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Measuring Equilibrium Sorption Coefficients with the Miscible-displacement Method

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Abstract

The miscible-displacement method is one commonly used approach for measuring equilibrium sorption coefficients. The objective of this research was to examine the impact of experiment conditions (detection limit, input-pulse size, input concentration) on the measurement of retardation factors and sorption coefficients for a system that exhibits significant nonideal sorption behavior. A series of miscible-displacement experiments was conducted wherein effluent solute concentrations were monitored over a range of approximately seven orders of magnitude, allowing characterization of asymptotic tailing phenomenon, which was significant. The magnitude of K_d increased asymptotically with the increase in the extent of the elution tail measured. The results also showed that the fraction of the tail required to obtain close-to-maximum measures of K_d is greater for smaller input pulses. Investigating the impact of analytical detection limit (equivalent to relative concentrations of 10^{-3} and 10^{-7}) revealed that the magnitude of K_d was invariant with input pulse for the 10^{-7} detection limit. Conversely, the measured K_d values were significantly smaller at low input pulses for the 10^{-3} detection limit.

Keywords

distribution coefficient; nonlinear sorption; column experiment

INTRODUCTION

Sorption is a primary process mediating the transport and fate of contaminants in subsurface environments. Mathematical modeling of contaminant transport and fate requires measurement or estimation of parameter values, including retardation factors and equilibrium sorption coefficients. The two primary methods for measuring equilibrium sorption coefficients are batch and miscible-displacement (column) techniques.

There are some advantages inherent to the miscible-displacement method. First, the conditions under which the experiments are conducted are typically more representative of subsurface contaminant transport (e.g., similar fluid flow and solids:solution ratio) in comparison to batch systems. Second, in some cases, depending upon magnitudes and rates of sorption, less time may be required to conduct experiments. There are also some potential limitations associated with the miscible-displacement method. A primary one is the potential

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for underestimation of equilibrium sorption coefficients due to poor characterization of effluent concentration tailing.^[1–3] This potential is of special concern for systems that are significantly influenced by rate-limited and/or nonlinear sorption, given the extensive tailing typically associated with such phenomena.

The objective of this research was to examine the impact of experiment conditions (detection limit, input-pulse size, input concentration) on the measurement of retardation factors and sorption coefficients for a system that exhibits significant nonideal sorption behavior. Effluent solute concentrations were monitored over a range of approximately seven orders of magnitude, allowing characterization of asymptotic tailing phenomenon.

MATERIALS AND METHODS

Methods

Trichloroethene (TCE) (Aldrich Chemical Co., Inc., Milwaukee, WI) was used as the model organic compound. Pentafluorobenzoic acid (PFBA) (Aldrich Chemical Co., Inc.) was used as a conservative tracer to determine the hydrodynamic properties of the packed columns. An electrolyte solution containing 0.01 N CaCl₂ was used for all experiments. Eustis sandy soil (siliceous, thermic Psammentic Paleudults), collected from the University of Florida campus, was used for the experiments. This soil is composed of 96% sand, 1% silt, 3% clay, and 0.38% organic carbon.

The miscible-displacement experiments were conducted using stainless-steel columns (7-cm long by 2.1-cm diameter) to avoid artifacts associated with contaminant interactions with the apparatus. The columns were wet-packed in small increments to establish a uniform bulk density. The mean bulk density and porosity for the packed columns were 1.76 kg L⁻¹ and 0.33, respectively. The packing procedure resulted in consistent values of bulk density and porosity for all of the columns, with coefficients of variation (COV) of less than 2% and 4%, respectively. Stainless-steel distribution plates were placed on either end of the column to promote uniform flow. After packing, the columns were saturated by injecting de-aired electrolyte solution at a low flow rate into the bottom of the vertically positioned column. Complete saturation was assumed once a constant mass was attained for the column.

