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Diffusion and Sorption of VOCs through Soil-Cement Materials

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Abstract

This paper presents a laboratory study that assesses the diffusive and sorptive parameters of three volatile organic compounds (benzene, ethylbenzene, and trichloroethylene) though cured, monolithic, soil-cement materials. A double-reservoir diffusion test setup is used to determine the effective diffusion coefficient (D_e) and distribution coefficient (K_d) for laboratory-prepared soil-cement specimens at three water-to-cement ratios. Batch testing was also performed to provide a measure of the distribution coefficient independent of the diffusion testing. Values of K_d determined from batch testing, diffusion testing, and theoretical estimates from the literature ranged from 0 to 1.3 cm^3/g and were in general agreement. Values of D_e determined from laboratory testing ranged from 1.50×10^{-10} m^2/s to 3.0×10^{-10} m^2/s.

Practical applications of the laboratory testing methodology and results are discussed with respect to how they may be used in the pre-design and design phases of cement solidification/stabilisation (s/s) treatment. An illustrative example shows how the laboratory testing results could be used to estimate contaminant transport from a site and to provide an indication of the relative importance of the diffusive and sorptive parameters obtained from laboratory testing.

Keywords

Waste management & disposal; Land reclamation; Pollution.

List of notation

ATSDR	is the Agency for Toxic Substances and Disease Registry
c	is concentration
c_b	is the concentration in the receptor solution
c_{bo}	is the initial concentration in the receptor solution
c_{bf}	is the final concentration in the receptor solution
c_t	is the concentration in the source reservoir
c_{to}	is the initial concentration in the source reservoir
c_{tf}	is the final concentration in the source reservoir
D_e	is the effective diffusion coefficient
f_b	is the mass flux of contaminant into the receptor reservoir
f_{oc}	is the fraction of organic carbon
f_t	is the mass flux of contaminant from the source reservoir
G_S	is specific gravity
H_b	is the equivalent height of the receptor reservoir (volume per unit area)
H_r	is the equivalent height of source reservoir (volume per unit area)
i	is the hydraulic gradient
ITRC	is Interstate Technology & Regulatory Council
k	is the hydraulic conductivity
K_d	is the distribution coefficient
K_{oc}	is the partition coefficient of a compound between organic carbon and water
K_{ow}	is the octanol-water partition coefficient
n_e	is the effective porosity
q_c	is the volume of leachate collected per unit area per unit time
RMSE	is root-mean-square error
s/s	is solidification/stabilization
t	is time
TCE	is trichloroethylene
v	is darcy velocity
VOC	is volatile organic compound
w	is water content
W:C	is water-to-cement ratio
ρ_d	is the dry density
λ	is the first order decay constant
γ_w	is the unit weight of water

1. Introduction

Many environmentally impacted sites such as those historically used for oil and gas processing, wood-treating, and pesticide and herbicide manufacturing may contain both organic and inorganic chemical substances at levels that compel treatment (ITRC, 2011). As there are relatively few processes that effectively treat both organic and inorganic contaminants, it may often be practical to treat these sites using cement-based solidification/stabilisation (s/s), which has been used to treat sites contaminated with both organic and inorganic substances (USEPA, 2009). To understand how cement-based s/s treatment will perform in the long-term, it is essential to have the resources to estimate contaminant migration through soil-cement materials.

Volatile organic compounds (VOCs) are known to pose a threat to human health and the environment at relatively low concentrations (USEPA, 2010; ATSDR, 2007). Hence, there has been significant research investigating the diffusion of VOCs through a number of materials including compacted clay liners (Barone et al, 1992; Kim et al., 2001), geomembranes (Rowe and Hrapovic, 1995), and geosynthetic clay liners (Lake and Rowe, 2004). However, there is a paucity of experimental investigation on the diffusion of VOCs through soil-cement (e.g., cement-based s/s) materials.

The objective of this work is to demonstrate that conventional double-reservoir diffusion testing techniques (as discussed by Shackelford, 1991 and Rowe et al., 2004) can be used to measure contaminant migration parameters of organic contaminants for monolithic soil-cement specimens. Results of these diffusion tests may be incorporated in contaminant migration models to estimate contaminant transport. This paper investigates diffusion and sorption of three volatile organic compounds (i.e., benzene, ethylbenzene, and trichloroethylene) for cured, monolithic, laboratory-prepared soil-cement specimens at three different water-to-cement ratios. The purpose of these diffusion tests is to examine the effective diffusion coefficient (D_e) and distribution coefficient (K_d) of three different soil-cement mixtures. The interaction of these VOCs during testing is examined by testing trichloroethylene with three other organic compounds in one test versus testing it in isolation.

2. Experimental Method

2.1 Specimen Preparation and Laboratory Testing Programme

Specimens were prepared by mixing 80% silica sand with 20% kaolinite (by dry weight) in a 20 L plastic bucket with sufficient water to result in a 13 % water content. A cement grout at a 1:1, 3:2, or 2:1 water-to-cement ratio (depending on mixture, see Table 1) was mixed into the sand-kaolinite blend until homogenous. CSA Type 10, general use, normal Portland cement was used to formulate the grout. Details of mixing and sample preparation are described in Goreham (2014). To allow for comparison, the mixtures are the same as three mixtures used for the tritiated water diffusion tests discussed by Goreham and Lake (2013) and hence, for continuity, the sample naming system used in that paper is continued. A summary of the proportions of water, cement, and soil (comprising 80% silica sand and 20% kaolinite) for each of the three mixtures is presented in Table 1.

Table 1. Summary of diffusion test conditions and mixture properties.

Mixture	No. of Replicates	Source Solution	Cement[a] (%)	Total W:C[b]	Grout W:C[c]	Total Fraction (by weight) Cement	Soil	Water
c	3	GROUP	15	2.87	2	0.10	0.63	0.27
c	2	Trichloroethylene	15	2.87	2	0.10	0.63	0.27
h	2	GROUP	15	2.37	1.5	0.10	0.66	0.24
h	2	Trichloroethylene	15	2.37	1.5	0.10	0.66	0.24
g	2	GROUP	15	1.87	1	0.10	0.70	0.20
g	2	Trichloroethylene	15	1.87	1	0.10	0.70	0.20

Note: GROUP refers to benzene, ethylbenzene, trichloroethylene, and naphthalene being tested simultaneously.

[a] Cement content as a percentage of dry soil mass.

[b] Total water-to-cement ratio (weight : weight) including water content of soil at mixing (13%).

[c] Water-to-cement ratio (weight : weight) of cement grout.

Immediately after mixing, the specimens were cast in 69-mm diameter by 30-mm long cylindrical polyvinylchloride moulds. Evenly distributed tamping over the cross-section was performed using pressure just sufficient to ensure uniform filling of the moulds. Specimens were placed in separate, tightly sealed, plastic bags and stored at 21 ± 2 °C. After 56 days, specimens were extruded from their moulds and promptly returned to the plastic bags. All specimens were allowed to hydrate for a minimum of 28 additional days (84 days total) before the start of testing.

Diffusion testing and batch testing were performed using a solution containing benzene, ethylbenzene, trichloroethylene, and naphthalene. To investigate the effect of contaminant interaction between the VOCs, both diffusion and batch testing were also performed using trichloroethylene as the sole contaminant.

