologic control creating the bottom. Inspection of two continuous cores through the plume in the cross section indicates that the contaminated aquifer segments above and below the clay layer are nearly homogeneous. Unlike what is observed at the Ontario and New Hampshire sites, the locations of some of the local maxima at the Florida site do coincide with observable changes in aquifer texture, but not always.

In summary, detailed sampling along the cross sections at the three study sites showed three common features of importance. First, the local maxima (i.e., high concentration zones) within the plumes are suspended above the bottoms of the aquifers. The occurrence of the local maxima



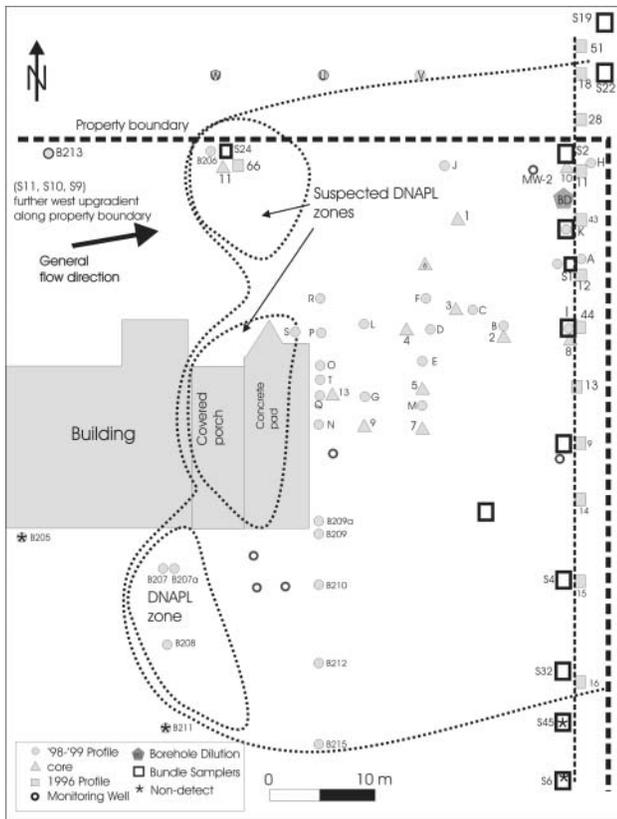
**Figure 7.** Results of ground water sampling along the cross section at the New Hampshire site. (a) PCE distribution, expressed as percent of DNAPL solubility (240 mg/L), projected onto the cross section. (b) Major profiles of PCE concentration (mg/L) versus depth.

above the aquifer bottoms indicates that the remnant DNAPL zones in the source area are also suspended in the aquifers at each site. Extremely subtle geologic heterogeneity likely causes the suspension. Second, the local maxima typically have abrupt transitions above and/or below in which the concentrations change by 2 or more orders of magnitude over very short vertical distances. Third, each of the cross sections shows multiple local maxima and the peak PCE or TCE concentrations within these maxima are in the range of 1% to 62% of DNAPL solubility. The observation that the peak concentrations in the local maxima are below DNAPL solubility is likely due to a combination of three factors. First, based on analytical modeling by Anderson et al. (1992b), the effect of vertical transverse dispersion can cause considerable mixing (dilution), particularly for contaminant zones emanating from their horizontal DNAPL layers. Second, even though the scale of sampling is small (i.e., the sample volume and spacing), the sampling points may not be positioned exactly on the highest concentration points in the plume. Third,

mixing occurs when the samples are drawn from the aquifers, which would dilute the highest concentration water.

### Sample Spacing

The local maxima on the cross sections at the three sites were found because the sample spacing was extremely small, particularly in the vertical direction. If much larger intervals had been used, many of the local maxima would not have been seen and peak concentrations would have been underestimated. Figure 10 shows a concentration profile from the Ontario cross section used to illustrate the effect of vertical sampling scale. This profile (labeled F on Figure 5), which was sampled at 15 cm vertical spacing, shows one distinct local maximum with a peak PCE concentration of 24 mg/L. Only two sample points, 15 cm apart, are situated at and near this peak and the next sampling points, 15 cm above and below, are much lower (< 7 mg/L). Also, profile AP-01-1 (Figure 5) has only one sample point



