

토양 내 PCE 제거과정에서 가스 분배추적자기법을 이용한 공기노출 PCE의 잔류량 검출

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Measurement of Gas-Accessible PCE Saturation in Unsaturated Soil using Gas Tracers during the Removal of PCE

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ABSTRACT

In this laboratory study, the changes in gas-exposed perchloroethene (PCE) saturation in sand during a PCE removal process were measured using gaseous tracers. The flux of fresh air through a glass column packed with PCE-contaminated, partially water-saturated sand drove the removal of PCE from the column. During the removal of PCE, methane, *n*-pentane, difluoromethane and chloroform were used as the non-reactive, PCE-partitioning, water-partitioning, and PCE and water-partitioning tracers, respectively. *N*-pentane was used to detect the PCE fraction exposed to the mobile gas. At water saturation of 0.11, only 65% of the PCE was found to be exposed to the mobile gas prior to the removal of PCE, as calculated from the *n*-pentane retardation factor. More PCE than that detected by *n*-pentane was depleted from the column due to volatilization through the aqueous phase. However, the ratio of gas-exposed to total PCE decreased on the removal of PCE, implying gas-exposed PCE was preferentially removed by vaporization. These results suggest that the water-insoluble, PCE-partitioning tracer (*n*-pentane in this study), along with other tracers, can be used to investigate the changes in fluid (including nonaqueous phase liquid) saturation and the removal mechanism during the remediation process.

Keywords : Soil, Unsaturated zone, Remediation, Contamination, PCE, NAPL, Partitioning tracer

1. Introduction

In many nonaqueous phase liquid (NAPL)-contaminated sites that require remedial action, the evaluation of the extent and quantity of NAPL are of great importance for designing a feasible remediation process. Among these evaluation techniques, the use of chemical tracers is relatively new, but has been proven effective for measuring the quantity of NAPL, as well as the spatial distribution of NAPL in a contaminated area (Jin et al., 1995).

The tracer technique has been evolved for analyzing the

characteristics of fluids in flowing domains. In most cases of tracer application for measuring the quantity of NAPL within the subsurface environment, a set of chemicals consisting of reactive and nonreactive tracers is used. Reactive tracers are the chemicals applied into a flowing fluid, which are intended to interact with the physical domains of interest other than the flowing domain. During advective flow, reactive (or partitioning) tracers may partition into other fluids. Low molecular weight alcohols (e.g. isopropanol and pentanol) are often used as NAPL-partitioning tracers when applied via the aqueous phase (Jin

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et al., 1995; Nelson et al., 1999). A number of field applications of aqueous alcohol solutions as tracers have been reported (Nelson and Brusseau, 1996; Hunkeler et al., 1997; Annable et al., 1998(a); Annable et al., 1998(b); Young et al., 1999). From analyzing the concentration profiles of these NAPL-partitioning tracers, the volume of NAPL can be estimated (Valocchi, 1985). The use of a nonreactive tracer is essential for the applications of reactive tracers.

Flowing fluid may be in either an aqueous or gas phase, which means that the tracers are applied in either an aqueous or gas state. Water-insoluble gases, which are sufficiently inert not to partition into any of the physical compartments of the flowing domain, have been used as gaseous nonreactive tracers. Inert gases, such as helium and argon, are good candidates as gaseous nonreactive tracers (Whitley et al., 1999). Methane has occasionally been used as a gaseous nonreactive tracer, as it can be easily detected by FID (flame ionization detector), a common GC detector (Deeds et al., 1999). A gaseous tracer technique has also been used for detecting NAPL in soil (Whitley et al., 1999; Deeds et al., 1999; Mariner et al., 1999). And the use of gaseous water-partitioning tracers has also been found to be feasible for measuring the degree of water saturation of water-unsaturated soils (Kim et al., 1999; Nelson et al., 1999; Keller and Brusseau, 2003).

Reactive gaseous tracer techniques have been further refined in recent studies. Gases and vapors, with different partitioning properties, were introduced to investigate the physical arrangement of fluids, as well as their volumes (Kim et al., 2007). Gases or vapors, which partition only into NAPL and are insoluble in the aqueous phase, are used as partitioning tracers for measuring the gas-exposed NAPL saturation. Some gaseous chemicals that partition only into the aqueous phase, with sparing solubility into NAPL, can be used for determining water saturation. Vapors that partition into both the aqueous phase and NAPL can be used to detect total NAPL saturations.

The purpose of this study was to investigate the applicability of the gaseous reactive tracer technique for evaluating the volume changes of fluids, including NAPL (perchloroethene used in this study), during the removal of NAPL via vaporization/volatilization. The degree of NAPL

depletion and the ratio of NAPL saturation exposed to the mobile gas phase compared to the total NAPL have been found to be correlated, and are of great interest in understanding the removal processes of sparingly water-soluble, volatile NAPL during gas-driven remediation techniques, such as SVE (soil vapor extraction).

