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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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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.

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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 h to 4 years ($\sim 2 \times 10^6$ 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 1-h contact time to almost 9000 for the 4-year contact time. These results indicate that a contact time of less than 1 h 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.

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-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; Kleineidam 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

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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 h 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. Pentafluourobenzoic 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 5 M 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 μg g^{-1} for Al, Fe, and Mn, respectively.

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

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 h, then air dried for 24 h 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 h and periodically for the remainder of the experiment (100 d).

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 h 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 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, NY), 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