Table 2 presents a selection of physical and chemical properties for benzene, ethylbenzene, and trichloroethylene. Although all three VOCs are considered to have relatively low solubility in water, solubility varies by an order of magnitude between the least soluble (ethylbenzene) and most soluble (benzene). Relative solubility and the hydrophilicity of a compound influence the potential for that contaminant to be sorbed to soil materials (Rowe et al. 2004).

Table 2 — Select physical and chemical properties of benzene, ethylbenzene, and trichloroethylene.

Properties	Molecular Weight[a] (g/mol)	Boiling Temperature[a] (°C)	Solubility in Water @ 20°C[a] (g/L)	Log K_{ow}[a] @25°C	Dielectric Constant[a] @20°C	D_o @25°C[b] (m^2/s)	Specific Density @20°C[a] (g/cm^3)
Benzene	78.1	80	1.79	2.13	2.3	1.16×10^{-9}	0.88
Ethylbenzene	106.2	136	0.17	3.15	2.5	9.16×10^{-10}	0.87
TCE	131.4	87	1.20	2.42	3.4	9.93×10^{-10}	1.46

[a] Schwarzenbach et al. (2003).
[b] Yaws (2010).

2.2 Diffusion Testing

There have been a number of studies investigating the diffusion of organic compounds through clay barriers (e.g., Barone et al., 1992; Sawatsky et al., 1997; Donahue et al., 1999; and Krol and Rowe 2004) derived from a method proposed by Rowe et al. (1988). A similar method (adapted for soil-cement materials) used in the work discussed herein is summarised in the following paragraphs.

In each diffusion test, a reservoir with a known initial concentration (the source reservoir) is placed on one side of a soil-cement specimen and water is placed on the other side (the receptor reservoir). The concentration in each reservoir is measured intermittently as time progresses. The experimental concentrations are compared with results of theoretical modelling to determine the best-fit contaminant migration parameters.

A sketch of a typical diffusion cell used in this study is presented in Figure 1. The diffusion cells were constructed of 70-mm internal diameter glass cylinders with thick flanges at both the top and bottom to support glass top and bottom plates. Each soil-cement specimen was trimmed to fit snugly into the apparatus, and a thin coating of bentonite (with a water content of approximately 100 %) was placed around the exterior perimeter of the specimen to provide a hydraulic seal between the specimen and the cell. A glass support was then placed in the bottom reservoir to prevent the specimen from moving within the cell. Using a two-part epoxy-resin (3M Scotch-DP 100) the top and bottom glass plates were attached to the top and bottom flanges, respectively. To ensure bentonite hydration, approximately 50 mL of water was immediately placed in the source reservoir, which was above the specimen. After two days, the apparatus was inverted and 50 mL of water was added to the receptor reservoir. After two additional days, the water was drained from the apparatus before the reservoirs were filled to start diffusion testing. No leakage around the perimeter of the specimen was observed throughout this procedure.

The initial source reservoir concentrations for each test are presented in Table 3. Diffusion testing was performed using a solution containing benzene, ethylbenzene, trichloroethylene, and naphthalene. To investigate the effect of contaminant interaction between the VOCs, diffusion testing was also performed using trichloroethylene as the sole contaminant. The receptor reservoirs were initially filled with ultrapure water. With an initial concentration of 1.0 g/L sodium azide to act as a biocide.

Table 3. Initial source reservoir concentrations and reservoir volumes for VOC diffusion tests.

Specimen	Volume		Initial Source Reservoir Concentration, C_o			
	Source (mL)	Receptor (mL)	Benzene (mg/L)	TCE (mg/L)	Ethylbenzene (mg/L)	Naphthalene (mg/L)
c4	132.0	175.0	28.2	11.7	11.3	5.3
c5	131.0	170.0	26.5	13.7	10.4	5.0
c6	145.4	166.5	26.0	21.1	12.0	5.1
c7	135.1	170.4	-	34.9	-	-
c8	120.8	172.3	-	33.4	-	-
h4	128.9	168.3	50.0	47.0	46.7	4.2
h5	120.9	173.3	46.8	43.2	41.7	3.8
h6	132.0	175.9	-	37.7	-	-
h7	124.1	195.5	-	40.0	-	-
g4	138.9	165.1	50.1	47.8	49.0	3.9
g5	134.7	173.6	50.9	47.9	49.4	3.8
g6	148.9	165.8	-	32.5	-	-
g7	136.4	172.4	-	46.5	-	-

Concentrations of the source and receptor reservoirs were typically measured twice-weekly by removing 100 µL samples from each reservoir and testing them using gas chromatography. Immediately after sampling, the volume of solution removed from each reservoir was replaced with ultrapure water

2.3. Soil-Cement VOC Diffusion and Distribution Coefficient Estimation

When modelling the diffusion tests, finite mass boundary conditions were used to represent the source and receptor reservoirs. These boundary conditions are used when there is a finite amount of mass in the system and the concentration at each boundary is constantly changing with time due to mass transfer through the specimen. The concentration at any time in the source reservoir, $c_t(t)$, may be described mathematically by Equation 1 (Rowe et al., 2004).

$$c_t(t) = c_{to} - \frac{1}{H_r}\int_0^t f_t(t)dt - \frac{q_c}{H_r}\int_0^t c_t(t)dt \tag{1}$$

Where: c_{to} is the initial concentration in the source solution [ML^{-3}], H_r is the equivalent height of source fluid (volume of source fluid per unit area) [L]; $f_t(t)$ is the mass flux of contaminant into the soil-cement at any time t [$ML^{-2}T^{-1}$]; q_c is the fluid collected for sampling per unit area, per unit time [LT^{-1}]. The concentration in the receptor compartment (ultrapure water at the beginning of the test), $c_b(t)$, may similarly be expressed mathematically by Equation 2.

$$c_b(t) = c_{bo} + \frac{1}{H_b}\int_0^t f_b(t)dt - \frac{q_c}{H_b}\int_0^t c_b(t)dt \qquad (2)$$

Where: c_{bo} is the initial concentration in the receptor solution [ML^{-3}], H_b is the equivalent height of the receptor reservoir (volume of receptor reservoir per unit area) [L], and $f_b(t)$ is the mass flux of contaminant into the receptor reservoir at any time t [$ML^{-2}T^{-1}$].

As discussed by Rowe et al. (2004), the theoretical equation for transient one-dimensional contaminant transport through a porous medium such as soil-cement, may be expressed by Equation 3.

$$n_e\frac{\partial c}{\partial t} = n_e D_e\frac{\partial^2 c}{\partial z^2} - n_e v\frac{\partial c}{\partial z} - \rho_d K_d\frac{\partial c}{\partial t} - n_e\lambda c \qquad (3)$$

Where: c is the concentration in the pore space of the soil-cement at depth z and time t [ML^{-3}], n_e is the effective porosity of the soil-cement [-], D_e is the effective diffusion coefficient [L^2T^{-1}], v is the Darcy velocity [LT^{-1}], ρ_d is the dry density of the soil-cement [ML^{-3}], K_d is the distribution coefficient [$M^{-1}L^3$], and λ is the first order decay constant [T^{-1}]. This equation neglects dispersion, which is a transport mechanism associated with relatively high advective flux and hydraulic conductivities. In diffusion-controlled systems with low advective flux, contaminant transport due to dispersion is generally negligible (Rowe et al., 2004; Malviya and Chaudhary, 2006).