2. Theoretical Background

The travel velocities of gaseous tracers under gas-flowing conditions in water-unsaturated soils are affected by the partitioning processes. The ratio of the travel velocity of the nonreactive tracer to that of a reactive tracer is known as the retardation factor (R_t , dimensionless) (Eq. 1);

$$R_t = \frac{v_g}{v_t} = \frac{\bar{t}_i}{\bar{t}_g} \quad (1)$$

where v_t and v_g are the linear velocities (cm/min) of the tracer and the gas phase, respectively, and \bar{t}_i and \bar{t}_g are the mean residence times (min) of the tracer in the medium and in the gas phase, respectively. The velocity (and thus the residence time) of the mobile gas phase is measured using a nonreactive tracer, the travel velocity of which is expected to be the same as that of the mobile gas (flowing domain). Reactive tracers selected for fluid volume measurement travel in the mobile gas phase at slower velocities than the mobile gas due to partitioning into the stationary fluids, where no transport occurs. The magnitude of the retardation factor is a function of the volumetric saturation of the partitioning phases and the partitioning coefficients (Eq. 2) (Kim et al., 2007):

$$R_t = 1 + \frac{S_w}{K_H S_g} + \frac{K_n (S_{na} + S_{mw})}{S_g} \quad (2)$$

where S_w , S_g , S_{na} and S_{mw} are the volumetric fluid saturations (cm³-fluid/cm³-total fluid) of the aqueous phase, gas phase, and the NAPL exposed to the mobile gas, as well as that not exposed to the mobile gas, respectively, and K_n is the partition coefficient (dimensionless) of a chemical (tracer) between the NAPL and gas phase (Eq. 3):

$$K_H = \frac{C_n}{C_g} \quad (3)$$

where C_n and C_g are the molar concentrations (mol/L) of the tracer in the NAPL and gas phases, respectively, and K_H Henry's law constant (dimensionless)(Eq. 4):

$$K_H = \frac{C_g}{C_w} \quad (4)$$

where C_w is the aqueous concentration (mol/L) of the tracer.

The value of S_g can be obtained from the travel time (\bar{t}_g) of the nonreactive tracer and the flow rate of the mobile gas. Suppose the partitioning coefficients, K_H and K_n , of a tracer are known, the fluid saturations (S_w , S_{na} , S_{nw}) shown in Eq. 2 can be calculated using experimentally determined tracer retardation factors. Water partitioning tracers that do not partition into the NAPL (thus $K_n=0$) would have slower travel velocities than a nonreactive tracer due to the second term, $S_w/(K_H S_g)$, in Eq. 2, resulting in a retardation factor larger than unity. Tracers that are water insoluble and NAPL soluble may partition into the NAPL exposed to the mobile gas. The retardation factors of these kinds of tracers can be used to estimate S_{na} (Eq. 2), assuming $S_{nw}=0$. The saturation of NAPL separated from the mobile gas by the resident water can be measured using a tracer partitioned between the NAPL and aqueous phases, which would detect all of the NAPL ($S_{na}+S_{nw}$), regardless the NAPL exposed to the mobile gas, by combining the results from the aforementioned NAPL-partitioning tracer.

The transport of a tracer is monitored by analyzing the tracer concentration over time at a location a finite distance from the tracer injection point. The mean residence time, \bar{t}_i of the tracer molecules can be calculated from the time-concentration profile, called the breakthrough curve (BTC)(Valocchi, 1985):

$$\mu' = \frac{\int_0^\infty C(t)tdt}{\int_0^\infty C(t)dt} = \bar{t}_i \quad (5)$$

where μ' is the normalized temporal first moment (min) of the tracer, which is equivalent to the mean residence time, $C(t)$ the concentration (mol/cm³) of the tracer, and t the time (min). The retardation factors of reactive tracers are calculated using the residence times of reactive and nonreactive tracers (Eq. 1). The gas saturation (S_g) is directly related to the residence time of a nonreactive tracer:

$$S_g = \frac{\bar{t}_N q_g}{V_T} \quad (6)$$

where \bar{t}_N is the residence time (min) of nonreactive tracer, q_g the flow rate (cm³/min) of the mobile gas, and V_T the total volume (cm³) of the fluid domain.

3. Materials and Methods

3.1. Materials

Quartz sand, with a diameter range of 200 - 500 μ m, was used as the porous medium. Reagent grade perchloroethene (PCE), *n*-pentane, chloroform and difluoromethane (DFM) were supplied from Aldrich Chemical Co., and used as NAPL, the NAPL-partitioning tracer, NAPL and water-partitioning tracer, and water-partitioning tracer, respectively. Methane (> 99.99%), provided by Aldrich Chemical Co., was used as the nonreactive tracer. Purified air was used as the mobile gas during the PCE removal experiments. Double distilled (DI) water was used throughout the experiments. The properties of the chemicals relevant to this study are listed in Table 1.

3.2. Experimental Set-up

A schematic diagram of the experimental set-up used in this study is shown in Fig. 1. The length and inner diameter of the sand column were 81.0 and 5.25 cm, respectively.

Table 1. Properties of the chemicals used in this study (25°C)

Chemical	Use	Mw	Vapor pressure ^a (kPa)	K_H ^b	K_n ^c for PCE
methane	non-reactive tracer	16.04	–	–	–
DFM	water-partitioning tracer	52.02	–	0.505 ^d	3.25
<i>n</i> -pentane	NAPL-partitioning tracer	72.15	68.4	50.5 ^a	197
chloroform	NAPL-water-partitioning tracer	119.40	25.6	0.153 ^a	721
PCE	NAPL	165.83	2.48	0.93 ^a	–

^a Mackay and Shiu, 1981, ^b dimensionless (Eq. 4), ^c experimentally determined in this study, dimensionless (Eq. 3), ^d Keller and Brusseau, 2003,