**Figure 8. Location of the primary monitoring cross section at the Florida site, comprising locations sampled using the Waterloo profiler in 1996 and 1999, cluster wells sampled in 1999 and 2000, cores and monitoring wells and borehole dilution test.**

defining the peak zone with the vertically adjacent points much lower. Figure 10 shows that 45 cm spacing would either miss this peak entirely or encounter the peak by chance, depending on the elevation at which the sampling begins. This figure also demonstrates that the area under the concentration profile, which is a measure of the PCE mass per unit horizontal aquifer segment, changes greatly depending on sample spacing and starting elevation. The aquifer at the Ontario site, as at the other two sites, varies only slightly in hydraulic conductivity (< 1.5 orders of magnitude). Therefore, given that concentrations for these chemicals can vary by up to 5 or 6 orders of magnitude within these plumes, the chlorinated solvent concentration distribution is the most important factor in the total plume discharge. The area under the concentration profile is obtained by interpolating linearly between data points. Therefore, if a peak value is encountered by chance at one of the sampling points in a large-spacing profile, such as the 120 cm spacing illustrated in Figure 10d, then the calculated area is larger than the actual area and the calculated mass-discharge is overestimated. However, an underestimation of mass is more probable, because large sample spacing is more likely to miss concentration peaks.

The features of the Ontario site that indicate close vertical sample spacing is necessary to identify peak concentration zones are also common to the other sites, as illustrated in Figure 11. Figure 11 shows that the maximum observed change in concentration, expressed on the vertical axis as the ratio of the maximum to the minimum values,

occurred between sampling points situated at 60, 60, and 90 cm apart for the Ontario, New Hampshire, and Florida sites, respectively. For an explanation of how this figure is constructed, consider the New Hampshire site where a total of 147 pairs of sample points were located exactly 30 cm apart. For these pairs, the maximum change in concentration was > 3 orders of magnitude. Figure 11 also shows that, at all three sites, a change in concentration > 2 orders of magnitude was observed for samples situated 30 cm apart or more, and > 1.5 orders of magnitude when situated 15 cm apart. This suggests that the maximum concentration zones are extremely small and that even sample intervals of 15 to 30 cm are inadequate to identify the peak values within the local maxima. However, as discussed earlier, a spacing < 15 cm would probably cause profile distortion due to overlapping of the spherical sampling zones for vertically adjacent samples. Therefore, smaller sample spacing may not give a better representation of the in situ reality, given the equipment used.

Although the interval between profiles is larger than the space between vertical sampling locations, the horizontal spacing of profiles in this study was deemed appropriate for each site based on the plume characteristics. The horizontal spacing at the Ontario site was 0.5 to 2 m, and at the New Hampshire and Florida sites it was 2 to 5 m and 4 to 10 m, respectively. The decision to cease drilling more sampling holes at each site was made once it became apparent that additional sampling was not identifying more local maxima or finding much higher peak concentrations within the local maxima. At the Ontario site, we completed a second cross section 20 m downgradient of the section shown in Figure 5 using bundle wells. This section identified the same local maxima within the plume with much lower peak concentrations, as expected. This consistency between transects provided confidence in the upgradient (i.e., near-source zone) transect results. At the New Hampshire and Florida sites, such consistency was also found with downgradient transects. Also, at the Florida site, the main cross section (Figure 9) was resampled in detail a year later, using bundle wells rather than the Waterloo profiler, which produced the same number of local maxima with similar concentrations.

The number and distances between profile holes along a cross section are often limited by time and financial constraints, and therefore the horizontal spacing likely will be greater than the vertical spacing within the profiles. However, we believe that the horizontal spacing can be larger than the vertical spacing without causing excessive uncertainties in the delineated concentration distribution. This belief is supported by several lines of evidence. First, DNAPL release experiments in the Borden Aquifer, which is nearly homogeneous and has a beach sand origin, showed thin suspended DNAPL accumulations with horizontal dimensions orders of magnitude larger than the DNAPL layer thicknesses (Kueper et al. 1993; Brewster et al. 1995). The large aspect ratio attributed to the DNAPL layers is expected to produce local maxima downgradient in the plume that also are much larger in the horizontal than in the vertical dimension, as proposed by Anderson et al. (1992b). Second, the major textural interfaces of sandy beach and fluvial deposits are primarily horizontal or near