The effective diffusion coefficient, D_e, is related to the free-solution diffusion coefficient, D_o, by the tortuosity factor, τ, as shown in Equation 4.

$$D_e = \tau D_o \qquad (4)$$

D_o represents the maximum rate of diffusion a species can experience under ideal conditions (i.e. over a microscopic scale, in pure water at infinite dilution. Under non-ideal conditions (i.e. macroscopic scale, concentrated solutions) a number of other effects (e.g. electroneutraility, solute-solute, and solute-solvent interactions) influence diffusion (Daniel and Shackelford, 1988).

The purpose of any laboratory diffusion test is to obtain parameters describing diffusion (e.g., n_e, D_e, and K_d). Therefore, at the time of testing, these parameters are unknown. Any theoretical concentrations generated by solving Equations 1 to 3 require an assumption for these values.

Pollute v.6 (Rowe et al,. 1998), a finite layer computer program, was used to solve these equations using a trial-and-error approach to match theoretical source and receptor reservoir curves with observed experimental data. Trial values of D_e were varied by increments of 0.25×10^{-10} m^2/s and trial values of K_d by increments of 0.1 cm^3/g. The best-fit to the experimental data, as determined by the least root-mean-square error (RMSE), allowed for the interpretation of D_e and K_d for the specimen and contaminant examined. To reduce the number of unknown parameters, the data was analysed using two assumptions for the value of n_e.

- Firstly, the experimental data was analysed assuming that n_e was equal to the average value of n_e determined from tritium diffusion testing (Goreham and Lake, 2013) for each mixture (0.34, 0.30, and 0.27 for mixtures c, h, and g, respectively).
- Secondly, the data was analysed assuming that the value of n_e is equal to the average total porosity determined from water content upon oven-drying of all specimens of that mixture (0.48, 0.42, and 0.37 for mixtures c, h, and g, respectively).

The best-fit D_e and K_d were determined for each assumption of n_e.

2.4. Batch Testing

Batch tests were performed to examine the capacity of the VOCs to sorb to the soil-cement materials used in diffusion testing using procedures similar to those described by Lake et al. (2013). Prior to batch testing, specimens were cured for a minimum of 84 days, pulverised using a ceramic mortar and pestle, sieved through a 2 mm (U.S. No. 10) sieve, and oven-dried to a constant mass at 60°C. The testing was performed in 50-mL pyrex centrifuge tubes with open-top caps lined with polytetrafluoroethylene septa.

Batch testing was performed using a solution containing trichloroethylene as the sole contaminant and a solution containing trichloroethylene, benzene, ethylbenzene, and naphthalene together. To develop sorption isotherms, the VOCs were generally tested in triplicate at eight different concentration levels ranging from 0.5 to 50 mg/L. Due to a vial breaking during testing, only duplicate results are available for mixture g at the 10.0 mg/L concentration level for the solution containing the group of chemicals. The batch tests on the group of contaminants had naphthalene concentrations at approximately 10% of those of the concentration of each VOC (i.e., ranging from 0.5 to 5.0 mg/L). A group of vials containing solutions at the same concentrations and subject to the same procedures presented above, but without any soil-cement material, were used as a control. All solutions used in the batch tests included 1.0 g/L of sodium azide to act as a biocide.

Three grams of crushed soil-cement were placed in each centrifuge tube which was filled with ultrapure water until the headspace was minimized. Over the range of mixtures and concentrations tested, the mass of solvent ranged from 46.3 g to 51.4 grams. A Hamilton gastight syringe was used to inject varying amounts of stock solution (to yield the desired concentration) into each centrifuge tube. The centrifuge tubes were promptly capped and then mechanically agitated, end-over-end, for 24±2 hours at 21±2 °C. After agitation solids and solution were separated using a Thermo IEC Centra GP8R centrifuge at 2500 rpm for 30 minutes. Three aliquots were taken from each tube and measured using gas chromatography.

3. Results and Discussion

3.1 Water Content, Porosity, and Dry Density

The different proportions of water added to the different mixtures allowed for a range of porosities to be examined in this study. Table 4 compares the average water content and porosity (assuming saturation) of the cured specimens for each mixture used in this testing programme to the average for the same mixture used in the previous tritiated water diffusion testing programme (Goreham and Lake, 2013).

Table 4. Comparison of average water content, porosity, and dry density for specimens made for this study and similar specimens used for tritiated water diffusion testing (Goreham and Lake, 2013).

Mixture	Grout W:C	Specimens from VOC Diffusion Testing Programme			Specimens from Tritium Diffusion Testing Programme		
		Water Content	Porosity	Dry Density (g/cm^3)	Water Content	Porosity	Dry Density (g/cm^3)
c	2:1	34%	0.47	1.36	35%	0.48	1.35
h	3:2	29%	0.43	1.47	30%	0.42	1.47
g	1:1	22%	0.37	1.63	23%	0.37	1.63

Although the degree of saturation was not directly measured on the specimens used for VOC diffusion testing, the water contents are very similar to those measured for specimens in the tritiated water diffusion testing programme (which were calculated to range from 99% to 108% saturation). The average dry density (ρ_d, ML^{-3}) of each of these mixtures was calculated using Equation 5.

$$\rho_d = \frac{G_S \gamma_w}{1 + wG_S} \qquad (5)$$

Where: G_s, is the specific gravity [-], w is the average water content [-], and γ_w is the unit weight of water [ML^{-3}].

3.2 Diffusion and Batch Test Results

The results of diffusion testing were first interpreted assuming that n_e was equal to the average value of n_e determined from diffusion testing of tritiated water on the same mixture (from Goreham and Lake, 2013). The result of a typical diffusion test analysed using this assumption is presented in Figure 2a. In this figure, the upper data points (starting at c/c_o=1) show the decrease in contaminant concentration with time in the source reservoir due to contaminant migration into the soil-cement specimen. The lower data points (starting at $c/c_o=0$) represent the increase in contaminant concentration in the receptor reservoir with time. Both the experimental data (solid circles) and theoretical best-fit (dashed lines) are presented. Figure 2b shows the same experimental data with the best-fit D_e and K_d determined by assuming that n_e was equal to the average total porosity determined based on the water-content of all specimens of that mixture.

Table 5 summarises the results of the 13 diffusion tests and presents the values of D_e and K_d derived from them for each assumption of n_e. Also included in Table 5 are the 95 % confidence intervals of K_d determined from batch testing and the final normalized (to initial concentration of the source reservoir) source and receptor reservoir concentration.

Table 5. Summary of batch and diffusion test results.