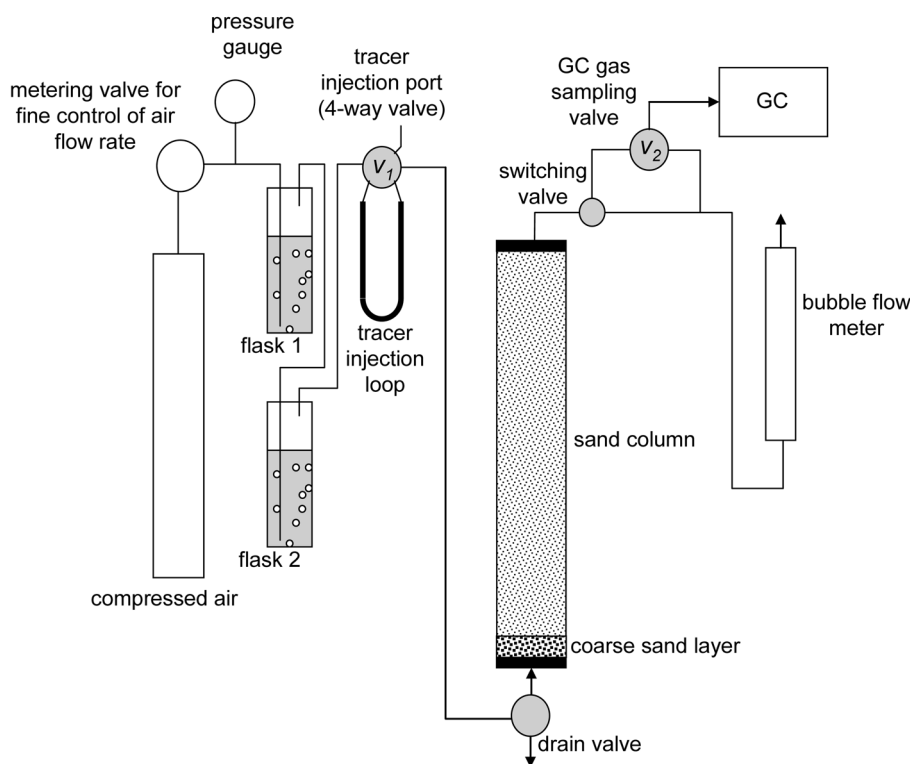


Fig. 1. Schematic diagram of the experimental set-up; flask 1 was filled with DI water; flask 2 was filled with PCE.

Table 2. Experimental conditions for the column experiment

	Experiment I	Experiment II
Total volume of column (cm ³)	1,786	
Total mass of sand (g)	2,660	
Porosity	0.44	
Bulk density of sand (g/cm ³)	1.49	
PCE mass introduced (g)	31.1	
PCE volume introduced (cm ³)	19.2	
Water saturation	0	0.11
Gas flow rate (cm ³ /min)	10.0	14.5

Coarse sand (diameter range of 0.1 - 0.2 cm) was packed into the bottom 3 cm of the sand column for better distribution of the injected air during the experiments. The PCE-contaminated sand was packed in the column, with no open space, on top of the coarse sand layer. A pre-determined mass of PCE was mixed with a known mass of clean dry sand for packing [target PCE saturation (S_g) was about 0.03]. Two gas washing bottles (flask 1 filled with DI water and flask 2 filled with PCE, as shown in Fig. 1) were set between a compressed air cylinder and the column to provide the column with vapor (water and/or PCE)-saturated air when necessary. A 20 cm long stainless steel

loop (0.43 cm i.d.) was installed for injection of the tracer. A GC (Younglin Co. Ltd., Model 6000M) was connected to the column to analyze the PCE and tracers in the column effluent gas during the experiment. A Rheodyne valve, with a sample loop capacity of 200 L, was installed at the column outlet, which was used as the GC sampler. The conditions for the GC analysis were as follows: column Alltech Co., model OV101, and inlet, oven and detector temperatures of 150, 180 and 250°C, respectively, and an injection volume of 200 µL. The experimental conditions used in this study are summarized in Table 2. All the experiments were conducted at 25 ± 1°C .

3.3. Experimental Procedure

Two sets of tracer experiments were conducted: Experiment I - tracer experiments with a column packed with dry (no water introduced), PCE-contaminated sand. The aim of Experiment I was to quantify the PCE saturation and K_n value of DFM; Experiment II - tracer experiments with the same sand column used in Experiment I, but under wet conditions, with water saturation of 0.11 ± 0.01 . Tracers were introduced onto the column, while water vapor-saturated air flowed through the system. Experiments were continued until the PCE concentration was below the detection limit of the GC.

3.3.1. Experiment I

After dry packing the column with PCE-contaminated sand, a constant air flow of $10.5 \text{ cm}^3/\text{min}$ was passed through the system. The column inflow air was passed through the PCE-containing gas washing bottle to saturate the air with PCE vapor and prevent PCE mass loss due to vaporization from the residual PCE in the column during the tracer experiment. However, the other gas washing bottle was bypassed so as not to introduce water into the column.

Tracer experiments were conducted in a sequential manner, starting with methane. Upon completion of one experiment, the next tracer experiment was conducted. A compressed methane bottle was connected to the switching valve (v_1 in Fig. 1) and the loop filled with methane gas at ambient pressure. The methane experiment was started when the methane gas was introduced onto the column. The methane concentration in the column effluent gas was analyzed using the GC until the concentration dropped below the detection limit of the instrument. The same procedure was used for DFM. Since *n*-pentane and

chloroform are liquids under ambient conditions, a small amount of liquid tracer ($100 \mu\text{L}$ for *n*-pentane, $500 \mu\text{L}$ for chloroform) was introduced into the loop. The loop was plugged at both ends, and then placed in an oven at 50°C for 30 minutes to allow vaporization. The loop was cooled before being reinstalled into the system. The tracer injection was continued for less than 4 minutes, which was considered sufficient to push all the gas or vapor onto the column.