# Florida TCE Site

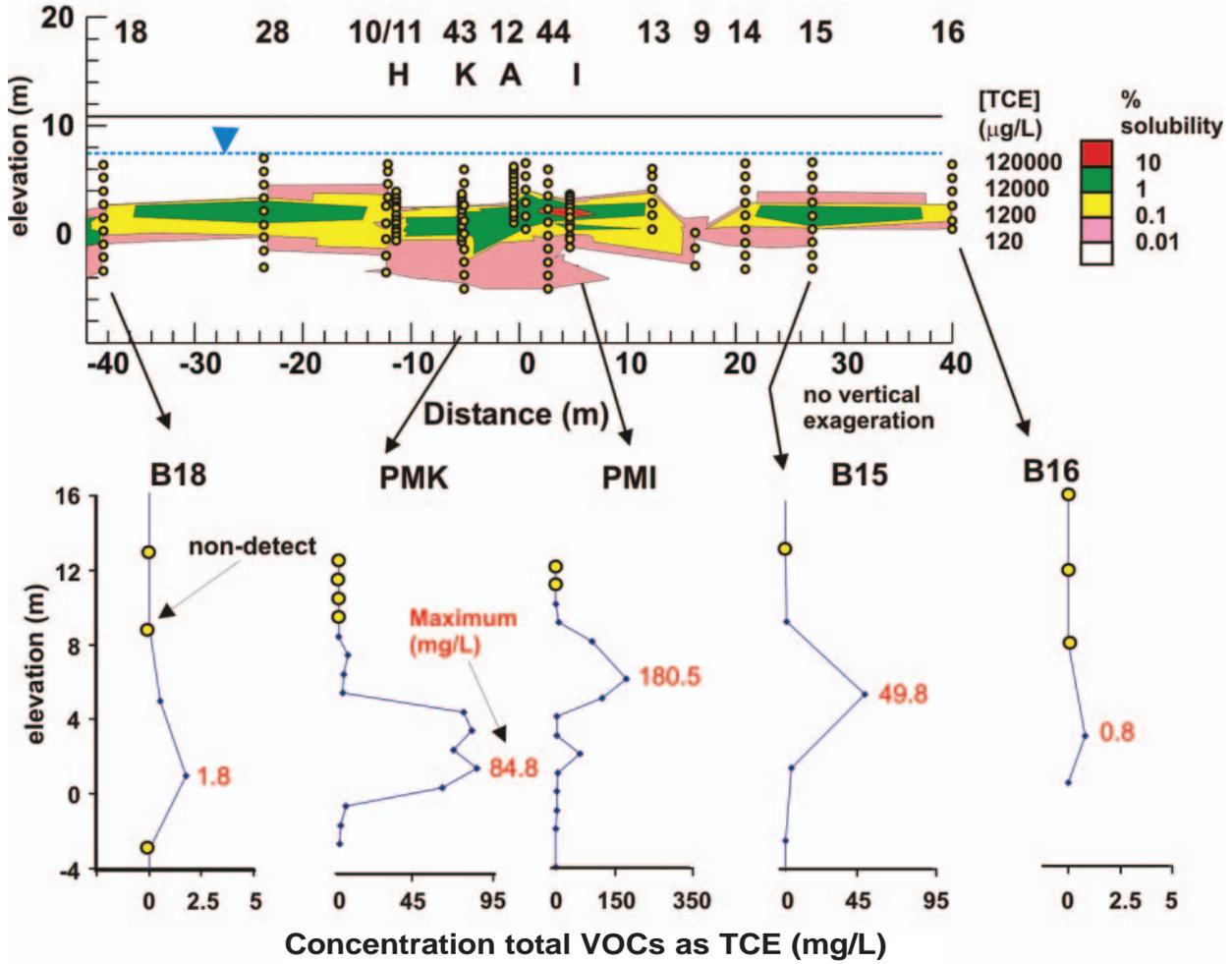


Figure 9. Results of ground water sampling along the cross section at the Florida site. (a) Equivalent TCE distribution (1.35 c-DCE+TCE), expressed as percent of solubility (1200 mg/L), projected onto the cross section. (b) Major profiles of equivalent TCE concentration (mg/L) versus depth.