Specimen	Tracer	Batch Testing	Diffusion Testing									
					n_e from Tritium Diffusion Testing				n_e from Oven-Drying			
		Batch Testing K_d (95% CI[a])	Normalized Final Source Reservoir Concentration (C_{tf}/C_{to})	Normalized Final Receptor Reservoir Concentration (C_{bf}/C_{to})	n_e	K_d	D_e ×10^{10}	RMSE[c]	n_e	K_d	D_e ×10^{10}	RMSE[c]
		(cm^3/g)	(-)	(-)	(-)	(cm^3/g)	(m^2/s)	(-)	(-)	(cm^3/g	(m^2/s)	(-)
c4	B	0.1 – 0.2	0.57	0.19	0.34	0.1	2.25	0.03	0.48	0.0	1.75	0.03
c5			0.55	0.17		0.1	2.50	0.10		0.0	1.75	0.10
c6			0.59	0.20		0.2	2.25	0.02		0.0	1.75	0.02
c4	TCE	0.4 – 0.8	0.51	0.14		0.4	2.50	0.03		0.3	1.75	0.03
c5			0.52	0.17		0.4	2.50	0.03		0.4	1.75	0.03
c6			0.49	0.15		0.5	2.50	0.03		0.4	1.75	0.03
c4	EB	0.4 – 0.7	0.60	0.15		0.4	2.00	0.02		0.2	1.50	0.02
c5			0.59	0.15		0.4	2.25	0.04		0.3	1.50	0.04
c6			0.59	0.15		0.7	2.25	0.02		0.5	1.75	0.02
c7	TCE[b]	0.3 – 0.5	0.54	0.15		0.5	2.50	0.02		0.4	1.75	0.02
c8			0.54	0.16		0.3	2.50	0.02		0.2	1.75	0.02
h4	B	0.7 – 0.8	0.52	0.14	0.30	0.6	3.00	0.03	0.42	0.5	2.25	0.03
h5			0.60	0.12		0.5	2.25	0.03		0.4	1.50	0.03
h4	TCE	0.5 – 0.6	0.55	0.11		0.8	2.50	0.03		0.7	1.75	0.03
h5			0.64	0.09		0.7	2.00	0.04		0.6	1.50	0.04
h4	EB	1.0 – 1.3	0.51	0.12		1.0	2.75	0.02		0.9	2.00	0.02
h5			0.56	0.08		1.0	2.25	0.03		0.9	1.50	0.03
h6	TCE[b]	0.2 – 0.4	0.47	0.16		0.5	3.00	0.03		0.4	2.25	0.03
h7			0.49	0.15		0.4	3.00	0.02		0.3	2.00	0.02
g4	B	0.3 – 0.6	0.55	0.14	0.27	0.6	3.00	0.02	0.37	0.5	2.25	0.02
g5			0.57	0.14		0.5	2.75	0.02		0.4	2.00	0.02
g4	TCE	0.6 – 1.0	0.50	0.11		0.9	2.50	0.04		0.8	2.00	0.04
g5			0.63	0.10		0.6	2.25	0.04		0.5	1.75	0.04
g4	EB	1.1 – 1.2	0.49	0.10		1.3	3.00	0.03		1.3	2.25	0.03
g5			0.55	0.10		0.9	2.75	0.03		0.8	2.00	0.03
g6	TCE[b]	0.3 – 0.5	0.52	0.13		0.6	3.00	0.03		0.7	2.25	0.03
g7			0.53	0.10		0.8	2.75	0.02		0.7	2.00	0.02

B = Benzene, TCE= Trichloroethylene, EB = Ethylbenzene

[a] Confidence interval.

[b] Tested alone (without other VOCs).

[c] Root-mean-square error for best-fit parameters and laboratory diffusion test results.

When using n_e determined from tritium diffusion testing in the interpretation of the diffusion tests, D_e was found to range from 2.00×10^{-10} to 3.00×10^{-10} m^2/s for all three VOCs. When assuming n_e was equal to the total porosity derived from oven-drying, D_e was found to range from 1.50×10^{-10} to 2.25×10^{-10} m^2/s

The values of D_e determined when assuming that n_e was equal the values obtained from tritium diffusion testing were always larger than those determined when assuming n_e was equal to the porosity determined from oven-drying. This is as expected as a slightly larger assumed value of n_e requires that the value of D_e be smaller to result in in the same diffusive flux (Equation 3). The value of $n_e\times D_e$, which is directly related to the diffusive flux, was found to range from 6.0×10^{-11} to 9.0×10^{-11} m^2/s when using the values of n_e obtained from tritium diffusion testing and 6.3×10^{-11} to 9.5×10^{-11} m^2/s when using values of n_e based on oven-drying.

Unlike the results of diffusion testing on tritiated water (Goreham and Lake, 2013) no trend in $n_e\times D_e$ was observed with water-to-cement ratio. This may be due, in part, to the difficulty of VOC diffusion testing and analytic measuring relative to testing with and measuring a conservative, non-volatile, compound such as tritiated water.

The three VOCs tested have relatively high solubility compared to other non-polar organic compounds (e.g., naphthalene) and hence the relatively low values of K_d measured in both batch testing and diffusion testing are not surprising. It is interesting to note the similarity in K_d values obtained from batch and diffusion testing; Figure 3 plots average values of K_d determined from batch testing against average values of K_d obtained from diffusion testing for each mixture and each VOC. The values of K_d determined from diffusion testing presented in this plot were attained using n_e determined from tritium diffusion testing. The results of a linear regression through the origin which resulted in a slope of 0.98 and an R^2 of 0.74 is also plotted on Figure 3. Overall, K_d determined from batch testing and diffusion testing are similar. Batch testing is a relatively quick and simple approach to establish values of K_d compared to double-reservoir diffusion testing.

Overall, the value of K_d was generally found to decrease with increasing water-to-cement ratio and based on compound in the following order $K_{dEthylbenzene} > K_{dTrichloroethylene} > K_{dBenzene}$. For the mixture with the lowest water-to-cement ratio (mixture c) diffusion testing indicates a $K_{dBenzene}$ ranging from 0.0 to 0.2. The authors believe that the measured values of zero indicate low amount of sorption with some sample variability rather than an absolute value of zero. There was no substantial difference in the values of K_d obtained when trichloroethylene was tested in isolation and those when trichloroethylene was tested simultaneously with the other organic compounds. Additionally, there was no substantial difference in the values of D_e or $n_e\times D_e$ for trichloroethylene obtained from the tests where trichloroethylene was tested in isolation and those where it was tested with the other organic compounds as co-solutes. These results suggests that under the specific conditions of this study (e.g., concentrations) there was negligible interaction between trichloroethylene and the other VOCs in solution (i.e., there were negligible competition effects).

For organic compounds, K_d [$M^{-1}L^3$] may be normalised to the fraction of organic carbon, f_{oc} [-], to produce the organic carbon-water partition coefficient, K_{oc} [$M^{-1}L^3$], as shown in Equation 6 (Karickhoff et al., 1979; Schwarzenbach et al., 2003).

$$\boldsymbol{K_{OC}} = \frac{\boldsymbol{K_d}}{\boldsymbol{f_{oc}}} \tag{6}$$

Furthermore, Karickhoff et al. (1979) present an empirical correlation to predict K_{oc} (cm^3/g) for a particular organic compound based on the octanol-water partition coefficient, K_{ow} (-) (Equation 7).

$$\mathbf{log}\,\boldsymbol{K_{OC}} = \mathbf{log}\,\boldsymbol{K_{OW}} - \mathbf{0.21} \tag{7}$$

The weighted average f_{oc} of the solids (sand, kaolinite, and cement) for each of the three soil-cement mixtures is 0.13% as measured by Afshar (2008). This testing was performed on the same batches of materials used in this study as part of the research group that performed the work discussed herein.

Using this value and the values of $\log K_{OW}$ of presented in Table 2, the calculated values of K_d based on Equations 6 and 7 were determined to be 0.11, 1.10, and 0.21 cm^3/g, respectively. These values are presented alongside average values of K_d from batch testing and diffusion testing for each compound in Table 6. The results show that experimentally measured and calculated theoretical values of K_d compare relatively well.

