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Nonideal Transport of Contaminants in Heterogeneous Porous Media: 9. Impact of Contact Time on Desorption and Elution Tailing

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Abstract

A series of miscible-displacement experiments was conducted to examine the impact of sorption contact time on desorption and elution of trichloroethene from a well-characterized soil. A large number of contact times were examined, spanning 1 hour to 4 years ($\sim 2 \cdot 10^6$ h). Effluent trichloroethene concentrations were monitored over a range of greater than six orders of magnitude, allowing characterization of potential asymptotic tailing. The results of the column experiments showed that trichloroethene exhibited extensive elution tailing for all experiments. Each increase in contact time resulted in a successive increase in the extent of tailing. In total, the number of pore volumes of water flushing required to reach the analytical detection limit increased from approximately 1000 for the one-hour contact time to almost 9000 for the four-year contact time. These results indicate that a contact time of less than one hour produced a sorbed phase that is relatively resistant to desorption, and that a progressive increase in resistance to desorption occurred with increased contact time. A mathematical model incorporating nonlinear, rate-limited sorption/desorption described by a continuous-distribution reaction function was used to successfully simulate the measured data. The nonlinear sorption, the apparent rapid development of desorption resistance, and the progressive increase in resistance with increasing contact time are consistent with behavior anticipated for sorbate interactions with hard-carbon components of the soil.

Keywords

Sorption; Aging; Hard carbon; Rate limited

1. Introduction

The sorption-desorption process is a primary factor mediating the transport and fate of hydrophobic organic compounds in subsurface environments. The widely-observed rate-

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limited nature of desorption has a wide array of potential impacts, including for example reducing bioavailability and constraining contaminant removal during remedial operations. One significant manifestation of rate-limited desorption under advective transport conditions is that of asymptotic elution tailing, which has been routinely observed in the miscible-displacement studies that have employed analytical methods with sufficiently low detection levels (e.g. Piatt and Brusseau, 1998; Johnson et al., 2003, 2009; Kleinedam et al., 2004; Deng et al., 2008; Kempf and Brusseau, 2009; Russo et al., 2010).

The impact of sorption contact time or contaminant “aging” on the magnitude and rate of desorption has been investigated as a means to elucidate the recalcitrance of sorbed-phase contaminants. The results of such experiments, typically conducted using batch methods, have generally shown measurable increases in resistance to desorption with longer sorption contact times (e.g. Pignatello, 1990, 1991; Connaughton et al., 1993; Deitsch and Smith, 1995; Hatzinger and Alexander, 1995; Cornelissen et al., 1997; Chung and Alexander, 1998; Abu and Smith, 2006; Chai et al., 2008). The use of miscible-displacement methods to examine the impact of desorption processes, specifically potential effects on elution behavior, is of interest as it directly addresses conditions inherent to contaminant transport in subsurface systems. This approach has been used in a few prior studies to examine the impact of contaminant aging by comparing the elution of freshly added contaminant to that of aged contaminant (Brusseau et al., 1991; Pignatello et al., 1993; Johnson et al., 2009).

The objective of this research is to examine the impact of sorption contact time on desorption behavior. In contrast to prior studies (both batch and miscible-displacement), which typically evaluate two or three contact times, we employ a large number of contact times that span 1 hour to 4 years. The miscible-displacement method is used to directly examine the impact of contact time on elution of sorbed contaminant under advective-transport conditions.

2. Materials and Methods

2.1. Materials

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 CaCl_2 was used for all experiments.

Eustis sandy soil (siliceous, thermic Psammentic Paleudults), collected from the University of Florida campus, was used for the experiments. Pertinent properties of the soil are presented in Table 1. The geochemical composition of the organic-carbon fraction was characterized following procedures similar to those previously employed (Johnson et al., 2009), and outlined in Jeong and Werth (2005). Those treatment steps included phosphoric acid (10%) addition to remove carbonates, followed by 0.1 M sodium hydroxide to remove the humic and fulvic acid fraction, and finally, treatment by acid dichromate (0.1 M potassium dichromate and 2 M sulfuric acid) to remove kerogen. The organic carbon in the bulk media was found to be composed of approximately 37% hard carbon (kerogen and black carbon) and 63% soft carbon (humic/fulvic acids, lipids) (Table 1) (Russo et al., 2010).

