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## Abstract

A major challenge in ground water remediation is locating nonaqueous phase liquids (NAPLs). Partitioning tracers can be used to identify NAPL sources between injection and extraction wells. NAPLs are only slightly soluble in water, pose a long-term source of groundwater contamination, and can be difficult to remove. The complexity of recovery processes requires the development of new technologies that guarantee cost-effective methods for locating and quantifying NAPLs. Traditional methods like soil coring have been inefficient since they underestimate the quantity of NAPLs and are expensive. Partitioning tracer tests are some of the most recent methods developed for locating these contaminants and determining the volume of the NAPL present in the inter-well zone. The results of the tests can be used to develop remediation techniques to recover NAPLs entrapped in the contaminated zone. Fluorescent dyes may be useful as partitioning tracers. They can be analyzed quickly at the field site, resulting in a shorter analysis time and lower costs than other partitioning tracers. This project pursued the selection of suitable tracers and the development of partitioning tracer techniques to locate and quantify NAPLs in the subsurface.

## Introduction

Partitioning tracer methods consist of the simultaneous injection of a conservative (nonpartitioning) tracer along with one or several partitioning tracers. The average NAPL saturation is determined on the basis of the retardation of the partitioning tracer relative to the nonpartitioning tracer (Jin et al., 1995; Hunkeler et al., 1997; Annable et al., 1998a). An ideal partitioning tracer should have the following properties: a) the ability to mimic the velocity pattern of the groundwater movement in the absence of NAPL; b) be somewhat hydrophobic and water-soluble; c) have low retardation in the absence of NAPL and have delayed of breakthrough relative to non-partitioning tracer in presence of NAPL; d) be easily detected in very low concentrations; e) be inexpensive, f) be nonhazardous, nontoxic; and g) be nondegrading (Seaman, 1998; Aley, 1998; Annable et al., 1998b).

The most important characteristic of fluorescent tracers is sorption (Hadi et al., 1997). Sorption properties are due to the polar or non-polar character in their functional groups. Hydrochemical conditions such as temperature, salinity, pH, background fluorescence of dye-free sample, turbidity, and suspended solids may affect the structure and analysis of the dyes (Feuerstein and Selleck, 1963). Changing the pH can change the spectral properties of the dye molecules. The fluorescence of fluorescein and pyranine was observed to decrease at low pH values as a function of the ions causing the pH change. The absorbency of these species was

increasing with decreasing pH (Behrens, 1986). Sorption properties of rhodamine WT (RWT) were also observed to increase with decreasing pH (Smart and Laidlaw, 1977).

Previous research works have been performed to find appropriate partitioning fluorescent dyes. Fluorescein and RWT were evaluated as adsorbing ground-water tracers. Experimental results indicated the tracers were effective for characterization of atrazine and alachlor (Sabatini and Austin, 1991). Soerens and Sabatini (1996) examined the effects of experimental methods and conditions on sorption parameters determined for RWT. They found that multiple compounds or isomers in RWT could originate significant errors in contaminant transport studies if they are not recognized in batch or column data. Structural isomers for RWT were also studied by Shiao et al. (1993) in two surface media. Batch and column studies demonstrated that the isomers were responsible for the two-step sigmoidal breakthrough curve. Rhodamine B (RB) and RWT were evaluated as potential partitioning tracers for detection and measurement of tetrachloroethylenene (Stainton and Soerens, 1997). Retardation factors found from batch tests were comparable to those calculated from column tests. RB was determined not to be a suitable partitioning tracer. In this study, RWT did not exhibit the two-step breakthrough curve predicted.

This project pursues the selection of suitable fluorescent tracers to identify zones of residual DNAPLs by inter-well tests. The objective of this study is to evaluate the use of some fluorescent dyes as suitable tracers in a water-saturat-

ed porous medium with tetrachloroethylenene (PCE) using laboratory column and batch studies.

### Materials and Methods

**Materials.**—Five fluorescent dyes were tested. They are fluorescein, as a conservative tracer, and eosine, RWT, sulforhodamine B (SRB), and pyranine, as partitioning tracers. PCE was chosen as the NAPL to be tested in this study. Ottawa sand was used as the sorbent for batch and column experiments. For batch experiments, the sand was washed with tap water until clear, then rinsed five times with distilled water, and oven dried at 100°C for 24 hours. Distilled water was used in all experiments.