Table 6 — Comparison of calculated and average measured values of K_d for benzene, ethylbenzene, and trichloroethylene.

	K_d (cm^3/g)			
VOC	Calculated based on f_{oc} and K_{ow} (Karickhoff et al., 1979)	Average determined from batch Testing	Average determined from diffusion testing assuming n_e from tritiated water diffusion tests	Average determined from diffusion testing assuming n_e from oven-drying
Benzene	0.11	0.42	0.37	0.32
Ethylbenzene	1.10	0.92	0.81	0.70

Trichloroethylene	0.21	0.35[a]/0.65[b]	0.61[a] /0.52[b]	0.45[a] /0.53[b]

[a] When benzene, ethylbenzene, trichloroethylene, and naphthalene were being tested simultaneously.

[b] When trichloroethylene was the only compound being tested.

4 Practical Application of Results: Contaminant Transport Modelling

During pre-design, where decisions may be made about the type of containment technologies employed, values from literature (such as those presented in this paper) are often relied on to define material properties in the absence of specific test data. Contaminant transport modelling can show the relative effects of how a change in the value of a given parameter influences contaminant migration. This section demonstrates how contaminant migration modelling may be performed and shows the relative effects of the three parameters studied (n_e, D_e, and K_d) over a range of values through the use of an illustrative example. The simplified geometry of a theoretical site is shown in Figure 4. Modeling was performed using the finite-layer computer program Pollute v.6 (Rowe et al,. 1998).

The following assumptions were used in the illustrative example:

- The potential for contaminant migration is only lateral (i.e., one-dimensional) and the hydraulic gradient, i, is a constant 1%.
- The neighbouring soil consists of a silty sand with the following properties, $k = 1\times10^{-7}$ m/s, $n_e = 0.40$, $D_e = 5.0\times10^{-10}$ m^2/s, and $K_d = 0$ μg/L).
- The impacted portion of the site has a uniform initial concentration of trichloroethylene of 3.4 g/m^3.
- There is no volume increase of the soil due to cement-based s/s treatment.
- The properties of the soil beyond the property line (i.e., to the right in Figure 4) are constant to an infinite extent.
- There is no biological degradation, volatilisation, or transformation of contaminants.
- Dispersion through the soil and soil-cement materials is negligible.
- The soil-cement material and neighbouring soil will maintain constant material properties for at least 1000 years.

Nine different cases were modelled and a summary of the transport properties used in each case are summarised in Table 7. The properties of soil-cement materials are likely to change with time due to the effects of aging, hydration, and weathering. Previous studies have indicated that factors such as chemical attack, cycles of wetting/drying, and exposure to freeze/thaw cycles influence the structure of soil-cement materials (Klich et al., 1999; Fitch and Cheeseman, 2003; Jolous Jamshidi et al., 2015). However, to limit the complexity of the modeled example, it has been assumed that the material parameters are constant with time. It is also likely that the neighbouring soil would have some level of sorption; this has not been included in the model to simplify the model and highlight the relative effects of cement treatment. In practice, these (and other) details would have to be considered with care as they may have a substantial effect on the results.

Table 7 — Contaminant transport parameters used in modelling and the modelled concentration of trichloroethylene at the property boundary after 1000 years for the theoretical site.

Case	Mixture	TOTAL W:C[a]	GROUT W:C[b]	Soil-Cement Monolith Properties				Concentration at boundary after 1000 Years (µg/L)
				n_e	D_e (m^2/s)	k (m/s)	K_d (cm^3/g)	
1	c	2.87		0.34	2.5×10^{-10}	3.3×10^{-9}	0	164
2	h	2.37	2.0	0.30	2.6×10^{-10}	4.2×10^{-10}	0	49
3	g	1.87	1.5	0.27	2.6×10^{-10}	4.6×10^{-10}	0	52
4	c	2.87	1.0	0.34	2.5×10^{-10}	3.3×10^{-9}	0.4	70
5	h	2.37	2.0	0.30	2.6×10^{-10}	4.2×10^{-10}	0.6	18
6	g	1.87	1.5	0.27	2.6×10^{-10}	4.6×10^{-10}	0.7	16
7	c	2.87	1.0	0.48	1.8×10^{-10}	3.3×10^{-9}	0.3	70
8	h	2.37	2.0	0.42	1.9×10^{-10}	4.2×10^{-10}	0.5	18
9	g	1.87	1.5	0.37	2.0×10^{-10}	4.6×10^{-10}	0.7	15

[a] Total water-to-cement ratio (by weight) including water content of soil at mixing (13%).

[b] Water-to-cement ratio (by weight) of cement grout.

The nine cases consider results of diffusion testing (i.e., D_e and K_d) for the three mixtures using both the assumption that n_e is equal to the value determined from tritium diffusion testing (cases 1-6) and the assumption that n_e is equal to the value determined based on oven-drying (cases 7-9). Cases 1-3 illustrate cases with no sorption (i.e., K_d=0) while cases 4-9 illustrate cases with sorption. The hydraulic conductivity used in each case was equal to the average hydraulic conductivity determined for each mixture (Goreham and Lake, 2013).

Figure 5 shows the concentration of trichloroethylene at the property boundary (10 m down gradient from the soil-cement monolith) for times up to 1000 years and Table 7 summarises the concentration at the property boundary after 1000 years for each case.

Referring to Figure 5 and Table 7 the key results of this modelling are:

- The concentrations at the property boundary for the cases representing soil-cement material with the highest water-to-cement ratio (cases 1, 4, and 7) are substantially higher than those representing the other two mixtures.

- Considering the cases modelled without sorption (cases 1, 2, and 3), the higher values of k and D_e in case 1 results in a concentration of 164 μg/L after 1000 years compared to the 49 and 53 μg/L observed for cases 2 and 3, respectively.
- Considering a moderate level of sorption (K_d = 0.4 to 0.7 cm^3/g) is considered (cases 4-6), concentrations at the property boundary after 1000 years are reduced to 70, 18, and 16 μg/L from 164, 49, and 53 μg/L when no sorption is modelled (cases 1-3).
- The assumption used to define n_e in the interpretation of the diffusion tests has a negligible effect on the modelled concentrations. When using n_e determined from tritium diffusion testing and the associated D_e and K_d, the modelled concentrations at the property boundary after 1000 years were 70, 18, and 16 μg/L for mixtures c, h, and g, respectively. When using n_e determined from oven-drying (and the associated D_e and K_d) the concentrations were 70, 18, and 15 μg/L, respectively.

It has been illustrated above that the choice of n_e used to interpret the diffusion test results does not have a substantial effect on their interpretation. Therefore, for simplicity, when interpreting diffusion test results from double-reservoir diffusion tests, it is likely sufficient to estimate n_e based on oven-drying.

Considering the relative influence of K_d on the results of contaminant migration modelling, when developing a contaminant migration model, it may often be sufficient to conservatively estimate D_e (e.g., based on the results of the testing performed in this thesis) and to measure K_d using batch tests or to estimate it from established relationships (e.g., Karickhoff et al. 1979). This approach may offer significant efficiency as batch testing or measuring the fraction of organic content of the soil is substantially less time- and material-intensive than diffusion testing. In many cases this approach may be sufficient to estimate the contaminant migration from a particular site with sufficient accuracy to guide decision-making related to the selection of the cement-based s/s versus other treatment options.

