

## **Using deuterated trichloroethene (TCE) in a tracer test to estimate the transport characteristics of a TCE plume**

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**Abstract** A trichloroethene (TCE) plume has been identified in an unconfined sand aquifer in Perth, Western Australia. This is the first known major occurrence of groundwater contamination by chlorinated aliphatic compounds in Perth. A small-scale (ca. 13 m), natural-gradient tracer test, utilizing deuterated TCE (TCEd1) and potassium bromide, was undertaken within the TCE plume to determine hydrodynamic and sorptive properties of TCE in the aquifer. No sorption of TCEd1 was observed, which is in contrast to a retardation coefficient estimate of 1.8, calculated from equations based on the organic carbon fraction of the aquifer sand. A low dispersivity of the aquifer material was calculated, indicating that dispersion was negligible with respect to the advective flow. Variable advective flow at distinct levels in the aquifer profile is shown to produce tailing of the depth-averaged breakthrough curves. The C-D bond of the deuterated TCE was stable, indicating the usefulness of deuterated TCE as a tracer within the contaminated zone.

## **INTRODUCTION AND BACKGROUND**

Groundwater supplies in the USA and Europe have become contaminated with volatile chlorinated hydrocarbons as a result of poorly designed hazardous waste disposal facilities, accidental spills and leakage from underground storage tanks. However, few water supply wells have been affected by these neutral hydrophobic compounds in Australia (Atwood & Barber, 1989). In 1992 the first major occurrence of groundwater contamination by TCE in Perth was detected in the shallow sand aquifer underlying the Perth metropolitan area (Benker *et al.*, 1994).

The TCE plume was found to extend ca. 900 m in groundwater down gradient from an industrial area, to be ca. 300 m wide and about 7 m thick. The peak concentration of 2000  $\mu\text{g l}^{-1}$  exceeds considerably the current Australian drinking water guideline for TCE of 30  $\mu\text{g l}^{-1}$  (NH&MRC, 1987). The detection, distribution and management of the plume was discussed by Benker *et al.* (1994), where preliminary mobility estimates were

presented. The TCE plume approximates the distribution of an ammonium plume, suggesting co-disposal of effluent waste water into waste lagoons within the industrial area.

There are many mechanisms that influence the movement of TCE (and other solutes) in groundwater (e.g. advection, sorption/desorption, chemical and biological transformation). Sorption, in particular, can play a significant role in the attenuation of organic compounds in groundwater, and in determining the effectiveness of remediation strategies.

The organic carbon partition coefficient,  $K_{oc}$  ( $\text{cm}^3 \text{g}^{-1}$ ), of the sorbate, which can be found in the literature, and the organic carbon fraction of the sorbent,  $f_{oc}$ , are commonly used for estimating sorption of neutral organic compounds such as TCE. The correlation  $K_p = K_{oc} \times f_{oc}$ , where  $K_p$  ( $\text{cm}^3 \text{g}^{-1}$ ) is the partition coefficient, is often used to estimate sorption (e.g. Stephanatos, 1991). The above equation, however, is not universal. For sandy aquifers, sorption coefficients in excess of what would be expected based on this formula have often been determined (e.g. Curtis *et al.*, 1986). This may be because the carbon-based correlation does not account for sorption due to mineral surfaces or for variations in composition of natural organic matter (e.g. Rutherford *et al.*, 1992).

Stephanatos (1991) reported misapplication of the  $K_{oc}f_{oc}$  concept in setting cleanup level standards and found that many site specific factors influenced the mobility, fate, and transport of the chemicals. He recommended the determination of site-specific partitioning of chemicals in the various environmental media.

To assess the partitioning of TCE in the low organic carbon aquifers of the Swan Coastal Plain, a natural gradient tracer test, utilizing TCEd1 and KBr, was undertaken within the TCE plume. This paper presents results from the tracer test, including estimates of hydrodynamic properties of the aquifer, sorption coefficients and aspects of the contaminant plume distribution and chemistry at the tracer test site.