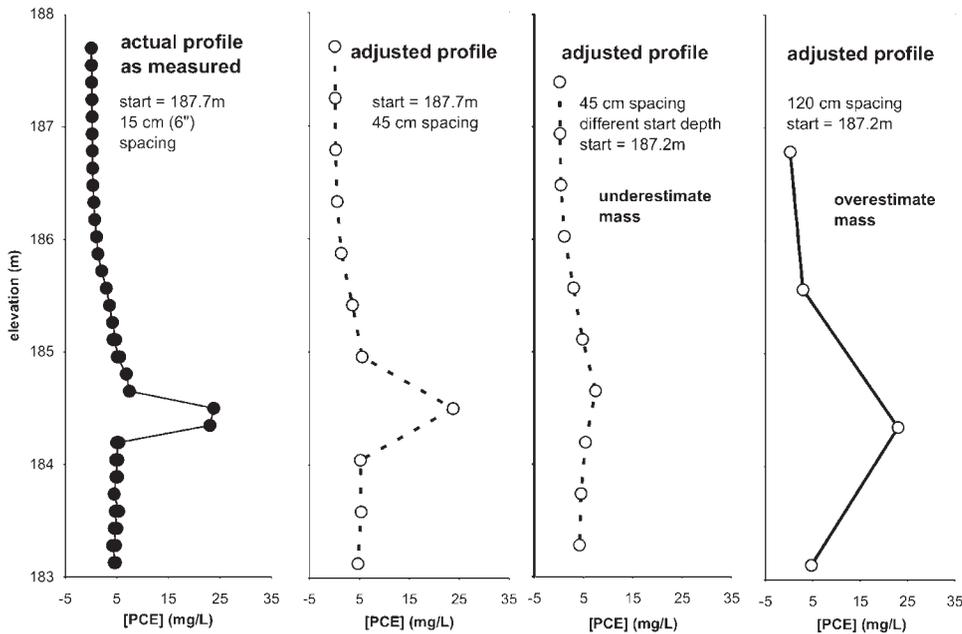
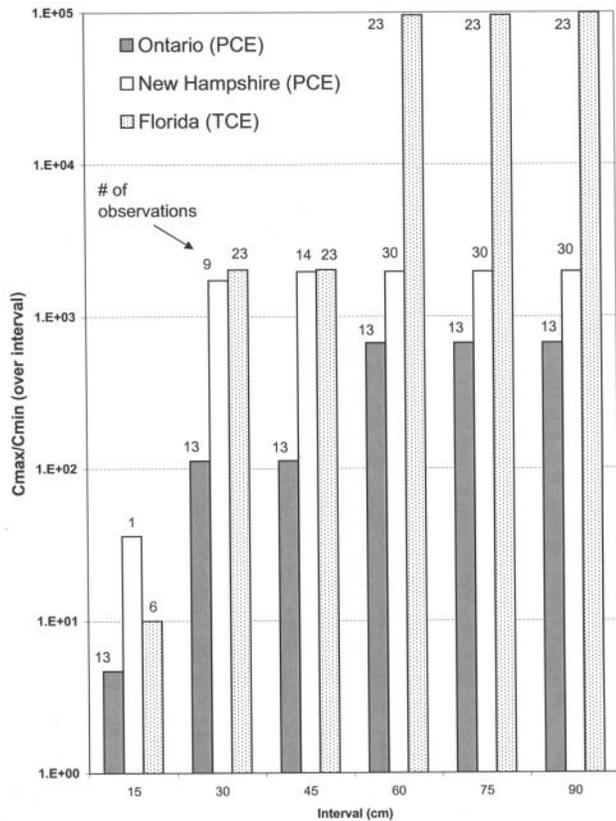


Figure 10. Profile F from the Ontario site showing (a) actual data collected at 15 cm vertical spacing, (b) the probability of detecting the peak if 45 cm spacing is used starting at the same elevation as field data, (c) underestimation or (d) overestimation of mass depending on spacing used.



**Figure 11. Maximum observed change in concentration (Cmax/Cmin) as a function of vertical sample interval showing large variations over small vertical distances.**

horizontal, which promotes formation of horizontal or near horizontal DNAPL layers. Third, results from the second cross sections at each site showed that no local maxima were missed and that the peak concentrations varied minimally, with changes of less than a factor of two at the Ontario and Florida sites.

Although it is evident that the positions of the local maxima on the cross sections at the three sites are determined by the positions of DNAPL zones situated upgradient of the cross sections, an alternative explanation based on heterogeneity of the hydraulic conductivity was considered. In this alternative explanation, the positions of high concentration zones are a manifestation of zones of much lower hydraulic conductivity where sluggish ground water flow has allowed contamination to linger while the contaminants are rapidly flushed out of the higher conductivity zones. Although some heterogeneity exists in the sand aquifers at the three sites, it does not include layers of low enough hydraulic conductivity to allow long-term lingering of contamination.

### Ground Water and Plume Fluxes

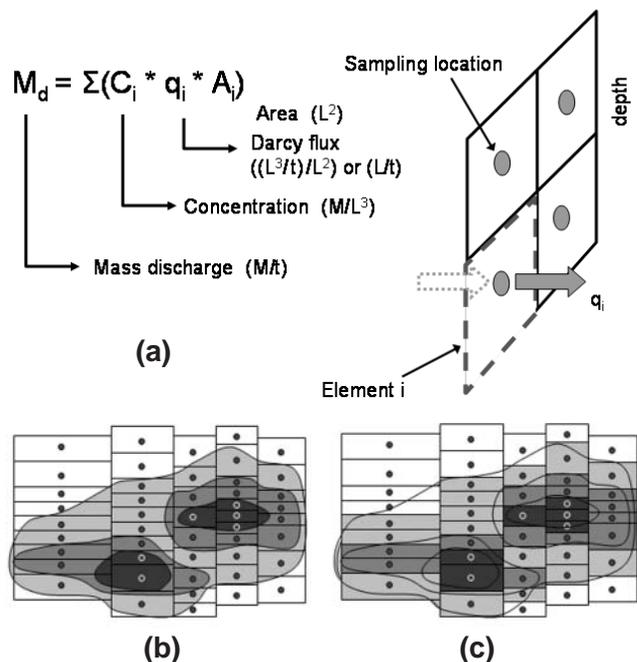
The total contaminant plume mass-flux, or mass-discharge ( $M_d$ ), was calculated for the cross section at each site using the contaminant distributions combined with ground water representative of Darcy's flux for the aquifer. The total plume flux is the sum of the mass-flux for each rectangular subarea, or element, into which each cross sectional area was divided (Figure 12a):