In cases where more investigation is warranted, such as in detailed design, diffusion testing may be performed as outlined above to estimate the diffusive and sorptive parameters based on site-specific details (mix design, contaminants of interest, etc.). Furthermore, the relative influence of K_d on the results of contaminant migration modelling suggests that the use of additives that promote sorption such as fly ash (e.g. Lake et al., 2013) or activated carbon (e.g. Arafat et al., 1999) may be an efficient way to decrease contaminant migration from soil-cement systems used in source-control remediation.

5 Summary and Conclusions

Thirteen diffusion tests were performed on three different laboratory-prepared mixtures of water, Portland cement, and soil (comprising 80% silica sand and 20% kaolinite by dry mass) using benzene, ethylbenzene, and trichloroethylene as tracers. Double-reservoir diffusion tests performed in glass diffusion apparatuses were adapted from those developed for clayey soils. In this analysis, two different assumptions were used for the value of n_e in the interpretation of the diffusion tests: a) that it was equal to the value n_e determined from tritium diffusion testing and b) that it was equal to the total porosity determined from oven-drying). The value of n_e selected was shown to have a negligible effect when applying the diffusion testing results to a contaminant migration analysis of a theoretical site.

Values of D_e determined from diffusion testing ranged from 1.5×10^{-10} to 3.0×10^{-10} m^2/s for the three water-to-cement ratios and three VOCs tested. No trends of D_e or $n_e \times D_e$ were apparent based on VOC or based on the water-to-cement ratio. K_d determined from batch testing and diffusion testing were found to range from 0 to 1.3 cm^3/g and compare relatively well to each other and to theoretical estimates based on f_{oc} and K_{ow}. Results of diffusion and batch testing using solutions of trichloroethylene in isolation and trichloroethylene in solution with the other organic compounds were similar and reveal no evidence of interaction or competition effects. Contaminant migration modelling of a theoretical site illustrated the relative importance of the diffusive and sorptive parameters obtained from testing (i.e., n_e, K_d, and D_e). For the range of values measured, K_d had a larger effect on the modelled concentrations than n_e or D_e.

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Figure 1. Typical diffusion testing apparatus used in this study.

Figure 2. Concentration profiles from laboratory diffusion experiments and best-fit curves for benzene a) using the assumption that n_e is equal to that determined from tritium diffusion testing b) using the assumption that n_e is equal to the total porosity determined from oven-drying.

Figure 3. Average K_d from determined from batch testing vs. average K_d obtained from diffusion testing for a given mixture and VOC (using the assumption that the effective porosity, n_e, was equal to the average value determined from tritium diffusion testing on the same mixture when analysing the diffusion tests).

Figure 4. Theoretical site used in example contaminant migration analyses.

Figure 5. Concentration at the property boundary for the theoretical site for modelling cases 1 to 9.

Figure 1

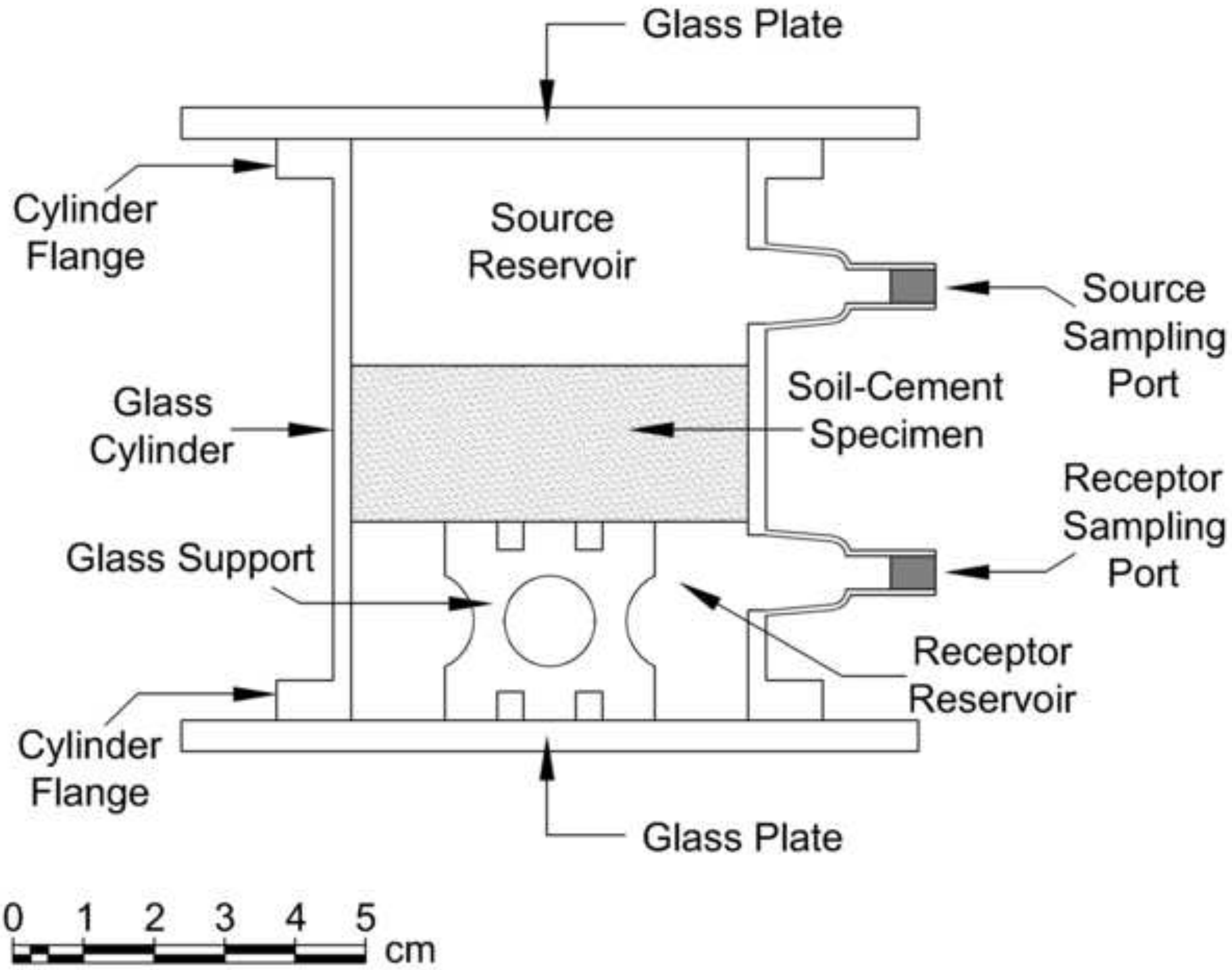

Glass Plate
Cylinder Flange
Source Reservoir
Source Sampling Port
Soil-Cement Specimen
Glass Cylinder
Receptor Sampling Port
Glass Support
Receptor Reservoir
Cylinder Flange
Glass Plate
0 1 2 3 4 5
cm