## SITE HYDROGEOLOGY

The Perth metropolitan area is predominantly underlain by unconsolidated sands, forming an extensive unconfined aquifer with a maximum thickness of about 55 m. Siltstone and shale form an impermeable base.

Local to the plume site, the soil profile in the saturated zone consists of yellow and grey sands down to about 22 m below ground surface (bgs), interbedded with a few thin silty layers. Clay was observed 22-23 m bgs, while beneath the clay, sand was again predominant. A clay layer at a depth of 27 m bgs forms the base of the aquifer. Soil samples at the site are characterized as medium grained, well sorted sands with median grain sizes 0.28-0.42 mm (uniformity coefficients in the range 1.8-3.1). Within the sands, the clay and silt size fractions are very low: 0.1-1.3%.

Groundwater levels at the site are 6.5-10.5 m bgs with annual fluctuations of about 1.0 m. The groundwater flow directions observed from August 1993 to August 1994 were on average  $240^\circ$  (southwesterly), varying by about  $5^\circ$ . The hydraulic gradient was observed to range from 0.0015 to 0.0023 with an average of 0.0018.

Estimates of some aquifer properties are given in Table 1. The K values measured in the laboratory were low for medium grained sand, and may indicate K anisotropy, since hydraulic conductivities were measured using vertical field cores. A preliminary

**Table 1** Estimates of aquifer properties.

Porosity	Bulk density ( $\text{g m}^{-3}$ )	Fraction organic carbon <sup>a</sup>	Water temperature ( $^{\circ}\text{C}$ )	Hydraulic conductivity ( $\text{m day}^{-1}$ ):	
				$K^b$	$K^c$
0.35	1.75	0.14	19	4.3	35
( $\pm 0.05$ )	( $\pm 0.06$ )	( $\pm 0.08$ )	( $\pm 0.5$ )	( $\pm 2.6$ )	( $\pm 18$ )

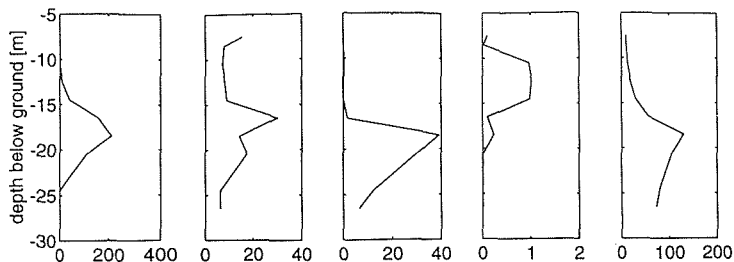
<sup>a</sup> Wackley and Black (e.g. Rayment & Higginson, 1992).

<sup>b</sup> Constant head permeameter (geometric mean).

<sup>c</sup> Estimate after Hazen.

natural-gradient tracer test, utilizing KBr, was carried out over a distance of 1 m to provide a direct measure of the magnitude and direction of the groundwater velocity. This test confirmed the flow direction and resulted in average velocities of 55–80  $\text{m year}^{-1}$  at different levels within the aquifer profile.

A vertical profile of TCE and inorganic species concentrations at the tracer test site is shown in Fig. 1. Unlike the ammonium concentrations, the TCE concentrations showed considerable variability. The dissolved oxygen content was generally below 0.5  $\text{mg l}^{-1}$ . A low redox potential of  $-100$  mV was found at the depth of the peak ammonium concentrations. Eh values of about  $+200$  mV and  $+100$  mV were found above and below this depth, respectively. Small patches of groundwater with high ammonium concentrations and very low redox potential, however, were also observed above the depth that showed continuous, high ammonium concentrations.