$$M_d = \sum (C_i A_i q_i)$$

where  $C_i$  is the PCE or TCE concentration within a rectangular element of area  $A_i$  with Darcy flux  $q_i$ . Each cross section was discretized into rectangular elements of varying sizes based on the spacing of ground water sample points as illustrated in Figures 12b and 12c. The dimensions of each element are defined by half distances to adjacent sampling points in the vertical and horizontal directions. For those elements at the periphery of the contaminated area, which have only one adjacent sampling point in either direction, the outer distance from the sampling point is set equal to the inner distance.

The Ontario, New Hampshire, and Florida cross sections were divided into 322, 257, and 146 rectangular elements, respectively, based on the number of sampling points in each cross section. The mean area for each element was 0.5, 1.8, and 6.1 m<sup>2</sup>, respectively (Table 2). The resulting total plume fluxes for the Ontario and Florida sites represent the entire plume fluxes for these two industrial properties. However, the total plume flux for the New Hampshire site applies only to one of the major source areas at this site. The segment of plume width attributed to this source area is about half of the total plume width.

The aquifers at each of the sites are only moderately heterogeneous with respect to visual grain size features and hydraulic conductivity, and the variability in heterogeneity mainly occurs at the centimeter scale, which is relatively small. Therefore, except for the Florida site, no spatial variability was assigned to the hydraulic conductivity in the ground water discharge calculations. This assumption of



**Figure 12. (a) Schematic of procedure for calculating mass-discharge; transect is divided into rectangular elements. Schematic of discretized cross section showing (b) hypothetical plume cross section with contoured concentrations and (c) actual node concentration assignment to each element.**

homogenous hydraulic conductivity in sand aquifers is commonly used in calculations of plume mass-discharge (Semprini et al. 1995; Wilson et al. 2000). A single hydraulic gradient was also assigned to each cross section, and therefore the Darcy flux was considered to be the same for all elements within the respective Ontario and New Hampshire cross sections. For the Florida site, the aquifer was divided into two flow zones: the zone above the thin clay layer in the middle of the plume and the zone beneath this clay layer. The hydraulic conductivity of the clay layer is orders of magnitude less than that of the aquifer and the hydraulic gradient in this layer is strongly vertical. Therefore, the clay layer was not included in the flux calculations and the thickness of the clay layer was subtracted in the elements where it was present.

The hydraulic conductivity of the aquifer at each of the sites was determined by two methods: falling head perme-

ameter and grain size analyses. The falling-head permeameter tests were conducted on samples taken from cores obtained using the piston corer (Zapico et al. 1987), which were repacked in the permeameter. This method was established by Sudicky (1986) for study of cohesionless media and fine-grained aquifer materials. Core samples were also used for grain size analyses using sieves in the manner described by Ingram (1971). For the Ontario site, the single value used for calculations of the Darcy flux through the cross section was obtained by performing permeameter tests on eight core samples selected from three core holes distributed longitudinally along the plume. Each sample was chosen to be representative of a relatively uniform textural unit in the aquifer zone occupied by the plume. The resulting flux values fell within a narrow range, from  $0.13 \times 10^{-2}$  to  $1.8 \times 10^{-2}$  cm/s. Application of the Hazen formula (Freeze and Cherry 1979) to grain size analyses of separate