Figure 2

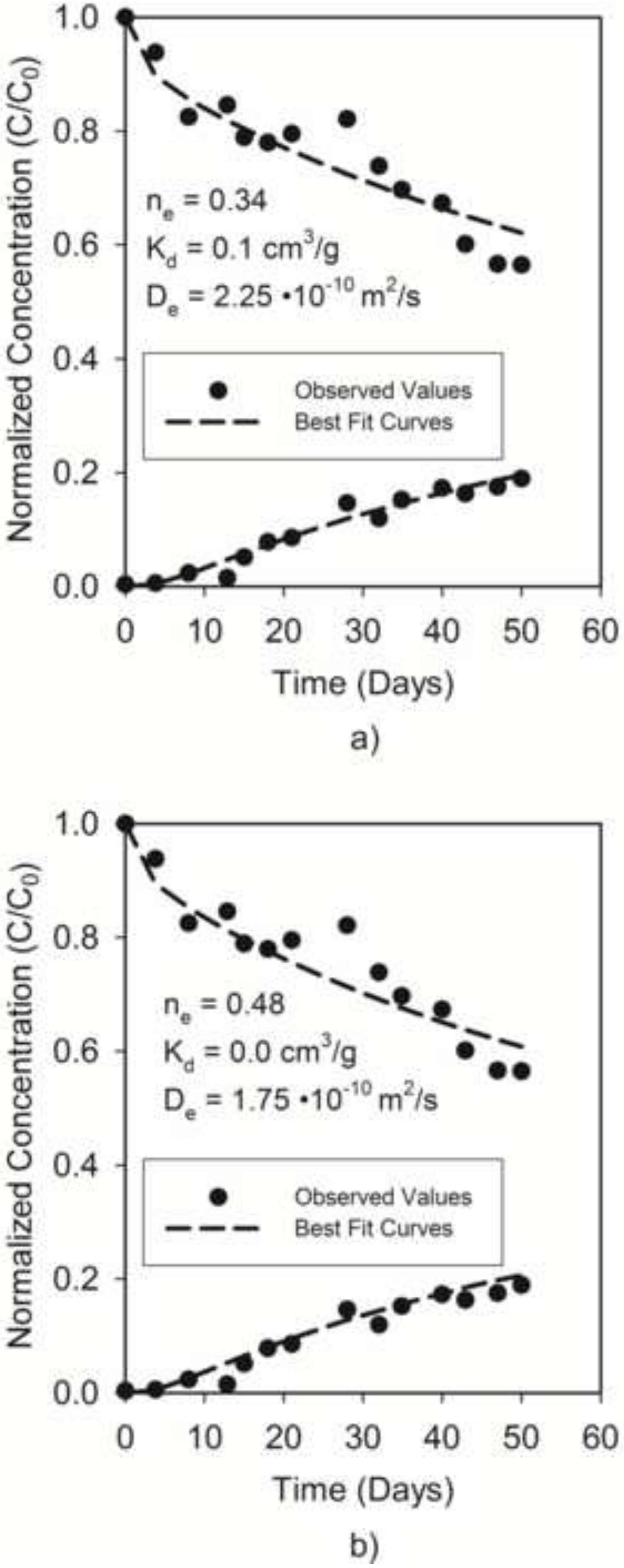

Normalized Concentration (C/C₀)
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Time (Days)
n_e = 0.34
K_d = 0.1 cm³/g
D_e = 2.25 •10⁻¹⁰ m²/s
● Observed Values
— — Best Fit Curves
a)
Normalized Concentration (C/C₀)
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Time (Days)
n_e = 0.48
K_d = 0.0 cm³/g
D_e = 1.75 •10⁻¹⁰ m²/s
● Observed Values
— — Best Fit Curves
b)