**Fig. 1** Vertical profiles of TCE and selected inorganic species concentrations in groundwater.

## EXPERIMENTAL PROCEDURE

The injection system was designed to approximate a cylindrical (1.2 m diameter), uniform distribution of the injected solutes (TCEd1 and KBr). The injection well was screened 15–16 m bgs, i.e. 7.8–8.8 m below the phreatic surface at the time of injection. The injection solution was prepared in four 2.5 l glass bottles. Each bottle was spiked with 30 g of KBr and 42.5  $\mu\text{l}$  of TCEd1. The bromide concentration was chosen following Thierrin *et al.* (1992) to achieve minimal gravity flow of the injected solution. The deuterated compound was chosen because of the stability of the C-D bonds and for ease of analysis. For the tracer test, two 200 l aluminium drums were filled with uncontaminated groundwater, into which the prepared solution was mixed and samples

were taken. The tracer solution (400 l) was injected into piezometer JX on 3 March 1994 over a period of 5 minutes.

Migration of solutes was monitored at seven bundled piezometer nests, consisting of 1/8" flexible nylon tubes, with 20 cm screens of slotted aluminium tubing covered by a polyester mesh. The nylon tubes are fastened as a bundle around a more rigid centre piezometer consisting of a 3/4" thick-walled PVC pipe. The bundled piezometers had nine ports placed at depths 14.3-16.9 m bgs. All piezometers were installed using a truck-mounted drill, with all placements determined to within 0.05 m. The location of the seven bundled piezometers is shown in Fig. 2.

Groundwater samples were obtained by applying suction with a syringe. Stagnant water was purged using 50-ml plastic syringes. Twenty ml glass syringes were used for all samples that were analysed for organic compounds. The organic analyses were carried out by gas chromatography and mass selective detector. A detection limit of ca.  $10 \mu\text{g l}^{-1}$  was obtained. Details of the analytical conditions and the extraction technique are given by Patterson *et al.* (1993).

Bromide was analysed using an Orion bromide electrode (model 94-35A). This electrode showed a linear response to bromide concentrations down to  $0.2 \text{ mg l}^{-1}$  and enabled measurements reproducible to within 2%. Bromide analyses on selected samples were also carried out by HPLC (conductivity detector) with a detection limit of  $0.1 \text{ mg l}^{-1}$ .

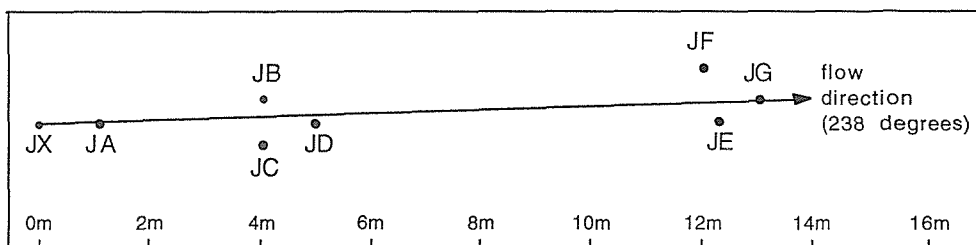


Fig. 2 Location of bundled piezometer nests with respect to the flow direction obtained by the tracer test.

## SOURCE DISTRIBUTION

The peak concentrations measured in the first monitoring bore (JA) were used to normalize all concentration measurements. The two dimensional plot (depth/time) for bromide for JA (Fig. 3) indicates that the solution, injected between  $-2$  and  $-3$  Australian Height Datum (AHD), covered a vertical interval of about 2.0 m. Only a minor amount of solute was below the injection interval, whereas a considerable amount was above this interval. The longitudinal extension of the tracer, measured for JA at the depth of the peak concentration, was ca. 1.2 m. Breakthroughs observed at the last piezometer row (13 m down gradient) indicate that the lateral extension of the plume would have been less than 1.0 m. The piezometers JA and JG seem to have been located very close to the centre of the flow path.