Electrolyte solution containing TCE at selected concentrations was injected into the column via a stainless-steel syringe pump (ISCO 500d) to minimize loss due to volatilization. The volume of TCE-saturated solution injected was varied between 2 and 1000 equivalent pore volumes. After injection of the TCE input pulse, the column was flushed with the electrolyte solution until the TCE concentration reached the quantifiable detection limit. Effluent samples were collected manually with 2-mL or 5-mL glass syringes (Popper & Sons, Inc, New Hyde Park, N.Y.), and analyzed immediately. The experiments were conducted at a flowrate equivalent to a mean pore-water velocity of approximately 20 cm hr⁻¹, which is within the range of velocities associated with induced-gradient conditions (e.g., pump-and-treat operations) at typical field sites. The data for three of the 20 pore-volume input-pulse experiments have been presented previously in Russo et al. (4).

Chemical Analysis

PFBA samples were analyzed using a UV-Vis spectrophotometer (SPD-10A Shimadzu) at a wavelength of 262 nm (quantifiable detection limit approximately 1 mg/L). Trichloroethene was analyzed by headspace gas chromatography (Tekmar-Dohrmann 7050 coupled with a Shimadzu GC-17A) using either a flame ionization (FID) or electron capture (ECD) detector depending on sample concentration. Chromatographic analysis was done using a glass

capillary column (SPB-624, 30-m length, 5- μm film thickness) with oven temperature programming. Specifically, analysis began with oven temperature set for two minutes at 40 $^{\circ}\text{C}$, ramped to 150 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}$ per minute, and held for two minutes. The injection port temperature was set at 180 $^{\circ}\text{C}$, with the detectors at 180 $^{\circ}\text{C}$ and 210 $^{\circ}\text{C}$ for the FID and ECD, respectively. Aqueous-phase standards were analyzed every 48 hours with check standards and blanks analyzed for quality assurance every 10 to 15 samples. The quantifiable detection limit for trichloroethene using headspace GC/ECD was 0.1 $\mu\text{g L}^{-1}$. Selected samples were also analyzed using UV-Vis spectrophotometry (QDL = 1 mg L^{-1}) to provide additional confirmation of analytical results.

Data Analysis

The retardation factor was determined by use of moments analysis of the break-through-curve. Absolute moments are given by:

$$\mu_n = \int_0^{\infty} t^n f(t) dt, \quad n=0, 1, 2, 3, \dots \quad (1)$$

Normalized moments are defined as:

$$\mu_n' = \frac{\mu_n}{\mu_0} \quad (2)$$

The zeroeth moment (μ_0) describes the total mass of tracer injected in to the column, whereas the first normalized moment (μ_1') represents the mean arrival time of the injection pulse. Trapezoidal rule integration was used for moment estimation such that μ_0 and μ_1' are given by:

$$\mu_0 = \sum_{i=2}^n \left(\frac{C_i + C_{i-1}}{2} \right) (t_i - t_{i-1}) \quad (3)$$

$$\mu_1' = \frac{\sum_{i=2}^n \left(\frac{t_i C_i + t_{i-1} C_{i-1}}{2} \right) (t_i - t_{i-1})}{\mu_0} \quad (4)$$

where t is dimensionless time given in pore-volumes, and C is taken as relative concentration. The retardation factor (R , dimensionless) was determined as the mean travel time of the sorbing compound:

$$R = \mu_1' - 0.5\mu_0 \quad (5)$$

Finally, the equilibrium sorption coefficient, K_d was calculated by solving the following relationship:

$$R = 1 + K_d \cdot \frac{\rho_b}{\theta} \quad (6)$$

Where ρ_b is bulk density (M L^{-3}) and θ is porosity.

RESULTS AND DISCUSSION

The breakthrough curves for the non-reactive tracer (PFBA) exhibited minimal spreading and tailing, and essentially complete mass recovery (data not shown). These results indicate relatively ideal hydrodynamic transport conditions. Mass recoveries for the TCE experiments ranged from 98–102%, which is within the range of analytical uncertainty. This indicates that the transport of TCE was not measurably influenced by transformation or irreversible-sorption effects.