Figure 3

Click here to download Figure: Figure 3.TIF

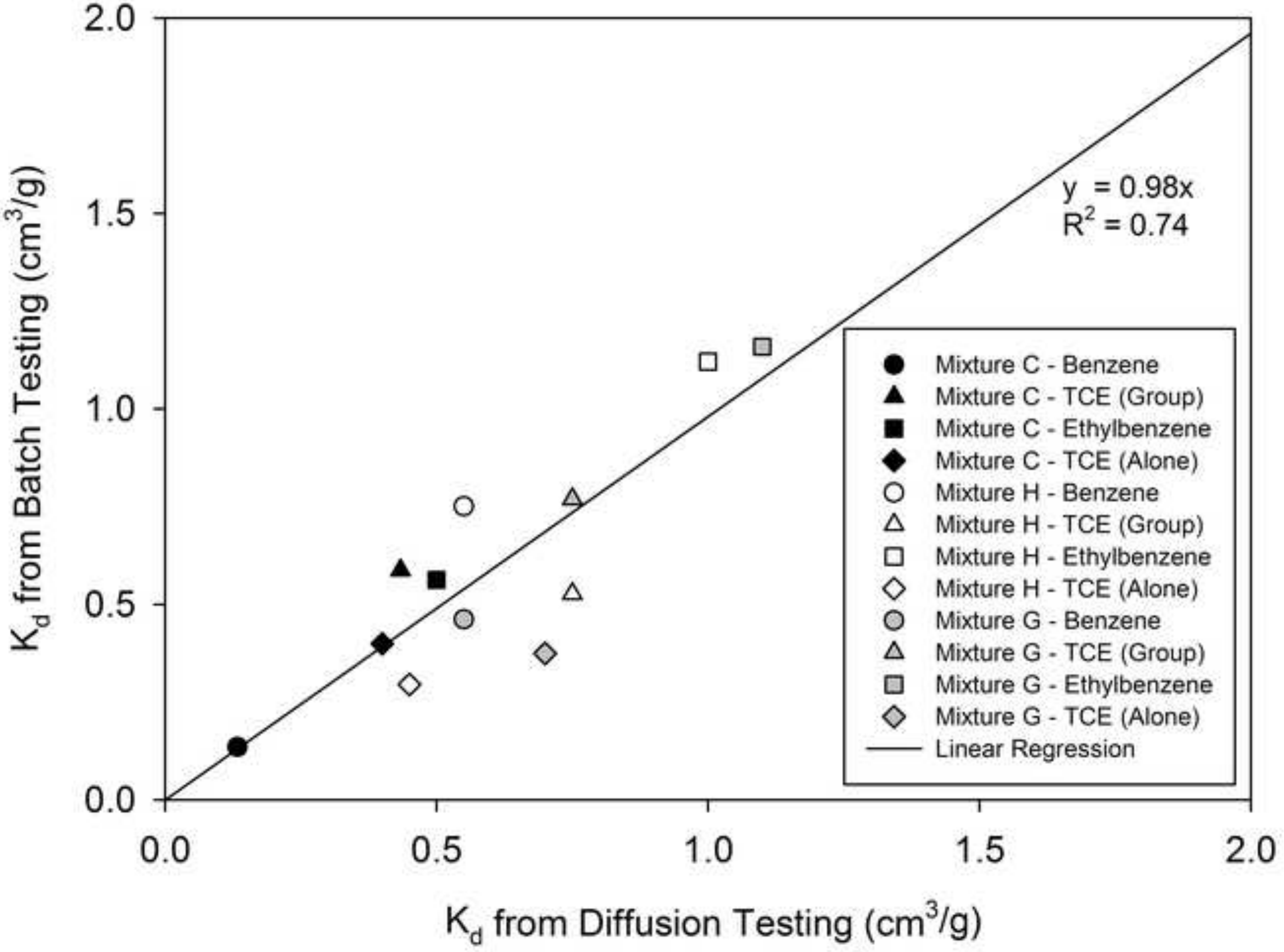


Figure 4

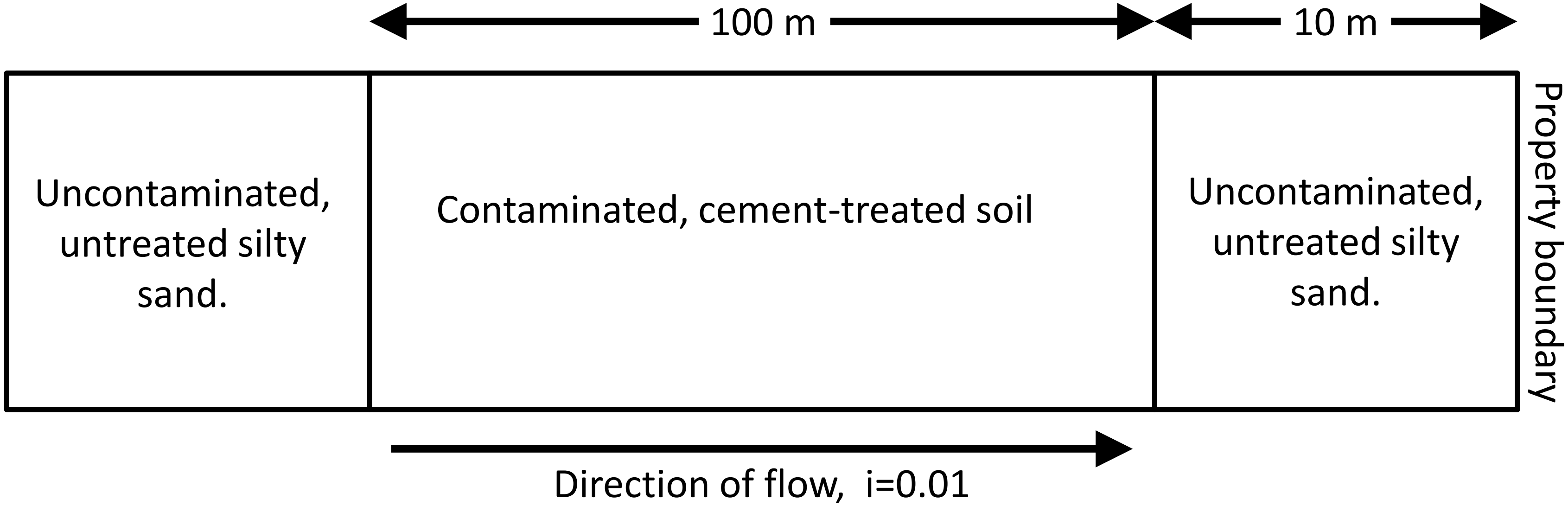
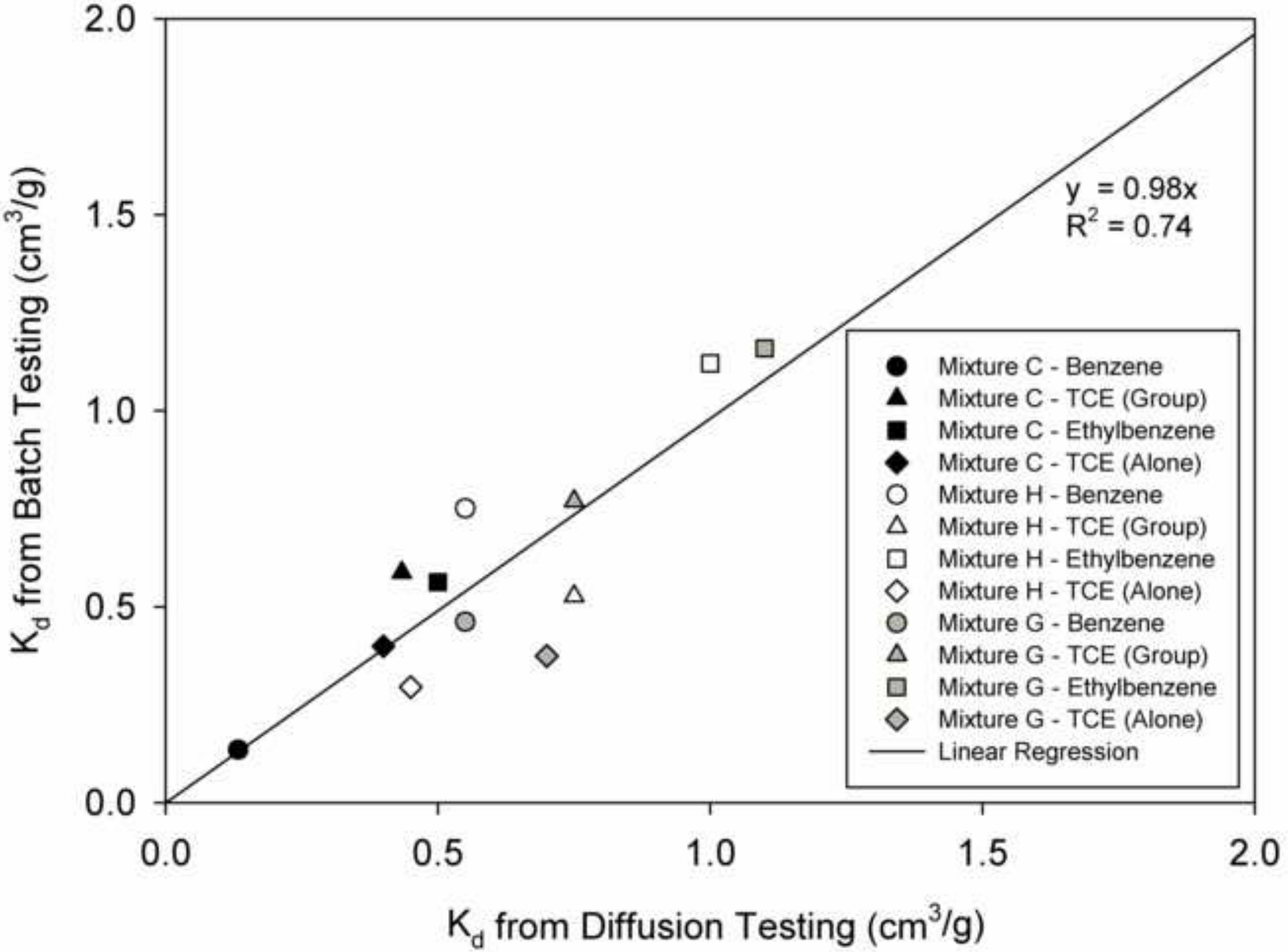

100 m
10 m
Uncontaminated, untreated silty sand.
Contaminated, cement-treated soil
Uncontaminated, untreated silty sand.
Property boundary
Direction of flow, i=0.01

Figure 5



2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
K_d from Batch Testing (cm³/g)
K_d from Diffusion Testing (cm³/g)
y = 0.98x
R² = 0.74
● Mixture C - Benzene
▲ Mixture C - TCE (Group)
■ Mixture C - Ethylbenzene
◆ Mixture C - TCE (Alone)
○ Mixture H - Benzene
△ Mixture H - TCE (Group)
□ Mixture H - Ethylbenzene
◇ Mixture H - TCE (Alone)
● Mixture G - Benzene
▲ Mixture G - TCE (Group)
■ Mixture G - Ethylbenzene
◆ Mixture G - TCE (Alone)
— Linear Regression