3.3.2. Experiment II

The same dry column used in Experiment I was also used for Experiment II. The air supply was momentarily replaced with CO_2 , which was passed through the PCE-containing gas washing bottle to replace the air in the column with CO_2 . An aqueous solution, pre-saturated with PCE, was then introduced onto the CO_2 -filled column via the drain valve. The resident CO_2 was expected to enhance the water-saturation process due to its higher water solubility than air. Flushing with water was continued until no gas pocket was observed, with the water in the column then drained from the drain valve.

Before the gas flush experiment, the mobile gas was switched back to air, with the flow of air onto the column set to pass through the gas washing bottles. A constant gas flow rate of $14.3 \text{ cm}^3/\text{min}$ was used throughout the experiment. When the gas flow rate had become constant, the gas washing bottle filled with PCE (flask 2 in Fig. 1) was bypassed, with the PCE removal experiment then started. The tracers were introduced onto the column in the same manner used in Experiment I. The time table for the tracer experiment is shown in Table 3.

When the PCE concentration in the column gas effluent was below the detection limit of the GC, the gas flush

Table 3. Tracer injection protocol in Experiment II: the lapse volume was calculated from the gas flow rate and the time of the injection

	methane	<i>n</i> -pentane	DFM	Chloroform
Injection lapse volume (L)		0.49		
	13.9	42.4		
	55.8	83.7	64.9	
	97.6	126.0	151.3	275.0
	140.5	168.2	277.1	
	182.0	211.3		
		265.7		

experiment was stopped. Methylene chloride (2 L) was used to extract the PCE from the sand for the determination of the residual PCE after the experiment. The PCE extract was analyzed using a GC (Younglin Co. Ltd., Model 6000M); column HP-5 (15 m × 0.25 mm × 0.25 μL), and inlet, oven and detector temperatures of 150, 80 and 250°C, respectively, with an injection volume of 10 μL.

3.3.3. Measurement of K_n Values

Two sets of batch experiments were also conducted to measure the K_n values of *n*-pentane and chloroform with respect to PCE. For each set, serum bottles, with 160 cm³ capacities, sealed with Teflon-lined caps, were used. 4 μL of a tracer was placed into each bottle, followed by vaporization in an oven at 35°C for 30 minutes. After the bottles had cooled, PCE was injected into each bottle, ranging from 0.5 to 3.0 cm³. The gas sample in the head space of the bottle was taken via a gas-tight syringe (200 μL), with the tracers analyzed using the same GC method as for the tracer experiment.

4. Results and Discussion

4.1. Experiment I and the K_n Values

Under dry conditions, with no water introduced into the sand column, the first temporal moment of methane was calculated from the BTC (Fig. 2), and then converted to the lapse volume, 0.78 liters, which was the measured volume of the gas phase (Table 4). The total empty volume of the column was estimated to be about 0.80 liters, based on the mass of sand and total volume of the column. Considering the volume of PCE introduced onto the column, with a

target saturation (S_n) of 0.03, this discrepancy can be explained by the volume of PCE (PCE saturation of 0.03 is equivalent to 0.024 liters). Thus, methane, used in this study as the nonreactive tracer, indeed behaved nonreactively with respect to the NAPL phase; no significant partition into PCE took place. The gas saturation (S_g) of the sand column was 0.98.

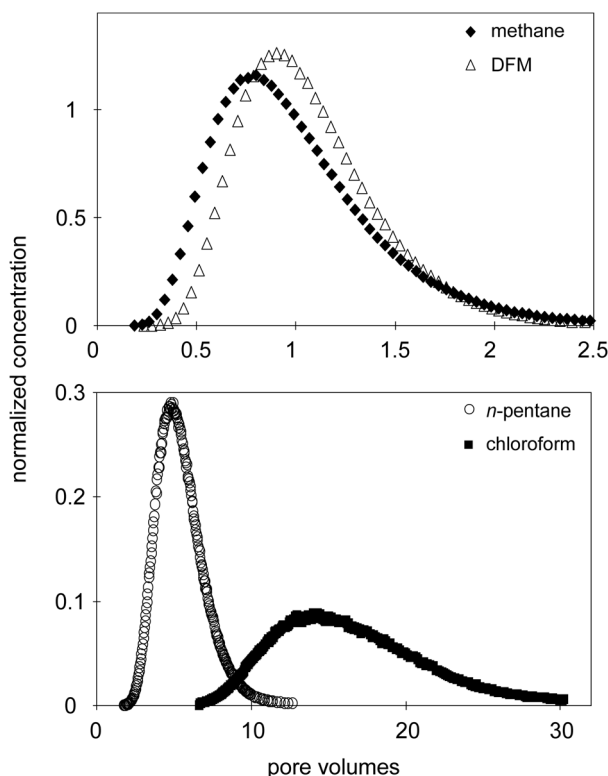


Fig. 2. BTCs of the tracers measured under dry conditions (Experiment I); normalized concentration - concentration normalized to the total area of the BTC so that the total area became unity; pore volume - cumulative lapse volume divided by the total volume of the gas phase.