The TCE and TCEd1 data indicated an almost linear decrease of TCE with increasing TCEd1 concentrations, indicating displacement of the TCE by the injected water containing TCEd1. For one sample, however, where high TCEd1 concentrations

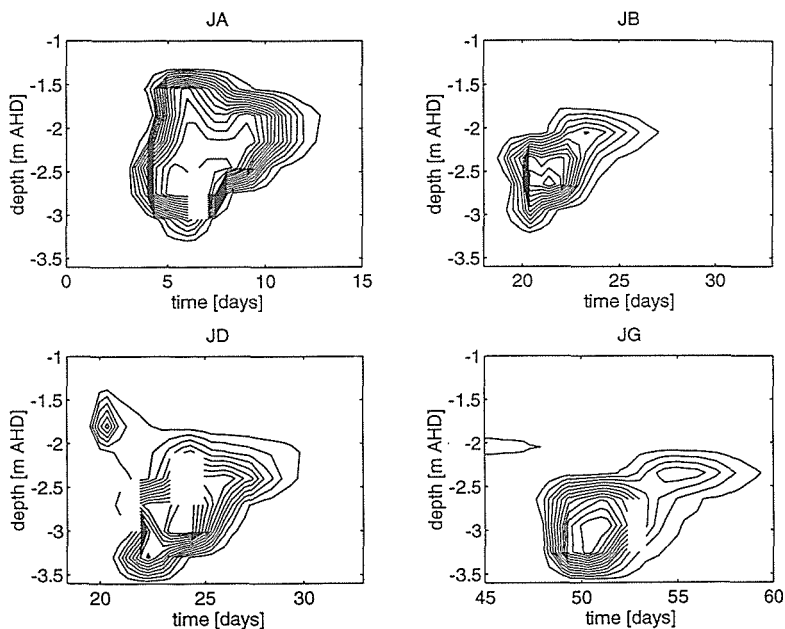


Fig. 3 Relative bromide concentration isolines at intervals of 0.07.

would have been expected, no TCED1 could be measured. However, the TCE concentration in this sample was unexpectedly high; about  $100 \mu\text{g l}^{-1}$ . This sample was easily distinguished from others, being darker in colour (presumably due to FeS precipitation). Initially, transformation of the deuterated compound to TCE was considered, but bromide in this sample was found to be at background concentrations. Therefore, it appears that no mixing occurred between the injected solution and the groundwater present in this patch.

## ADVECTION AND DISPERSION

The contour plots in Fig. 3 also show the relative bromide concentrations measured at the piezometers JB, JD and JG. Relative peak concentrations of 0.125 and 0.380 were measured in JC and JE, respectively. Very low relative concentrations, less than 0.02, were measured in JF. From the solute breakthrough at different piezometers, the flow direction of the tracer was estimated to be  $238^\circ$ . The vertical position of the peak concentration at JG was about 0.4 m below the peak location at JA. Vertical movement of the peak is likely to result from aquifer heterogeneity, since the injected concentrations were chosen to minimize gravity effects.

During the tracer test, an almost linear increase in hydraulic gradient was measured along the flow path of the solutes. Table 2 lists average hydraulic gradients, average linear groundwater velocities and average hydraulic conductivities for the sections JA-JD, JA-JG, and JD-JG, respectively. The increase in velocity was slightly higher than would be expected due to the increase in hydraulic gradient alone. Variability in average hydraulic conductivity (as indicated in Table 2) or effective porosity may account for this effect.

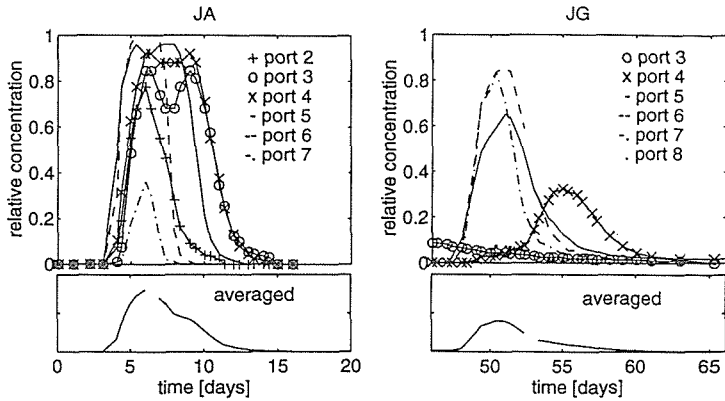
**Table 2** Variation of aquifer characteristics between tracer test piezometers.