Trichloroethene exhibited extensive elution tailing for all experiments, as illustrated by the data presented in Figure 1. The columns required several thousand pore volumes of water flushing to reduce effluent TCE concentrations to the quantifiable detection limit, despite relatively low retardation factors (~ 2.5). The results of replicate experiments showed good reproduction, as exemplified by the data presented in Figure 1. The nonideal behavior was attributed primarily to the impact of rate-limited sorption/desorption, with a minor contribution from nonlinear sorption. [4]

The tailing exhibited in Figure 1 is typically observed for transport of organic compounds in sorbing porous media when analytical methods of sufficient detection limits are employed. [4–9] However, methods with detection limits that are not sufficient to fully characterize such tailing are often used for transport studies. A central question for this situation is what fraction of the tail must be captured to accurately measure the equilibrium sorption coefficient? The impact of the extent of the elution tail measured and used for moment analysis is illustrated in Figure 2. The magnitude of K_d increases asymptotically with the increase in the extent of the elution tail measured.

The impact of the size of the input pulse (the volume of TCE solution injected) was investigated by varying the input pulse from 2 to 1000 pore volumes. The results are presented in Figure 3. Inspection of Figure 3 shows that the fraction of the tail required to obtain close-to-maximum measures of K_d is greater for smaller input pulses. For example, only 10% of the elution tail is required to obtain a K_d that is 90% of the maximum value for the experiment with an input pulse of 100 pore volumes. Conversely, more than 60% of the tail is required for the 2 pore-volume input-pulse experiment. These results illustrate that it is critical to capture a significant portion of elution tailing for experiments employing smaller input pulses. This is particularly relevant given that miscible-displacement experiments are often conducted with relatively small input pulses.

The impact of analytical detection limit on the extent of elution tail characterized, and the resultant impact on K_d values measured, was investigated by calculating K_d for two cases. For the first case, the entire elution tail was used for moment analysis, corresponding to a relatively sensitive detection limit (equivalent to relative concentrations of $\sim 10^{-7}$). For the other case, the elution tails were truncated at a relative concentration of 0.001, corresponding to a detection limit of approximately 1 mg L^{-1} . This detection limit is representative of those associated with standard methods such as UV-VIS spectrophotometry.

The results of the analysis are presented in Figure 4. The magnitude of K_d is invariant with input pulse for the 10^{-7} detection limit. Conversely, the measured K_d values are significantly smaller at low input pulses for the 10^{-3} detection limit. These results suggest that the impact of poor capture of elution tailing on K_d measurement can be overcome at least in part by conducting experiments with larger input pulses. This is consistent with prior research based on numerical simulations indicating that increasing the input-pulse size

decreases the effect of experimental error on calculated moments and reduces the sensitivity of calculated parameters to errors such as variations in flow rate or input concentration. ^[10]

The concentration of the compound in the injection solution (input concentration, C_0) is another important experiment variable that can influence K_d measurement. Specifically, the extent of the elution tail is directly correlated with C_0 . This is illustrated in Figure 1, wherein the lowest C/C_0 attained for the experiment conducted with a $C_0 = 9 \text{ mg L}^{-1}$ is two logs higher than that attained for the experiments conducted with a $C_0 = \sim 1200 \text{ mg L}^{-1}$. Correspondingly, the elution tail is approximately 1000 pore-volumes long versus almost 4000 pore volumes, respectively. The impact of C_0 will be exacerbated for systems with nonlinear sorption characterized by less favorable sorption at higher concentrations (e.g., Freundlich exponents less than 1), given that elution tailing is enhanced for such cases and that retardation is greater at lower C_0 values. Accurate measurement of K_d for such conditions would require characterizing as much of the elution tail as possible.