The soil was subjected to X-ray diffraction analysis to characterize the mineralogical composition of the inorganic fraction (see Table 1). Additional analysis was conducted to identify the composition of the clay mineral component, which comprises less than 2% of the total medium. The clay mineral fraction consisted almost exclusively of kaolinite. The metal-oxide composition was characterized by treating subsamples of the soil with 5M

Nitric acid, followed by analysis of the extractant solution via Inductively Coupled Plasma/Mass Spectrometry (Perkin Elmer Elan DRC II). The results showed element concentrations of 694, 314, and 19 $\mu\text{g g}^{-1}$ for Al, Fe, and Mn, respectively.

2.2. Batch Experiment Methods

Batch experiments were conducted to help evaluate potential nonideal (nonlinear, rate-limited) sorption behavior. Batch reactors consisted of 20-ml flame-sealed glass ampules (Wheaton), which eliminated the use of Teflon and other potentially reactive materials. The ampules were filled with 14–15 g of soil and approximately 8 ml of aqueous solution to minimize headspace. The resulting soil:water ratio was approximately 2:1, which was relatively close to the conditions of the miscible-displacement experiments while providing sufficient solution for analysis.

The Eustis soil was equilibrated with tracer-free electrolyte solution for 72 hours, then air dried for 24 hours to a volumetric water content of 0.5%. The material was then placed in the ampules, which were then filled with TCE solution and immediately flame sealed with an oxygen-natural gas sealing torch (Labconco). A range of five initial concentrations (1–1200 mg L^{-1}) were used. Each concentration was reproduced in several sets of triplicates, along with soil-free control samples. After sealing, the samples were rotated along the longitudinal axis at 4 rpm continuously for the first 24 hours and periodically for the remainder of the experiment (100 days).

Three sets of ampules for each concentration were sacrificed at selected times to measure TCE concentrations. Prior to sampling, the ampules were centrifuged at 1100 rpm for 30 min to achieve solid-water separation. After sampling, each ampule was oven-dried at 105°C for 24 hours to obtain dry soil mass. Mass loss of TCE during the experiments via volatilization to headspace and biotransformation was characterized by analysis of the controls for TCE concentrations and by checking all samples for degradation products (e.g., dichloroethene). No degradation products were detected, and the TCE concentrations for the controls were typically within approximately 2% of the initial concentrations.

2.3. Miscible-Displacement Methods

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 g cm^{-3} 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 1.6% and 3.4%, respectively. Stainless steel distribution plates were placed on either end of the column to encourage 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 aqueous solubility ($\sim 1200 \text{ mg L}^{-1}$) 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 to encompass a wide range of contact times (discussed in more detail in the following paragraph). 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 in 2-ml or 5-ml glass syringes (Popper & Sons, Inc, New Hyde Park, N.Y.), and analyzed immediately. The experiments were conducted at a flow rate equivalent to a mean pore-water velocity of approximately 20 cm h^{-1} , which is within the range of

velocities associated with induced-gradient conditions (e.g., pump-and-treat operations) at typical field sites.

As noted, the volume of TCE-saturated solution injected was varied to encompass a wide range of contact times. The specific input-pulse volumes used, in terms of column pore volume (water retention capacity), were 2, 4, 8, 20, 100, and 1000 pore volumes. The contact-time equivalents for these input pulses are 42 min, 1.4 h, 2.8 h, 7 h, 35 h, and 15 days, respectively. It should be noted that these contact times represent the time for which the soil was exposed to TCE prior to the start of the elution phase of the experiments. Some of the data for the 20 pore-volume input pulse experiments were previously presented in Russo et al. (2010); the results of all other experiments (including those discussed in the next paragraph as well as the batch experiments) have not been previously published.