**Batch Tests.**—Batch experiments were conducted to calculate the partitioning coefficient in two different systems: PCE/dye and soil/dye. In PCE/dye tests, a volume of dye solution ( $V_S$ ) was added to a volume of PCE ( $V_N$ ) in an Erlenmeyer flask. A PCE/dye ratio of 1:4 was used. Four reactors were prepared for tracer concentrations of 25, 50, 100, and 150  $\mu\text{g/L}$ . Flasks were capped to avoid evaporation. Reactors were continuously stirred at approximately 307 rpm for 2 hours; then all were allowed to settle for about 24 hours. The initial concentration ( $C_O$ ) and concentration of the tracer in the aqueous phase ( $C_W$ ) for each sample were determined from fluorometer readings. Measurements were compared to a control. The batch tests were conducted at room temperature ( $22 \pm 2^\circ\text{C}$ ). The PCE-water partitioning coefficient ( $K_{NW}$ ) was calculated using the following relationship:

$$K_{NW} = \frac{C_N}{C_W} \quad (1)$$

The concentration of the dye in the PCE ( $C_N$ ) is given by

$$C_N = \frac{(C_O - C_W) V_S}{V_N} \quad (2)$$

Values of  $C_N$  versus  $C_W$  were plotted to create a linear sorption isotherm, and the  $K_{NW}$  value was determined by regression analysis for each dye.

Soil/dye tests were conducted by placing a mass of Ottawa Sand ( $M_S$ ) in each of a series of sample vessels and adding a volume of dye solution ( $V_S$ ) at different concentrations. Several ratios of  $M_S:V_S$  (g/mL) were analyzed (20:20, 30:15, 30:10). Tests were conducted at room temperature ( $22 \pm 2^\circ\text{C}$ ). Two sets of reactors were evaluated for each group of conditions. After shaking, reactors were allowed to reach the equilibrium for a period of 24 hours. Following this period, reactors were placed in a centrifuge. Dye was

drawn off with a 10 mL syringe, and fluorescence was measured. The initial concentration ( $C_O$ ) and equilibrium concentration ( $C$ ) of the tracer were determined from fluorometer readings. The amount of dye sorbed to the soil ( $q$ ) was calculated by using

$$q = \frac{(C_O - C) V_S}{M_S} \quad (3)$$

Values of  $q$  were determined at different concentrations in the reactors. Plots of  $q$  versus  $C$  were used to define a linear sorption isotherm, where the slope is the sorption partitioning coefficient ( $K_p$ ). This value was determined by

$$q = K_p C \quad (4)$$

From batch tests,  $K_{NW}$  and  $K_p$  were used to predict values of  $R_f$  (Jin et al., 1997; Annable et al., 1998a, b; Wright et al., 1996).

$$R_f = \frac{t_p}{t_n} = 1 + \frac{K_{NW} S_N + \rho_b K_p}{(1 - S_N) \eta S_W}$$

where,  $\eta$  = porosity,  $t_p$  = average travel time for partitioning tracer,  $t_n$  = average travel time for non-partitioning tracer,  $\rho_b$  = bulk density,  $S_N$  = NAPL saturation, and  $S_W$  = water saturation.

**Column Tests.**—Experiments were conducted in a chromatography column, packed with Ottawa sand and then saturated with distilled water for 48 hours at room temperature ( $22 \pm 2^\circ\text{C}$ ). The weight of the column was measured before and after saturation. Column properties were calculated by mass balance. The results are as follows: pore volume ( $V_O$ ) = 97.7 ml, porosity 0.35 (dimensionless), and bulk density = 1.70 g/ml. Flow was pumped through the column vertically using a peristaltic pump. Two different experiments were performed for each dye to determine the  $R_f$  of the tracers, soil/dye and soil/dye/PCE. In the former, three pore volumes (PV) of tracer solution (300 mL) were injected through the top of the column followed by several PVs of distilled water flowing in the same direction. In the second experiment, columns were saturated with PCE, following the same procedure used by Stainton and Soerens (1997). The volume of NAPL ( $V_N$ ) was calculated by mass measurement. The average flow velocity was  $4.44 \pm 0.31$  m/d. Column effluent was collected in a fraction collector. Fluorometer readings ( $C$ ) were taken after the process was completed.

Results from partitioning tracer experiments in columns were represented by breakthrough curves (BTCs). Microsoft Excel Solver GRG2, a nonlinear optimization code, was applied to determine  $R_f$ . The analytical solution of the one-dimensional advection-dispersion equation was used to calculate the predicted concentration of the tracer in the BTCs

as follow

$$\frac{C}{C_o} = 0.5 \left\{ \operatorname{erfc} \left[ \frac{R_f - \frac{V}{V_o}}{2 \left( \frac{1}{P_e} R_f \frac{V}{V_o} \right)^{0.5}} \right] + \exp(P_e) \operatorname{erfc} \left[ \frac{R_f + \frac{V}{V_o}}{2 \left( \frac{1}{P_e} R_f \frac{V}{V_o} \right)^{0.5}} \right] \right\} \quad (6)$$

where  $P_e$  = Peclet number,  $V$  = volume of the sample, and  $\operatorname{erfc}$  = complementary error function.