**Table 2**  
**Calculation Results and Site Parameters**

	<b>Angus, Ontario</b>	<b>Milford, New Hampshire</b>	<b>Cocoa, Florida</b>
Average ground water temperature	10°C	10°C	20°C
Field episode dates	July–August, 1997 May 2000	October 22-30, 1997 April 15-25, 1998	1996 February 11-20, 1988 June 11-17, 1998 February, 1999 March, 1999
Number of profile locations	14	30	23
Number of water samples (Waterloo Profiler only)	323	869	534
Number of local maxima identified <sup>a</sup>	6 – Transect A1	15 – Transect S1	6 – Transect P3
Peak concentration (mg/L [% saturation])	38 [16%] – Transect A1	148 [61%] – Transect S1	180 [15%] – Transect P3
Average K (cm/s) <sup>b</sup>	2.80e-2	7.0e-3	(Upper zone) 6.2e-3 (Lower zone) 1.6e-3
Average hydraulic gradient <sup>c</sup>	0.011	0.061	(Upper zone) 0.005 (Lower zone) 0.003
Darcy flux (cm/d)	23	3.7	(Upper zone) 2.8 (Lower zone) 0.4
Average linear ground water velocity (cm/d)	65	11	(Upper zone) 8 (Lower zone) 1.2
Current plume discharge (kg/yr [U.S. gallons/yr])	Transect A1 – 20.5 [3.3]	Transect S1 – 15.0 [2.4]	Entire Transect P3 31 [5.6] PFC swath 45 [8.1]
Total discharge U.S. gallons <sup>d</sup>	(1970 to 1999) 96 – A1	(1950 to 1999) 118 – S1	(1966 to 2002) Entire Transect P3 290 PFC swath 201
Area of elements (m <sup>2</sup> ) (total, min, max, average)	Transect A1 162.2, 0.13, 2.1, 0.5	Transect S1 481, 0.17, 5.47, 1.79	Entire Transect P3 1171, 0.2, 19.9, 6.1

<sup>a</sup>Local maxima represent the zones of local high concentrations.

<sup>b</sup>Hydraulic conductivity calculated as average of falling head permeameter values and grain size analysis using the Hazen formula (except at the Florida site where permeameter results only were used for the lower aquifer zone)

<sup>c</sup>Measured from water table wells at the Ontario site, monitoring wells at the New Hampshire site, and bundle samplers at the Florida site

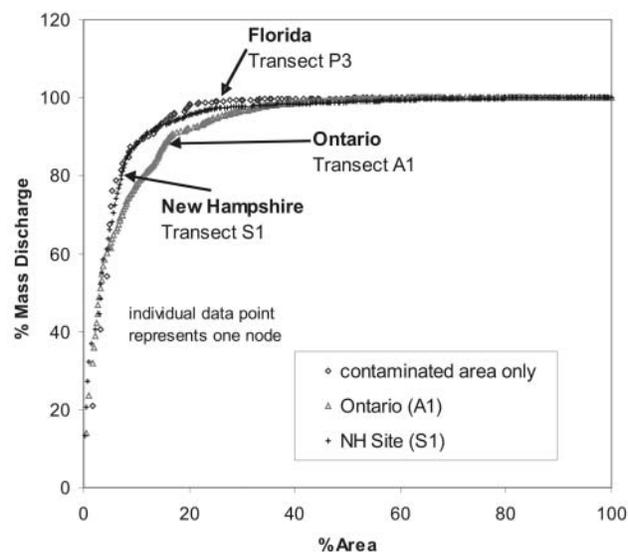
<sup>d</sup>Total discharge values were calculated assuming present-day discharge values since initial use of solvent at each site.

samples from the same eight depth intervals gave larger values, which varied only by a factor of two and had a narrower range of  $1.9 \times 10^{-2}$  to  $4.0 \times 10^{-2}$  cm/s. Combining the results of both sets of hydraulic conductivity values provided an arithmetic mean of  $2.4 \times 10^{-2}$  cm/s and a geometric mean of  $2.8 \times 10^{-2}$  cm/s. The geometric mean was used for the Darcy flux through the cross section. For the New Hampshire site, 12 samples from three core holes situated near the cross section were used to obtain hydraulic conductivity data by both methods. A geometric mean value of  $0.7 \times 10^{-2}$  cm/s, a minimum of  $0.14 \times 10^{-2}$  cm/s, and maximum of  $4.1 \times 10^{-2}$  cm/s were obtained.

For the Florida site, the upper and lower aquifer zones were considered as separate units for measurement of hydraulic conductivity and hydraulic gradient. For the upper zone, permeameter measurements were made on nine samples selected from two cores, and grain size analyses were done on three samples from the same two cores and a third core. All of these measurements provided a geometric mean of  $6.2 \times 10^{-3}$  cm/s, with a minimum of  $3.3 \times 10^{-3}$  cm/s and a maximum of  $8.2 \times 10^{-3}$  cm/s. This very narrow range in K values is consistent with the homogeneity of the upper aquifer zone apparent from visual inspection of core.