Table 4. Experimental results from the application of methane (non-reactive tracer)

	Injection lapse volume (L)	Temporal 1 st moment (L)	Calculated volume of water (L)	S_g	S_w
Experiment I	—	0.782	—	0.98	0
Experiment II	13.9	0.693	0.090	0.87	0.112
	55.8	0.683	0.104	0.85	0.130
	97.6	0.713	0.078	0.89	0.098
	140.5	0.709	0.086	0.89	0.108
	182.0	0.711	0.089	0.89	0.111
mean ± sd ^a		0.70 ± 0.013	0.089 ± 0.009	0.89 ± 0.04	0.11 ± 0.01

^a standard deviation

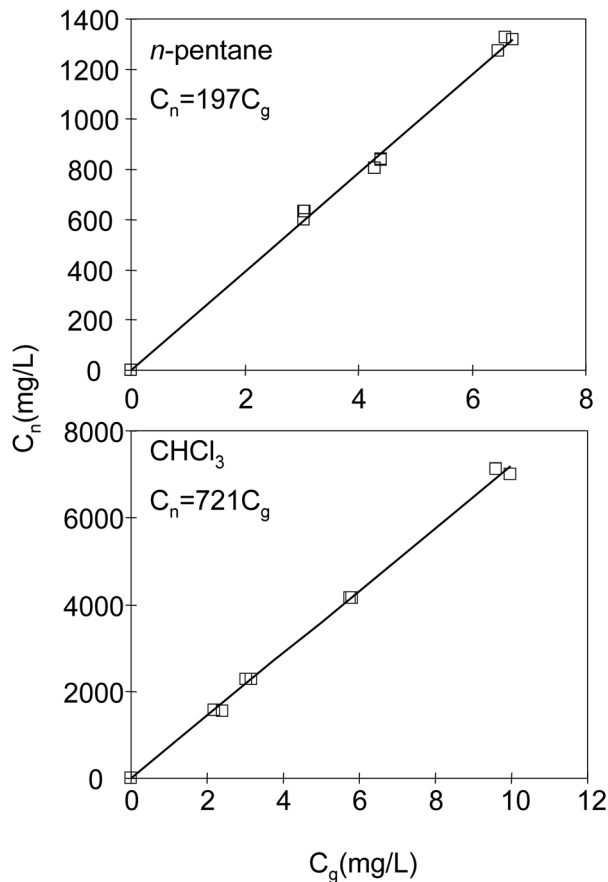


Fig. 3. Partition isotherms for *n*-pentane and chloroform (CHCl_3) into PCE.

In order to use Eq. 2 for estimating the value of S_n based on an R_t value, the partitioning coefficient (K_n) should be known. The K_n values for *n*-pentane and chloroform with respect to PCE were measured to be 197 and 721, respectively (Fig. 3). The retardation factor of *n*-pentane was calculated to be 5.72, using manual integration of the *n*-pentane BTC (Fig. 2). Assuming $S_w = 0$ (no water present), $S_{nw} = 0$ (all the PCE was considered to be exposed to the gas phase), and $S_g = 0.98$, and using K_n (197) and R_t (5.72) values, the S_n was calculated to be 0.024, which was equivalent to a PCE volume of 19.2 cm^3 . The S_n value calculated from the BTC of chloroform ($R_t = 17.7$) was 0.023, which was slightly lower than that of *n*-pentane, but in good agreement with that of *n*-pentane. The target S_n value was 0.03, which was calculated from the mass of PCE mixed with the sand prepared for column packing, which differed from the measured S_n values by 0.006. Vaporization of PCE during column packing was believed

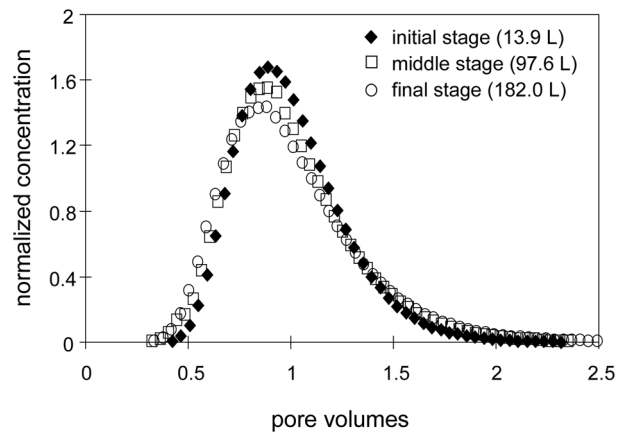


Fig. 4. Methane BTCs measured at different lapse times (converted to lapse volume) under wet conditions (Experiment II).

to be responsible for this mass loss.

The partitioning behavior of DFM into PCE was also investigated. Although DFM was selected as the water-partitioning tracer, because it was expected to partition exclusively into the aqueous phase, the K_n value was also estimated using the R_t value (1.08) calculated from the BTC (Fig. 2), and the S_n (0.024) value measured using *n*-pentane. Using Eq. 2, the K_n value of DFM was estimated to be 3.2, which was significantly lower than those of other partitioning tracers. This small value; however, can not be ignored when the S_w value is low compared to S_n . Since the K_n of DFM is similar (by factors) to the reciprocal of K_H (0.505), PCE partitioning must be taken into account unless the S_n value is significantly lower than S_w .

4.2. Experiment II – PCE Removal

The methane BTCs measured during the PCE removal experiment are shown in Fig. 4. Of the five measured BTCs, only three, which were measured at the beginning, middle and final stage of the PCE removal experiment, are shown in the figure. The BTCs were almost on top of each other, meaning that the volume of the gas phase remained unchanged during the PCE removal gas flush experiment.

The first temporal moments of methane, converted to the lapse volume by multiplying the time with the flow rate of the mobile gas, are shown in Table 4. As shown in Fig. 4, the first temporal moments were very close to each other, implying that the volume of the gas phase remained unchanged during the experiment. The mean gas volume

was 0.70 liters. The difference between that measured for the dry column (Experiment I) and the mean gas volume of the wet column was 0.082 liters, which mostly represented the volume of water introduced onto the column for the experiment under wet conditions. The exact estimation of the water volume (or S_w) based on the first moments of methane was slightly more complicated due to the presence of PCE, the volume of which decreased over time during the removal process, which increased the volume of the gas phase. Thus, the exact PCE volume has to be known to calculate the water volume (or S_w) based on the first moments of methane. The water volumes and S_w values calculated using PCE volumes and the first moments of methane are listed in Table 4 (removal of PCE will be discussed later).