### Results and Discussion

**Batch Tests.**—Batch tests were conducted for all the tracers except for fluorescein since previous studies have demonstrated that it is conservative (Sabatini and Austin, 1991; Hadi et al.; 1997; Stainton and Soerens, 1997).

In soil/dye experiments, RWT demonstrated linearity for different  $M_s/V_s$  ratios in 75% of the results. However, SRB isotherms followed a linear relationship in only one of the three experiments conducted, but  $R^2$  was still very low (0.72).  $K_p$  values for RWT were between 0.066 and 0.115  $\text{cm}^3/\text{g}$  (Table 1). For SRB only one value, 0.091  $\text{cm}^3/\text{g}$ , was acceptable.  $K_p$  was independent of the tracer concentration for both RWT and SRB.

Table 1. Soil/Dye Partitioning Coefficient ( $K_p$ ) from Batch Tests

Tracer	$M_s/V_s$ g/ml	$K_p$ $\text{cm}^3/\text{g}$	
		Set #1	Set #2
		RWT	20/20
	30/15	0.066	0.082
SRB	20/20	0.091	0.036 <sup>(NS)</sup>
	30/10	0.022 <sup>(NS)</sup>	ND

NS = unsuccessful  
 ND = no data

Problems with fluorescence were encountered for eosine and pyranine; both of these dyes enhanced their fluorescence after equilibrium conditions were reached. Two possible parameters were thought to have an effect in the final fluorescence of these dyes: a) background fluorescence, and b) pH. The former was measured using a control sample for each dye. Investigations demonstrated that the background fluorescence did not have noticeable influence on

the results. A buffer solution (potassium phosphate monobasic-sodium hydroxide, 0.05 M) was added to eosine and pyranine samples in order to adjust the pH to 7. The samples with the buffer corresponded to the  $M_s/V_s$  ratio of 25/20. In order to compare the effects of the pH in Pyranine, the buffer solution was added to set #2 prior to performing the batch tests. Fluorometer readings were taken before and after buffering the samples. The adjusted pH had little effect in changing the fluorescence of eosine or pyranine.

PCE/dye partitioning coefficients were represented by linear isotherms. Results are summarized in Table 2. SRB isotherms did not have a good linear regression fit since the higher  $R^2$  value was 0.39. Pyranine increased its fluorescence at the equilibrium stage after the batch test. However, a linear relationship was also observed with respect to fluorescence with a  $K_{NW}$  equal to -3.061. This was based on the slope of the isotherm and  $R^2 = 1.00$ . This behavior could be the result of a structural change in the pyranine molecules originated by a change in the pH or the formation of a different chemical compound.

Table 2. PCE/Dye Partitioning Coefficient ( $K_{NW}$ ) from Batch Tests

Tracer	$V_s/V_N$	
	ml/ml	$K_{NW}$
RWT	160/40	0.1703
SRB	160/40	0.0603
Eosine	160/40	0.049
Pyranine	160/40	-3.061

**Column Tests.**—Experiments with fluorescein were conducted at an average flow rate of 1.70 mL/min. Regression analysis for this tracer gave an average  $R_f$  value of  $1.08 \pm 0.07$  (dimensionless). For RWT, the flow rate was  $1.73 \pm 0.1$  mL/min. The average retardation factor was determined to be  $1.64 \pm 0.38$ . Retardation factors for SRB, eosine, and pyranine were 1.23, 1.45, and 2.97, respectively. Breakthrough curves from column tests without PCE were represented in Fig. 1. Pyranine demonstrated to be the most retarded among the nonconservative tracers, and SRB was the least retarded. RWT showed the two-steps produced by isomers, similar to the results found in previous studies (Sabatini and Austin, 1991; Shiau et al., 1993; Soerens and Sabatini, 1996). Effects of the flow velocity in the  $R_f$  were noticed for both fluorescein and RWT. Higher velocities resulted in lower retardation factors. Only one value for RWT did not follow this pattern.