In addition to varying the size of the input pulse, three experiments were conducted with soil that was pre-equilibrated with TCE for 30 days, 420 days, and 4 years, respectively. For these experiments, soil was placed in a container constructed of stainless-steel fine mesh that was suspended in a 3 L glass container filled with electrolyte solution, with TCE liquid emplaced in the bottom. The soil was suspended such that it did not directly contact the TCE liquid. Aqueous subsamples were collected from the bottle periodically to ensure the solution remained saturated with TCE. After a designated contact time, a subsample of the soil was collected (after mixing of the sample) and packed into the column. Several pore volumes of TCE-saturated solution were injected to ensure the column was water-saturated prior to the initiation of flushing with electrolyte solution.

2.4. 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- μ m film thickness) with oven temperature programming. Specifically, analysis began with oven temperature set for two minutes at 40 C, ramped to 150 C at a rate of 10 C per minute, and held for two minutes. The injection port temperature was set at 180 C, with the detectors at 180 C and 210 C for the FID and ECD, respectively. Aqueous-phase standards were analyzed every 48 h 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 approximately 0.1 μ g L⁻¹. Selected samples were also analyzed using UV-Vis spectrophotometry (QDL = 1 mg L⁻¹) to provide confirmation of analytical results.

2.5. Data Analysis

For batch experiments, the mass of TCE sorbed by the soil was calculated from the mass reduction measured for the aqueous solution, correcting for volatilization to headspace based on the control samples. The sorption isotherm was developed using the data collected during the last sampling rounds of the rate study, and was fitted with the Freundlich equation. For the miscible-displacement experiments, the total eluted solute mass was determined through analysis of the area under the concentration versus time curve (zeroth moment). The retardation factor, R ($R = 1 + K_d \rho/n$, where ρ is bulk density, n is porosity, and K_d is the distribution coefficient), was determined through moment analysis of the elution curves.

The transport data were simulated with a one-dimensional advective-dispersive equation wherein nonlinear, rate-limited sorption/desorption was represented with a continuous

distribution of domains and associated sorption/desorption rate coefficients (e.g., Connaughton et al., 1993; Pedit and Miller, 1994; Chen and Wagenet, 1995; Culver et al., 1997; Haggerty and Gorelick, 1998; Li and Brusseau, 2000; Saiers and Tao, 2000; Johnson et al., 2003; Zhang and Brusseau, 2004; Deng et al., 2008; Johnson et al., 2009; Russo et al., 2010). With this model, the impact of pore/grain-scale heterogeneity on sorption/desorption is accounted for with a continuous distribution of retention domains and associated mass-transfer rate coefficients. Parameters, calibration, and optimization procedures used for the modeling have been presented elsewhere (Johnson et al., 2003). Three variables are optimized through calibration of the model to measured data, the fraction of instantaneous desorption (F), the mean desorption rate coefficient ($\ln k_2$), and the variance of $\ln k_2$.

3. Results and Discussion

3.1. Batch Experiments

A batch sorption-rate experiment was conducted with Eustis soil to characterize rate-limited sorption. The changes in apparent K_d as a function of time for five different initial aqueous concentrations are presented in Figure 1. The results show that sorption of TCE is significantly rate limited. Sorption equilibrium appears to be attained by 100 days, with the possible exception of the lowest-concentration experiment. Sorption is nonlinear and is well described by the Freundlich isotherm, with an n value of 0.75 (see Figure 2).

3.2. Miscible-displacement Experiments

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. The retardation factors for TCE determined from moment analysis of the breakthrough curves were similar for all experiments (mean = 2.5, COV = 9.5%), with no evidence of trends as a function of contact time.

Trichloroethene exhibited extensive elution tailing for all experiments, as illustrated by the data presented in Figures 3 and 4. The columns required several thousand pore volumes of water flushing to reduce effluent TCE concentrations to the quantifiable detection limit, despite the relatively low retardation factors. The results of replicate experiments showed good reproduction, as exemplified by the data presented in Figure 3.