SUMMARY

Assessing and modeling the transport and fate of solutes in porous media requires measurement or estimation of equilibrium sorption coefficients, and one primary method for measuring such coefficients is the miscible-displacement technique. A series of miscible-displacement experiments was conducted to examine the impact of detection limit, input-pulse size, and input concentration on the measurement of sorption coefficients for a system that exhibits nonideal sorption behavior in the form of extensive elution tailing. The results of the experiments showed that the magnitude of K_d obtained from moment analysis of the breakthrough curves increased asymptotically as more of the elution tail was measured. These results are consistent with those of prior studies that have shown that failure to characterize the tails of breakthrough curves can cause underestimation of equilibrium sorption coefficients. ^[1–3]

Miscible-displacement experiments are often conducted with the use of relatively small input pulses. Additionally, elution curves are typically monitored for a limited extent wherein, for example, the reduction in relative concentration is less than three logs. The results of the study indicate that there is a high potential for underestimation of K_d for such conditions. The results of the study also provide strategies for minimizing such underestimation. One approach is to measure a great proportion of the elution tail. This may require the use of analytical methods with more sensitive detection limits. Another approach is to conduct experiments using larger input pulses, which require smaller fractions of the tail to be measured.

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References

1. Brusseau ML, Rao PSC, Jessup RE, Davidson JM. Flow interruption: a method for investigating sorption nonequilibrium. *J Contam Hydrol*. 1989; 4:223–240.
2. Young DF, Ball WP. Column experimental design requirements for estimating model parameters from temporal moments under nonequilibrium conditions. *Adv Water Resour*. 2000; 23:449–460.
3. Altfelder S, Streck T, Maraqa MA, Voice TC. Nonequilibrium sorption of organic compounds – compatibility of batch and column techniques. *Soil Sci Soc Am J*. 2001; 65:102–111.

4. Russo A, Johnson GR, Schnaar G, Brusseau ML. Nonideal transport of contaminants in heterogeneous porous media: 8. Characterizing and modeling asymptotic contaminant-elution tailing for several soils and aquifer sediments. *Chemo*. 2010; 81:366–371.
5. Deng J, Jiang X, Zhang X, Hu W, Crawford JW. Continuous time random walk model better describes the tailing of atrazine transport in soil. *Chemo*. 2008; 70:2150–2157.
6. Johnson GR, Zhang Z, Brusseau ML. Characterizing and quantifying the impact of immiscible-liquid dissolution and nonlinear, rate-limited sorption/desorption on low-concentration elution tailing. *Water Resour Res*. 2003; 39:6–1–6–8.
7. Johnson GR, Norris DK, Brusseau ML. Mass removal and low-concentration tailing of trichloroethene in freshly-amended, synthetically-aged, and field-contaminated aquifer material. *Chemo*. 2009; 75:542–548.
8. Kempf A, Brusseau ML. Impact of non-deal sorption on low-concentration tailing behavior for atrazine transport in two natural porous media. *Chemo*. 2009; 77:877–882.
9. Kleinedam S, Rugner H, Grathwohl P. Desorption kinetics of phenanthrene in aquifer material lacks hysteresis. *Environ Sci Technol*. 2004; 38:4169–4175. [PubMed: 15352457]
10. De Lasa H, Hazlett J, Fuller OM. Evaluation of the Moment Method Technique for the Definition of Adsorption Parameters in a Packed. *Bed Chem Eng Sci*. 1986; 41:1233–1242.

Figure 1.
Results of replicate miscible-displacement experiments (20 pore-volume input pulse).
Experiments 1–4 conducted using an input concentration of $\sim 1200 \text{ mg L}^{-1}$; experiment 5
conducted using an input concentration of $\sim 9 \text{ mg L}^{-1}$. Modified from Russo et al. (2010).

Figure 2.

Magnitude of the relative equilibrium sorption coefficient, K_d , (where relative K_d is the measured value normalized by the maximum value) as a function of the extent of elution tail used for moment analysis (20 pore-volume input pulse).

Figure 3.

Magnitude of the relative equilibrium sorption coefficient, K_d , (where relative K_d is the measured value normalized by the maximum value) as a function of the extent of elution tail used for moment analysis. Data presented for experiments conducted with different input-pulse volumes. Fractional relative pore volume is calculated as pore volume divided by the product of the retardation factor and the maximum pore volume eluted.

Figure 4. Magnitude of the equilibrium sorption coefficient, K_d , for two detection limits, as a function of the input pulse.