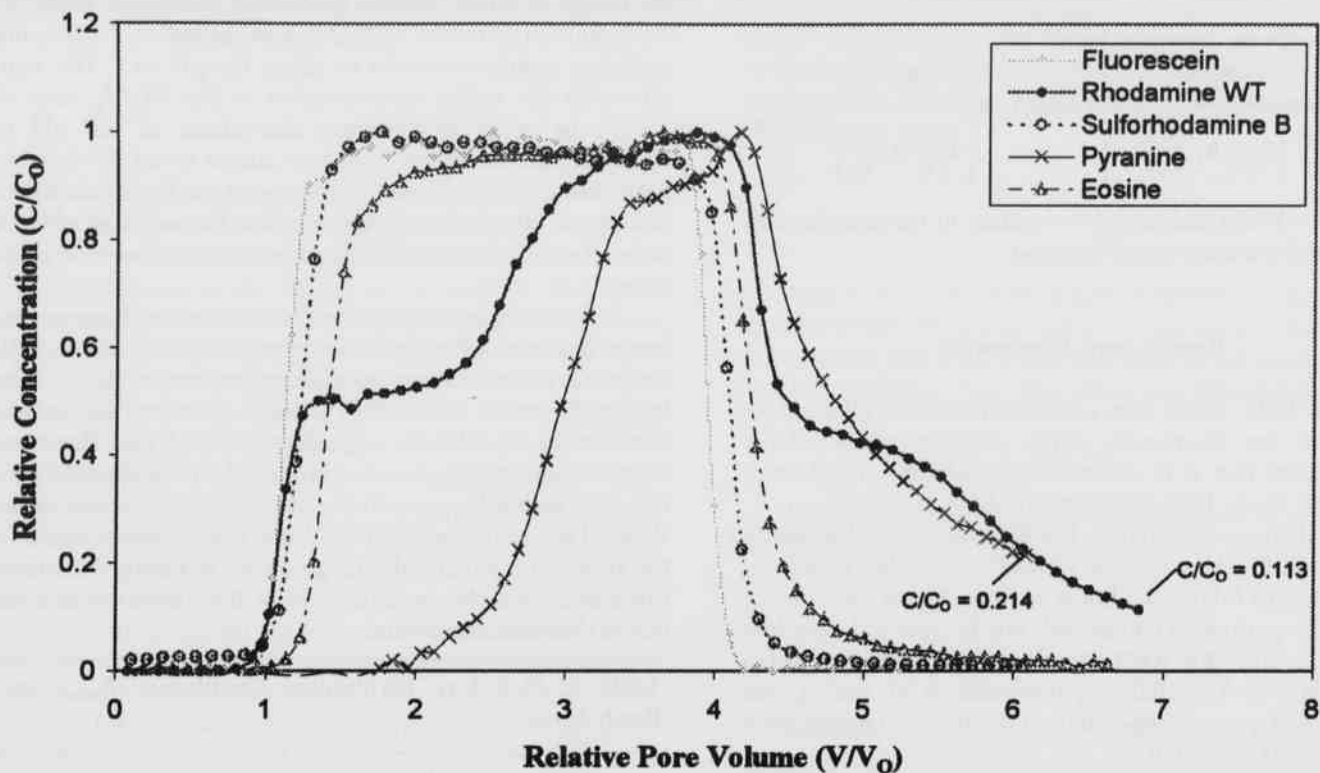


Fig. 1. Breakthrough Curves from Column Tests without PCE

Column results for the fluorescent tracers with PCE are illustrated in Fig. 2. As expected, in the presence of PCE, the retardation factors increased for all the tracers. The average flow rate was  $1.47 \pm 0.06$  mL/min. From regression analysis, measured  $R_f$  values were 1.31, 2.30, 1.33, 1.79, and 3.51, for fluorescein, RWT, SRB, cosine, and pyranine, respectively. All the dyes had retardation factors between 1.2 and 4.25. This approach makes them suitable as partitioning tracers. Among the nonconservative tracers, the least retarded was SRB and the most retarded was pyranine. Eosine produced a peak value  $C/C_0 > 1$ . BTCs, from experiments with PCE and without PCE, displayed similarity with respect to their shapes.

### Conclusions

Soil/dye partitioning coefficients for RWT and SRB demonstrated that the adsorption of these dyes into the soil was insignificant. Therefore, they are suitable as partitioning tracers. The increase of fluorescence for cosine and pyranine did not allow the  $K_d$  values determined. Background fluorescence and pH did not have an apparent effect on the final fluorescence of these dyes.

Partitioning coefficients for RWT, eosine, SRB, and PCE were very small. However, low  $K_{NW}$  values could be a consequence of the small range of concentrations tested, the PCE/tracer ratio, or the nature of the tracer itself. Pyranine enhanced fluorescence after reaching the equilibrium stage with PCE, following a linear isotherm with a negative slope. The formation of a different carboxylic group from a chemical reaction between pyranine and PCE was believed to be the cause of the increase in fluorescence of this tracer in batch tests.