The impact of contact time on TCE elution is presented in Figure 4. The results show that tailing became more extensive as the input pulse increased from 1 pore volume to 1000 pore volumes. Similar behavior was observed for the experiments conducted with soil that was pre-equilibrated with TCE, wherein the extent of tailing is greater for the experiment with the longest pre-equilibration time. The elution curve associated with the 1000 pore-volume input experiment, for which the contact time was 15 days, exhibits slightly less tailing than the curve associated with the 30-day pre-equilibration experiment. These observations indicate that the two methods used for the experiments, solution injection and external pre-equilibration, yielded consistent results.

The TCE elution curve exhibits significant tailing even for the experiments with a two pore-volume input pulse. This suggests that a contact time of less than one hour produces a sorbed phase that is relatively resistant to desorption. Each increase in contact time resulted in a successive increase in the extent of tailing (Figure 4). In total, the number of pore volumes of water flushing required to reach the detection limit increased from approximately 1000 for the two pore-volume input to almost 9000 for the 4-year pre-

equilibrated experiment. These results indicate that a progressive increase in resistance to desorption occurs with increasing contact time.

3.3. Mathematical Modeling

The transport model incorporating a continuous-distribution function for sorption produced good simulations of all of the measured data (i.e., all contact times). The goodness-of-fit is illustrated in Figure 3 for the 20 pore-volume input-pulse data sets. The model provides a good fit to the full elution curve, including the rapid decrease during the initial stage of flushing as well as the asymptotic elution tail. The values of the calibrated parameters were statistically similar for all of the experiments. The mean values were 1.3, 12.4, and 0.8 for $\ln k_2$, the variance of $\ln k_2$, and F , respectively, with COV values of approximately 10%. The results of sensitivity analyses indicated that the fitted parameters were robust, wherein it was observed that relatively small changes in the parameter values resulted in large differences in simulated behavior.

A comparison of model simulations including and excluding nonlinear sorption indicates that nonlinear sorption has a relatively minor impact on the observed elution tailing (see Figure 5). Thus, the extensive tailing is attributed primarily to the impact of rate-limited desorption. The nonideal trichloroethene elution behavior observed for these experiments could not be accurately simulated using the widely used two-domain approach (results not shown).

3.4. Discussion

Mechanisms potentially responsible for nonideal sorption of hydrophobic organic compounds by natural porous media are generally considered to primarily involve interactions with organic-carbon components of the sorbents, with some potential for contributions from inorganic components depending upon specific soil properties. The Eustis soil is composed primarily of quartz, with very small fractions of other minerals and metal-oxides. In addition, the clay mineral fraction is comprised essentially completely of kaolinite, a non-expanding clay. With these properties, it is anticipated that the inorganic components provide minimal contribution to sorption of TCE for Eustis soil. The relative contributions of organic carbon and inorganic components of the Eustis soil to sorption of hydrophobic organic compounds were investigated in prior research (Brusseau et al., 1989; 1991; Nkedi-Kizza et al., 1989). For this research, the soil organic carbon was reduced or removed by treatment prior to sorption experiments that were conducted in parallel with ones using the untreated soil. The results showed that the magnitude of sorption was significantly reduced (in some cases essentially to zero), and that rate-limited behavior was minimal, for the treated soil. These results indicate that sorption behavior for the Eustis soil is controlled by organic carbon.

Attention has recently focused on the hard-carbon components of organic carbon, such as black carbon and kerogen, as potential sources of nonideal sorption behavior (nonlinear sorption, recalcitrant desorption) for hydrophobic organic contaminants. Nonlinear sorption is considered a manifestation of the presence of variable and heterogeneous sorption energies associated with condensed, carbonaceous material. Recalcitrant desorption is associated with the mode of sorbate-sorbent interaction, which is envisioned to comprise retention and permeation of sorbate molecules within molecular-sized domains of a deformable sorbent matrix that has relatively long characteristic times of relaxation (e.g., Brusseau et al., 1991; Brusseau, 1993; Luthy et al., 1997; Xing and Pignatello, 1997; Weber and Young, 1997; Piatt and Brusseau, 1998; Bucheli and Gustafsson, 2000; Jonker and Koelmans, 2002a,b; Lu and Pignatello, 2002; Cornelissen et al., 2005; Abu and Smith, 2006;

Koelmans et al., 2006; Chai et al., 2007; Morelis and van Noort, 2008; Prevedouros et al., 2008).