The BTCs of DFM are shown in Fig. 5(a). All the BTCs were fairly close to each other, meaning the water saturation was not significantly changed during the experiment. Using the R_t values of DFM measured at the beginning, middle and final stage of the PCE removal process, the calculated S_w values, ignoring the presence of PCE [thus, $S_n (=S_{na} + S_{nw})$ in Eq. 3 assumed 0], were 0.11, 0.10 and 0.077, respectively. With the PCE saturation taken into account, the S_w became slightly lower (Table 5). Because low water saturation was maintained in this study, S_n can not be ignored when calculating S_w using the retardation factors of DFM. However, the errors associated with the calculation of S_w by neglecting S_n would be much less significant with increasing S_w values.

The S_w values measured using DFM were slightly lower than those using the nonreactive tracer. The R_t values of DFM were less than 1.3, with only 0.3 coming from the PCE partitioning and water partitioning processes, which was used to calculate S_w . Thus, a small measurement error

during the tracer test might result in an error in the calculated S_w .

The BTCs of *n*-pentane measured during the PCE removal process are shown in Fig. 6. It was very clear that *n*-pentane broke through the column faster as the PCE removal process progressed. The retardation factors calculated using the temporal first moments of *n*-pentane and methane are shown in Fig. 8(a). Since the retardation factor of *n*-pentane is a direct function of the saturation of

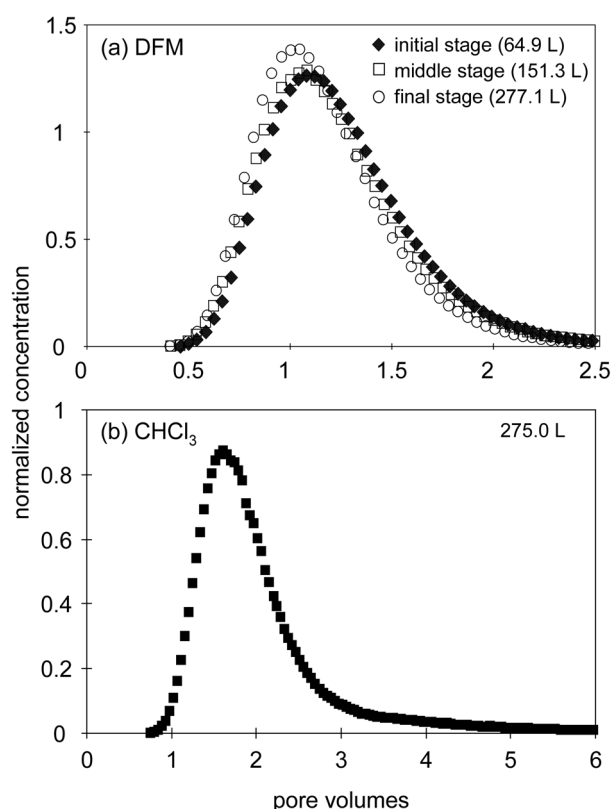


Fig. 5. BTCs for DFM and chloroform measured at different lapse times (converted to lapse volume) under wet conditions (Experiment II).

Table 5. Experimental results from the application of DFM (water-partitioning tracer)

	Injection lapse volume (L)	R_t	S_w^a	S_w^b	S_n^c
Experiment I	–	1.08	0	0	0.024
Experiment II	64.9	1.26	0.087	0.113	0.016
	151.3	1.23	0.093	0.102	0.006
	277.1	1.17	0.075	0.077	< 0.001

^a calculated from the 1st moment of DFM with S_n taken into account

^b calculated from the 1st moment of DFM assuming $S_n = 0$

^c measured from the *n*-pentane experiment (Experiment I) and PCE depletion profile (Fig. 7, Experiment II)

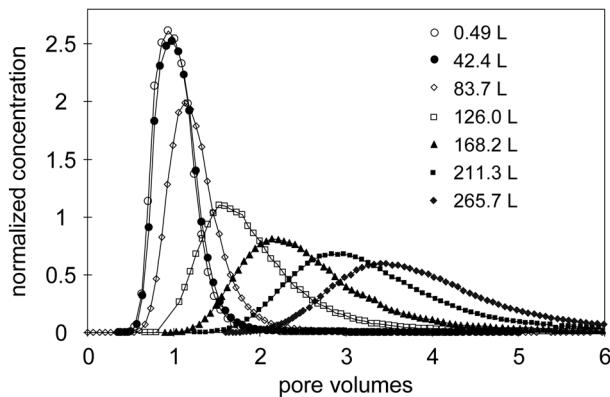


Fig. 6. BTCs for *n*-pentane measured at different lapse times (converted to lapse volume) under wet conditions (Experiment II).

PCE exposed to the mobile gas, the S_n measured using *n*-pentane at the beginning stage (injection lapse volume 0.5 liter, or lapse time 0.5 hour), divided by the S_n measured under dry conditions, is the ratio of the gas-exposed PCE saturation (S_{na}) to the total PCE saturation. Using the S_n (0.024) measured under dry conditions and S_{na} (0.016) measured under wet conditions, 65.4% of the total PCE was found to be exposed to the mobile gas at the beginning of the removal process. This ratio of S_{na} to S_n might be of great interest when the target NAPL is water insoluble, with only gas-exposed NAPL subject to transfer to the mobile gas phase by vaporization during the gas-driven remediation (e.g., soil vapor extraction) of NAPL-contaminated soil.