Column tests indicated that RWT, SRB, and eosine are theoretically suitable as partitioning tracers. Among the partitioning tracers evaluated in this study, pyranine was demonstrated to be the most retarded and SRB the least retarded. RWT showed the two-steps BTC produced by isomers present in its molecular structure. Fluorescein and SRB had similar retardation factors. Because these tracers fluoresce at different wavelengths, they can be injected simultaneously in field tests. Flow velocities had a noticeable effect on determination of retardation factors. Higher velocities resulted in lower retardation factors for both RWT and fluorescein.

This study has demonstrated that partitioning fluorescent tracers are a potential resource for detection and esti-

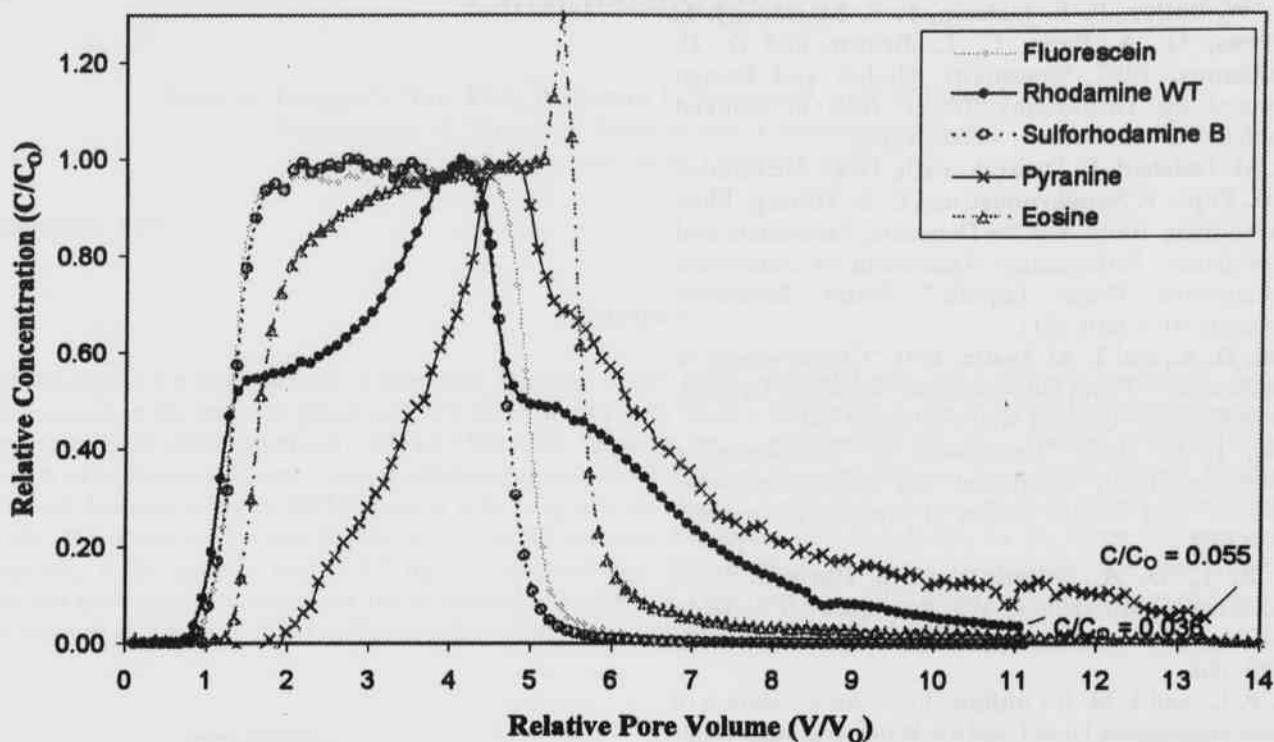


Fig. 2. Breakthrough Curves from Column Tests with PCE

mation of DNAPLs in saturated soils. However, the complexity of their molecular structure produced difficulty in understanding their properties and, consequently, the determination of partitioning coefficients between the tracers and PCE.

Different parameters, such as pH, temperature, PCE/dye ratio, tracer concentration, and orientation of the column, are involved in batch and/or column experiments. Conventional testing methods do not include the control of such variables. Thus, further studies should be done to determine the effect of these variables and design more accurate tests. On the other hand, additional fluorescent tracers should be evaluated in order to increase the number of dyes available for future work.

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