The hydraulic gradient through the cross section at each site was determined from water level measurements in monitoring wells and bundle wells conducted during a period of time that included much or all of the ground water sampling period at each site. Measurements in bundle wells or nested piezometers showed no measurable vertical component of the hydraulic gradient in each of the aquifers, which was expected based on the horizontality of the plumes and the lack of textural variability of the sand deposits. The horizontal gradient at the Ontario site was determined from three drive-point piezometers (Figure 4), which were monitored on six occasions distributed over a year between May 1998 and June 1999. During this time, the water table varied over 43 cm and the horizontal hydraulic gradient was somewhat larger when the water table was highest. The hydraulic gradient varied over a factor of two, from 0.008 to 0.017, with a mean of 0.011. A network of conventional monitoring wells was installed by consultants at the New Hampshire site in the mid-1980s and routine water level monitoring has been done for many years. A subset of these measurements was selected to obtain the gradient for use in the PCE mass-discharge calculations. Monthly water levels measured between March 1998 and June 1999 in a pair of wells located along the plume centerline provided a very small gradient range, from 0.0051 to 0.0075, with a mean of 0.0061.

At the Florida site, four conventional monitoring wells screened in the upper aquifer zone were monitored monthly between May 1997 and July 1999. The water table fluctuated over 1.2 m during this time and the gradient varied from 0.004 to 0.007, with a mean value of 0.005. This mean value is nearly identical to the mean gradient in the upper aquifer zone measured in a network of bundle wells on many other occasions. The hydraulic gradient for the lower zone was obtained from four bundle wells situated along the northern property boundary. Two multilevel monitoring events were performed in June and July 1999, providing a



**Figure 13. Relationship between mass-discharge and area for the three sites showing that most of the discharge occurs within a small cross sectional area for each transect.**

0.002 and 0.004 gradient, respectively, and a mean of 0.003. These same four bundles also provided a gradient in the shallow upper portion of the aquifer equal to 0.005, which compared well to the mean gradient from the conventional wells taken over a longer time period (monthly for a 26-month period). Therefore, although the monitoring period for the deeper zone was shorter, it is believed to be representative of the mean gradient for this zone.

Much of the total mass-discharge occurs in a small portion of each cross section. Figure 13 shows the cumulative mass-discharge versus percent cross sectional area for each of the three study sites. Each graph was constructed by ranking each elemental area on the cross section from the largest to the smallest elemental mass-discharge. The mass-discharge in each of these ranked elemental areas was then summed, beginning with the largest. Each data point position on the graph represents the mass-discharge for one additional element. Inspection of Figure 13 indicates that the first element on each graph constitutes 14% to 20% of the entire mass-discharge but represents only 0.2% to 1.8% of the cross sectional area. For each of the three sites, 60% of the plume mass-discharge occurs in 5% of the cross sectional area and 80% occurs in 10% or less of the area. The large percentages associated with such small areas derives from the characteristic features of the spatial concentration distributions, most importantly the occurrence of extremely small high concentration zones (local maxima). This illustrates quantitatively that, if cross sections immediately downgradient of the DNAPL source zones are not monitored in sufficient detail to find the local maxima and peak concentration, most of the actual plume mass-discharge will be omitted from the calculated discharge estimate.

Mass-discharge at the Florida site was determined four years after the cross section data were acquired in the study reported here, thereby providing an independent check on the plume mass-discharge. At the Florida site, the mass-discharge was determined by measuring the VOC concentrations from a line of pumping wells situated just west of the

cross section shown in Figure 9. The pumping wells captured the entire plume, and the resulting contaminant mass extraction rate was twice that obtained by the detailed cross sectional monitoring approach. The mass-discharge from the pumping wells was an average determined over the first six months of system operation. Given the inherent and measured variability in the values for hydraulic conductivity and gradient used in the cross sectional approach, agreement within a factor of two is considered excellent.

The calculation procedure for the graphs in Figure 13 used all of the elements comprising each cross section. Each element has a field sampling point, but some of the sampling points had no detectable contaminant concentrations. Therefore, the percentage of total cumulative mass-flux for a specified percent of the cross sectional area is slightly lower when only those elements with detectable concentrations are included.