	JA-JD	JA-JG	JD-JG
Average groundwater velocity (m day <sup>-1</sup> )	0.229	0.273	0.300
Average hydraulic gradient	0.001 58	0.001 79	0.001 94
Average hydraulic conductivity <sup>a</sup> (m day <sup>-1</sup> )	43.5	45.8	46.4

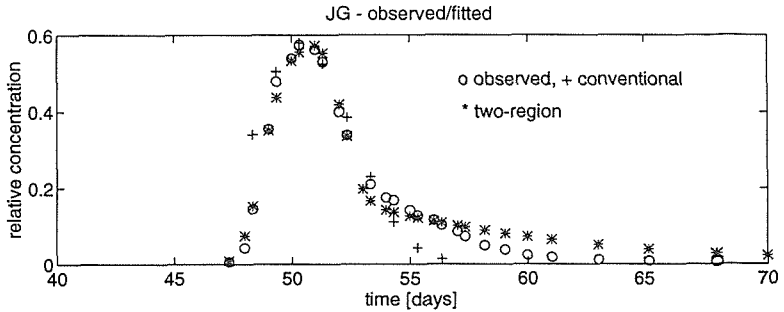
<sup>a</sup> Calculated from velocity assuming effective porosity of 0.3.

Breakthrough curves for individual ports on JG, and averages over six ports are given in Fig. 4. Integrating the areas under the depth-averaged breakthrough curves for JA and JG and multiplying these values by the measured velocities indicates conservation of solute mass. Individual ports are not directly comparable between multiport piezometers since the solutes moved vertically. The breakthrough curves obtained at distinct levels, however, can explain the features evident from the depth-averaged breakthrough curves.

A marked tailing of the breakthrough curve, evident at JG, was caused by a slightly lower average velocity at one of the four central ports. Less tailing was evident for the



**Fig. 4** Bromide breakthrough curves for individual ports and depth-averaged.



**Fig. 5** Observed (averaged over four ports) and simulated bromide breakthrough curves.

breakthrough at individual ports. Dispersion of the depth-averaged plume, therefore, was governed by small differences in advective velocities at distinct levels in the aquifer profile. A conventional advection-dispersion model, utilizing the observed breakthrough at JA as the input concentration distribution, and incorporating the observed linear increase in velocity with time, could not simulate the tailing and resulted in very small dispersivity estimates of about 0.015 m for the travel distance of 12 m. A two-region model gave similar dispersivity estimates, but proved more suitable in simulating the observed tailing (see Fig. 5).

## SORPTION

The retardation factor,  $R$ , of a solute, which is the ratio between the average linear groundwater velocity ( $v_g$ ) and the average velocity of the retarded compound ( $v_s$ ), is given by

$$R = 1 + (\rho/n)K_p = v_a/v_s$$

where  $\rho$  ( $\text{g cm}^{-3}$ ) is the bulk density of the porous medium,  $n$  is the effective porosity and  $K_p$  ( $\text{cm}^3 \text{g}^{-1}$ ) is the partition coefficient. Various correlation equations (e.g. Schwarzenbach & Westall, 1981) indicate that for TCE, the numerical value for  $K_p$  ( $\text{cm}^3 \text{g}^{-1}$ ) is expected to be about the same (in consistent units) as the value for the organic carbon content if this value is greater than 0.1%. Since the average organic carbon content at the site is 0.14%, the  $K_p$  value is estimated to be  $0.14 \text{ cm}^3 \text{g}^{-1}$ . With an average bulk density of  $1.75 \text{ g cm}^{-3}$  and an estimated effective porosity of 0.3, a retardation factor of ca. 1.8 can be calculated. This indicates that the velocity of TCE may be assumed to be about one-half of the average groundwater velocity.