The organic carbon for the Eustis soil is composed of approximately 37% hard carbon (kerogen and black carbon) and 63% soft carbon (humic/fulvic acids, lipids). The nonlinear sorption observed for TCE, as well as the apparent rapid development of desorption resistance, are consistent with behavior anticipated for interactions with hard carbon. As noted above, the retardation factors were similar for all contact times, which indicates that increased contact time did not result in an increased magnitude of sorption. This observation, in conjunction with the observed progressive increase in recalcitrance as a function of contact time indicates a temporal dynamism in the disposition or configuration of the sorbed phase. This may involve long-term permeation of sorbate within the sorbent matrix, and/or sorbate-induced modification of the local environment surrounding the sorbate molecules, such as deformation of the sorbent matrix.

4. Summary

A series of miscible-displacement experiments was conducted to characterize the impact of sorption contact time on desorption and elution of trichloroethene. Effluent trichloroethene concentrations were monitored over a range of greater than six orders of magnitude, allowing characterization of potential asymptotic tailing. The results of the column experiments showed that trichloroethene exhibited extensive elution tailing for all experiments. A mathematical model incorporating nonlinear, rate-limited sorption/desorption described by a continuous-distribution reaction function was used to successfully simulate the measured data. Similar values for the calibrated coefficients were obtained for all the experiments, which indicates that the model was sufficiently robust to represent the range of characteristic times of desorption associated with the system, as well as capture the impact of a very wide range of contact times.

The TCE elution curve exhibited significant tailing even for the experiments with a two pore-volume input pulse, which indicates that a contact time of less than one hour produced a sorbed phase that is relatively resistant to desorption. Each increase in contact time resulted in a successive increase in the extent of tailing. This indicates that a progressive increase in resistance to desorption occurred with increasing contact time. The nonlinear sorption, the apparent rapid development of desorption resistance, and the progressive increase in resistance with increasing contact time are consistent with behavior anticipated for sorbate interactions with hard-carbon components of the soil.

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Highlights

The impact of sorption contact time on desorption and elution of trichloroethene was investigated.

Trichloroethene exhibited extensive elution tailing for all experiments.

Increases in contact time resulted in greater extents of tailing.

Implications of the results for relevant sorption mechanisms are discussed.

Figure 1. Results of batch sorption-rate experiments. The values in the legend refer to nominal initial concentrations (mg L^{-1}).

Figure 2.

Isotherm data: measured and regression obtained with Freundlich equation [$S = 1.18 C^{0.75}$, $r^2 = 0.998$, where S is sorbed-phase concentration and C is aqueous-phase concentration]. The confidence intervals are approximately equal to or less than the size of the data points.

Figure 3. Results of replicate miscible-displacement experiments (20 pore-volume input pulse); simulated curve produced with a one-dimensional transport model for which sorption-desorption is represented by a continuous-distribution function. Modified from Russo et al. (2010).

Figure 4.
Results of miscible-displacement experiments with different sorption contact times, presenting one curve for each of the pore-volume input pulses employed.

Figure 5.
Comparison of simulated and measured TCE transport; simulations produced for cases with and without rate-limited or nonlinear sorption-desorption.

TABLE 1

Soil Properties

Analysis	Component	%
Bulk Soil Analysis	Organic carbon	0.38
	Sand	96
	Silt	1
	Clay	3
Organic Carbon Analysis	Black carbon	7
	Kerogen	30
	Lipids	10
	Humic/fulvic acids	53
Inorganic Analysis	Quartz	97.7
	K-feldspar	0.4
	Plagioclase	0.1
	Amphibole	0.1
	Clay Minerals	1.7