The PCE concentration profile in the column effluent is shown in Fig. 7(a). The PCE concentration was fairly consistent, between 140 - 170 mg/L, which was close to the maximum concentration (170 mg/L) in the gas phase calculated from the vapor pressure of PCE at 25°C (Table 1). The PCE concentration suddenly dropped at a lapse volume of 180 L, where most of the PCE on the column was believed to have been depleted. The cumulative PCE removal profile (Fig. 7(b)) gave almost a straight line until the PCE concentration dropped. With the removal of PCE, the retardation of *n*-pentane became smaller (Fig. 8(a)), as did the PCE mass and S_{na} remaining on the column (Fig. 8(b)), as calculated from the R_t values of *n*-pentane. The ratio of gas-exposed PCE saturation to the total PCE saturation, S_{na}/S_n , calculated using data from Fig. 8(b), is shown in Fig 8(c). This ratio decreased with the removal of PCE. This observation explains that the gas-exposed PCE

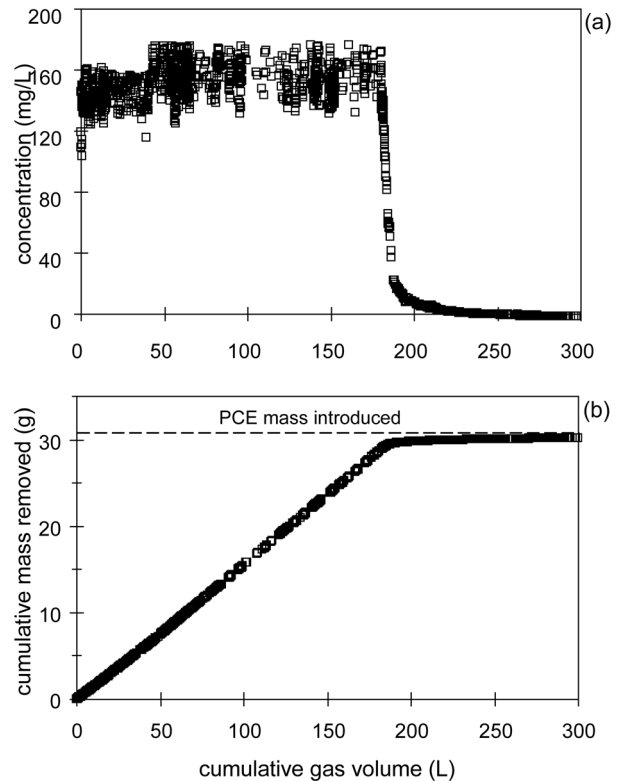


Fig. 7. (a) PCE concentrations measured during gas flush, (b) cumulative PCE mass removed during the experiment, where the dotted horizontal line represents the initial PCE mass introduced onto the column (measured in Experiment I).

was preferentially removed compared to PCE, which was separated from the mobile gas by water. If the NAPL is water insoluble and/or has a very low Henry's law constant, unlike PCE, the removal of the NAPL would be limited to the initial S_{na} , unless the water preventing the NAPL from contacting with the mobile air is disturbed, where the buried NAPL would become exposed. Since PCE has a moderate water solubility (151 mg/L) (Mackay and Shiu, 1981) and Henry's law constant (0.93), the PCE separated from the mobile gas would possibly be transferred to the mobile gas via dissolution and volatilization. However, the mass transfer rate due to vaporization (direct mass transfer from the NAPL to the gas phase) is generally known to be much faster than the dissolution-volatilization process. Thus, analyzing the S_{na}/S_n ratio might be very advantageous for investigating the removal mechanism of NAPL from water-unsaturated soils.

Chloroform was used at the final stage of the PCE removal process to measure the residual PCE. Based on the

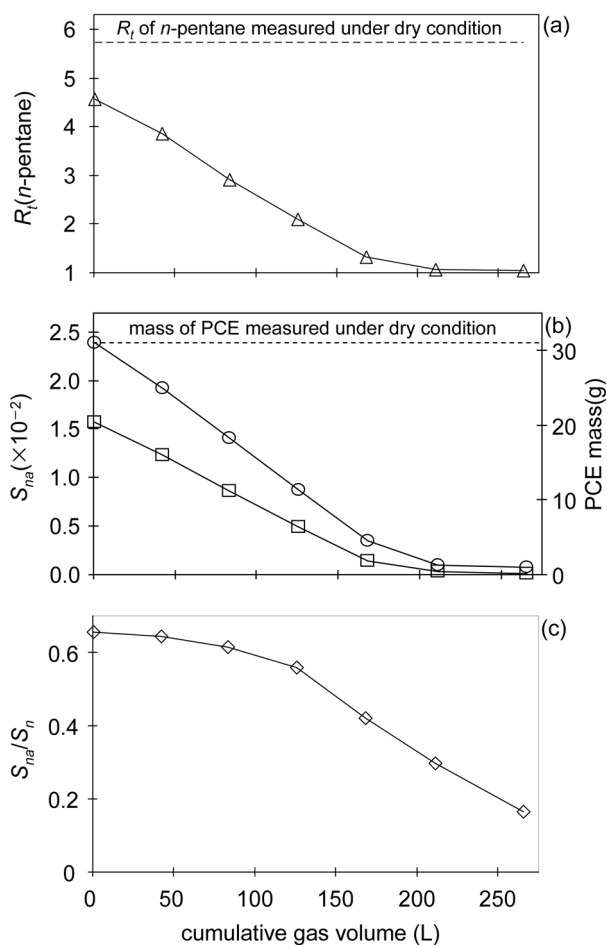


Fig. 8. (a) Retardation factors of n -pentane measured during the PCE removal experiment, (b) residual PCE on the sand column - circle: quantity of PCE calculated from the initial mass and the mass of PCE removed (by gas effluent analysis GC, Fig. 7), square: PCE quantity calculated from the R_t values of n -pentane, and (c) the ratio of the gas-exposed PCE mass to the total mass.