The plume mass-discharges for the three sites are in a narrow range even though the industrial operations that caused the contamination and the geologic origins of the aquifers are different (Tables 1 and 2). These plume discharge values represent conditions in the aquifer a few decades after the initial formation of the DNAPL source zones. Anderson et al. (1992b) indicate that, initially, the source zones in sandy aquifers can be conceptualized as horizontal DNAPL accumulation layers with connecting vertical fingers or pipes which were the residual pathways for vertical DNAPL flow. They presented calculations supporting the expectation that the vertical residual pathways disappear much more quickly due to dissolution in the flowing ground water than the horizontal DNAPL layers. Therefore, it is likely that decades of DNAPL dissolution at the three field sites have resulted in disappearance of much or all of the vertical residual trails. Consequently, in the early years following formation of the DNAPL source zones, the plume mass-discharges were likely higher than those observed now. Sale and McWhorter (2001) used an analytical mathematical technique to examine the mass-discharge and persistence of DNAPL in hypothetical source zones in sand aquifers with horizontal ground water flow. The source zones were comprised of multiple thin single-component DNAPL layers connected by narrow, diameter vertical fingers. Like Anderson et al. (1992b), they found that the fingers disappeared relatively quickly and that the DNAPL layers persist for a much longer time. However, they also found that each DNAPL layer evolves toward disappearance primarily by shrinkage from the downgradient end, and that this causes high concentrations to persist in the plume on cross sections immediately downgradient of the source zone until essentially all of the DNAPL layers have disappeared. Therefore, it is not surprising that the very high PCE or TCE concentrations are present at each of the three study sites even though mass removal by ground water flow has been in progress for decades. There is no reliable basis for estimating the total DNAPL mass that initially formed the source zones, and therefore it is not possible to use the plume mass-discharge measurements to estimate the mass remaining in the source zones, and hence the longevity of the zones.

## Conclusions and Implications

The concentration distributions of PCE or TCE delineated on the three cross sections situated immediately down-gradient of the DNAPL source zones showed multiple, distinct local maxima in which the peak concentrations were orders of magnitude above the minimum concentrations in the surrounding ground water. The local maxima occur at these sites even though the aquifers containing the plumes are nearly homogeneous with respect to hydraulic conductivity, which generally varies within less than half an order of magnitude. The extreme spatial variability of concentration distribution is attributed to spatial variability of the DNAPL distribution in the suspended source zones. For each site, 60% of the plume mass-discharge occurs in < 5% of the total monitored cross sectional area. In some of the sampling profiles, the concentrations varied by 2 to 4 orders of magnitude over a vertical space between sampling points of 15 to 30 cm. Therefore, to locate and quantify these extremely high mass-flux zones it was generally necessary to use vertical sampling of 15 to 30 cm and space the holes a few meters or less apart in the transverse horizontal direction. The use of closely spaced, depth-discrete ground water sampling methods identified the presence of the high flux contaminant zones, which likely would not have been detected by conventional monitoring wells or sparser spacing using direct-push or other multilevel techniques. Direct-push drilling equipment and rapid on-site VOC analysis helped to make this detailed sampling feasible.

The values of total plume flux, obtained for the three sites by combining the concentration distributions with hydraulic information, are in a narrow range, spanning from 15 to 45 kg/yr. The source zones causing the plumes have been losing mass over decades due to natural ground water flow and dissolution. Because the residual trails likely disappeared in the early years, and because the horizontal DNAPL layers are expected to have longevity, it is likely that the plume mass-discharges were higher in the early years than after decades of source zone aging, but that the plume will also persist. An implication of this study is that, in cases where the best possible accuracy of plume mass-discharge is needed, the measurement of the Darcy ground water flux should focus on the local maxima, which should be located prior to conducting hydraulic conductivity or ground water flow measurements. In this context, techniques for more direct measurement of ground water flux, such as borehole dilution (Freeze and Cherry 1979) or the Florida flux meter (Hatfield et al. 2001) offer advantages for both water and contaminant flux. Situations can exist, however, where only the plume mass-discharge is needed, without knowledge of the spatial concentration distribution within the plume. In these situations, the method described by Ptak et al. (1998), which involves integrating concentration measurements at pumping wells positioned in the plume, can be used to obtain mass-discharge.

Identification of the small, high concentration and high mass-discharge zones is important for consideration of in situ remedial options such as permeable reactive barriers and for assessing natural attenuation. Permeable reactive barriers (PRBs) comprised of zero-valent iron are used at

many solvent-contaminated sites to prevent solvent mass emanating from the source zones from continuing to feed the plumes. These PRBs require a particular residence time of the contaminants within the PRB to reduce the concentrations to a specified level. The presence of small, high concentration zones within a plume presents a problem for PRB design. To treat the high concentration zones can greatly increase the cost of the PRB and to not do so will result in breakthrough of such zones. In the assessment of natural attenuation it is necessary to show the degree to which the mass-discharge and peak concentrations decline within the plume in the downgradient direction. If the small high mass-discharge zones are not located in the downgradient monitoring, the results give the appearance of attenuation when the reality is otherwise. Conversely, if the higher concentration zone is identified farther downgradient, one might falsely interpret that there exists an additional DNAPL zone or source.

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