A comparison between the depth averaged breakthrough curves obtained at JG for TCEd1 and bromide is presented in Fig. 6. The peak concentrations of both solutes travelled at identical velocities. This result was surprising due to a variety of factors. The Wackley and Black method (e.g. Rayment & Higginson, 1992) used to determine the organic carbon content of the aquifer soil does not measure the total organic carbon fraction and therefore the bias for retardation estimates would generally be towards lower values. Also, batch sorption studies have been carried out using aquifer material from the tracer test site. These studies indicated that sorption of TCEd1 onto the aquifer

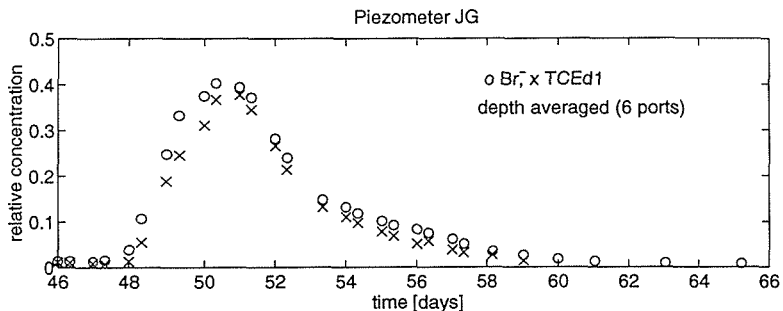


Fig. 6 Comparison of breakthrough data, averaged over six ports, for TCEd1 and bromide.

soil would be expected. Furthermore, the vastly different susceptibility of TCEd1 and bromide for mass loss during sampling and sample preparation as well as the different methods of analyses, would have been expected to affect the result. In the laboratory, sorption was observed onto the nylon and polyester materials used for construction of the piezometers. However, the time taken to sample groundwater was short, limiting the potential for significant sorption/desorption effects onto the materials used.

## DISCUSSION AND CONCLUSION

TCEd1 sorbed neither onto organic carbon nor onto mineral surfaces present in the sand aquifer and no evidence of TCE transformation was observed. The breakthrough curves of TCEd1 and KBr, which almost coincide, show that the groundwater sampling technique, the analytical procedures, as well as the aluminium, nylon, and polyester materials used in piezometer construction, are suitable for assessment of TCE transport. Also, the C-D bond of the deuterated compound was stable, indicating the usefulness of deuterated TCE as a tracer within a TCE contaminated zone.

The tracer test results also showed low dispersivity of the aquifer material. Even for long distances, longitudinal dispersion of practical significance is only to be expected if the solutes are initially distributed over a considerable depth. Therefore, in predicting the transport of the tracer, dispersion is negligible compared to the uncertainty involved in predicting the advective flow. The uncertainty with respect to the advective flow was partly due to uncertainties in estimation of the average hydraulic conductivity of the aquifer soil.  $K$  values based on grain size analyses agreed reasonably well with the estimate obtained by the tracer test. The constant permeameter test carried out on core samples, however, resulted in unreasonably low values, indicating  $K$  anisotropy and/or compaction of the core sample. A velocity increase with time was also observed, principally due to variations in hydraulic gradient. The organic carbon measurements, carried out on ground aquifer material, were highly variable. Using the average organic carbon fraction and applying commonly used correlations between soil organic carbon fraction and sorption coefficients would have resulted in considerable underestimation of the flow velocity for TCEd1.

The depth-averaged breakthrough curves at JG showed extensive tailing due to relatively small differences in advective velocities at distinct levels within the aquifer profile. The tailing is therefore expected to increase with the vertical extension of the solutes as a consequence of increased variability of the aquifer soil. Development of plumes, therefore, is difficult to predict without detailed knowledge of advective velocities and their directional trends at different levels within the aquifer profile. Therefore, a two-region model, although more suitable in simulating the observed tailing, does not necessarily improve the capability of predicting the future transport.

The tracer test results underline the importance of field transport studies. Controlled field studies are more likely to result in reliable estimates of transport parameters, which are particularly important if remediation of contaminated groundwater is planned.

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