measured BTC (Fig. 5(b)), the calculated R_t was 2.10. Using this value and the S_g value (0.11) measured using methane, the residual PCE mass was estimated to be 0.7 grams. The mass of residual PCE estimated from the initial mass of PCE (31.1 grams) under dry conditions and the total mass removed (30.3 grams) was 0.9 grams, which was in fair agreement with that measured using chloroform. The PCE mass extracted from the sand after the experiment was about 0.6 grams, which was close to that measured using chloroform.

5. Conclusions

This study showed that the use of the tracer (n -pentane

used in this study), which partitions only into the gas-exposed NAPL, when used with nonreactive and other reactive tracers, could provide critical information regarding the fluid arrangement in soils. For the column packed with partially water-saturated sand (water saturation 0.11), the ratio of gas-exposed PCE saturation to the total PCE saturation was measured during the PCE removal experiment, with the gas-exposed PCE found to be removed faster compared to the PCE isolated from the mobile gas by the aqueous phase. However, more PCE than that measured using n -pentane (that is the gas-exposed PCE) was removed from the column, implying volatilization, as well as vaporization, was also responsible for the mass depletion of PCE.

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References

- Annable, M.D., Jawitz, J.W., Rao, P.S.C., Dai, D.P., Kim, H., and Wood, A.L., 1998(a), Field evaluation of interfacial and partitioning tracers for characterization of effective NAPL-water contact areas, *Ground Water*, **36**, 495-502.
- Annable, M.D., Rao, P.S.C., Hatfield, K., Graham, W.D., Wood, A. L., and Enfield, C.G., 1998(b), Partitioning tracers for measuring residual NAPL: Field-scale test results, *J. Environ. Eng.*, **124**, 498-503.
- Deeds, N.E., Pope, G.A., and McKinney, D.C., 1999, Vadose zone characterization at a contaminated field site using partitioning interwell tracer technology, *Environ. Sci. Technol.*, **33**, 2745-2751.
- Hunkeler, D., Hoehn, E., Höhener, P., and Zeyer, J., 1997, ^{222}Rn as a partitioning tracer to detect diesel fuel contamination in aquifers: Laboratory study and field observations, *Environ. Sci. Technol.*, **31**, 3180-3187.
- Jin, M., Delshad, M., Dwarakanath, V., McKinney, D.C., Pope, G.A., Sepehrmoori, K., and Tilburg, C.E., 1995, Partitioning tracer test for detection, estimation, and remediation performance assessment of subsurface nonaqueous phase liquids, *Water Resour. Res.*, **31**, 1201-1211.
- Keller, J.M. and Brusseau, M.L., 2003, In-situ characterization

- of soil-water content using gas-phase partitioning tracer tests: Field-scale evaluation, *Environ. Sci. Technol.*, **37**, 3141-3144.
- Kim, H., Choi, K.-M., Rao, and P. Suresh. C., 2007, Measurement of gas-accessible NAPL saturation in soil using gaseous tracers, *Environ. Sci. Technol.*, **41**, 235-241.
- Kim, H., Rao, P.S.C., and Annable, M.D., 1999, Gaseous tracer technique for estimating air-water interfacial areas and interface mobility, *Soil Sci. Soc. Am. J.*, **63**, 1554-1560.
- Mackay, D. and Shiu, W.Y., 1981, A critical-review of Henry's law constants for chemicals of environmental interest, *J. Phys. Chem. Ref. Data*, **10**, 1175-1199.
- Mariner, P.E., Jin, M., Studer, J.E., and Pope, G.A., 1999, The first vadose zone partitioning interwell tracer test for nonaqueous phase liquid and water residual, *Environ. Sci. Technol.*, **33**, 2825-2828.
- Nelson, N.T. and Brusseau, M.L., 1996, Field study of the partitioning tracer method for detection of dense nonaqueous phase liquid in a trichloroethene-contaminated aquifer, *Environ. Sci. Technol.*, **30**, 2859-2863.
- Nelson, N.T., Brusseau, M.L., Carlson, T.D., Costanza, M.S., Young, M.H., Johnson, G.R., and Wierenga, P.J., 1999, A gas-phase partitioning tracer method for the in situ measurement of soil-water content, *Water Resour. Res.*, **35**, 3699-3707.
- Nelson, N.T., Oostrom, M., Wietsma, T.W., and Brusseau, M.L., 1999, Partitioning tracer method for the in situ measurement of DNAPL saturation: Influence of heterogeneity and sampling method, *Environ. Sci. Technol.*, **33**, 4046-4053.
- Valocchi, A.J., 1985, Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils, *Water Resour. Res.*, **21**, 808-820.
- Whitley Jr., G.A., McKinney, D.C., Pope, G.A., Rouse, B.A., and Deeds, N.E., 1999, Contaminated vadose zone characterization using partitioning gas tracers, *J. Environ. Eng.*, **125**, 574-582.
- Young, C.M., Jackson, R.E., Jin, M., Londergan, J.T., Mariner, P.E., Pope, G.A., Anderson, F.J., and Houk, T., 1999, Characterization of a TCE DNAPL zone in alluvium by partitioning tracers, *Ground Water Monit. Rem.*, **19**, 84-94.