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Nonideal behavior during complete dissolution of organic immiscible liquid
1. Natural porous media

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ABSTRACT

Experiments were conducted to investigate the complete dissolution of organic immiscible liquid residing within natural porous media. Organic-liquid dissolution was investigated by conducting experiments with homogeneously packed columns containing a residual saturation of organic liquid (trichloroethene). The porous media used comprised different textures (ranges of particle-size distributions) and organic-carbon contents. The dissolution behavior that was observed for the soil and aquifer sediment systems deviated from the behavior typically observed for systems composed of ideal sands. Specifically, multi-step elution curves were observed, with multiple extended periods of relatively constant contaminant flux. This behavior was more pronounced for the two media with larger particle-size distributions. Conversely, this type of dissolution behavior was not observed for the control system, which consisted of a well-sorted sand. It is hypothesized that the pore-scale configuration of the organic liquid and of the flow field is more complex for the poorly sorted media, and that this greater complexity constrains dissolution dynamics, leading to the observed nonideal behavior.

1. Introduction

Organic liquids are a persistent source of groundwater contamination at many hazardous waste sites. Understanding the mechanisms mediating the dissolution of organic liquids, and attendant source-zone mass flux, is critical for accurate risk assessment and effective remediation of sites contaminated by organic liquids. One issue of particular significance for organic-liquid-contaminated source zones is characterizing mass-removal behavior and associated mass-flux dynamics over long time frames [1]. Addressing and managing mass flux over the long term is central to reducing site risk.

The distribution, mass-transfer dynamics, and mass flux of organic liquids in the subsurface have been examined in numerous studies conducted over the past few decades. Thus, there exists a significant level of information and understanding about the behavior of organic-liquid contaminants in the subsurface. However, the current understanding of mass-transfer and mass-flux processes is far from complete, and many challenges remain [1]. For example, experiments to investigate the dissolution behavior of organic liquids have been conducted at the column, intermediate, and field scale (e.g. [2–20]). However, the laboratory experiments have been conducted using primarily glass beads or well-sorted sands, while relatively few have been conducted using natural soils and aquifer sediments (e.g. [10,11,16]). Additionally, few of these experiments have examined complete mass removal and associated long-term mass flux behavior (e.g. [10,16]). The objective of this study was to examine dissolution behavior for systems composed of natural soils and aquifer sediments, with a specific focus on characterizing long-term mass-flux behavior associated with complete dissolution of the organic liquid.

2. Materials and methods

2.1. Materials

Trichloroethene (TCE) (Aldrich Chemical Co., Inc., Milwaukee, WI) was used as the model organic liquid, given its widespread presence as a groundwater contaminant. Pentafluorobenzoic acid (PFBA) (Aldrich Chemical Co., Inc.) was used as a conservative tracer to determine the hydrodynamic properties of the columns. Calcium chloride (0.01 N) electrolyte solution was used as the aqueous solution for all experiments. Five natural porous media with varying compositions and particle-size distributions were used for the experiments. These included a sandy sub-soil collected from Alachua County, FL (Eustis), a silty soil from Pima County, AZ (Hayhook), a high organic-carbon content soil from Pima County, AZ

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Table 1
Properties of porous media.

Porous media	Sand %	Silt %	Clay %	Bulk density (g/cm^3)	Porosity	Median grain diameter (d_{50}, mm)	Organic-carbon content (% OC)	Uniformity coefficient (UC)[a]	R[b]
Well-sorted sand	100	–	–	1.67	0.37	0.35	0.03	1	~1
Borden soil	96.2	2	1.8	1.74	0.34	0.21	0.03	1.9	1.5
Eustis soil	95.9	1	4.4	1.69	0.36	0.27	0.38	2.3	2.4
Hayhook soil	85.5	4.3	10.2	1.64	0.38	0.26	0.08	16	1.3
Mt. Lemmon soil	60	24	16	1.17	0.56	0.11	10	22.6	8.2

[a] UC = d_{60}/d_{10}.
[b] R = retardation factor.

(Mt. Lemmon), and an aquifer sediment from Ontario, Canada (Borden). A well-sorted natural quartz sand (45/50 Accusand) was used as a control, representative of the type of porous medium used in most prior column studies of organic-liquid dissolution. The media encompass a range of particle-size distributions (reflected by the uniformity coefficients) and organic-carbon contents (Table 1). The columns, tubing, and fittings were constructed of stainless steel. Most of the experiments were conducted using columns that are 2.5 cm in diameter and 7 cm in length (referred to as the "medium-sized" columns). Additional experiments were conducted using two other sizes, 0.5 cm diameter by 4 cm long (small) and 7.6 cm diameter by 11 cm long (large).

2.2. Methods

The columns were uniformly packed with dry porous media. After packing, the columns were saturated by injecting de-aired aqueous solution into the bottom of the column. The flowrate was slowly increased from the equivalent pore-water velocity of 5–25 cm/h over 48 h. Complete saturation was assumed once a constant mass was attained for the column. A non-reactive tracer test was then conducted to determine hydrodynamic properties of the system. Additionally, experiments were conducted using aqueous solutions of TCE to characterize the contribution of sorption/desorption to transport and elution of TCE. These experiments were conducted by continuously injecting tracer solution until the effluent concentration of the tracer (PFBA or TCE) equaled the input concentration. Tracer-free aqueous solution was then injected until the effluent tracer concentration reached the detection limit.

To establish residual saturation for the dissolution experiments, pure-phase TCE was injected into the bottom of the vertically placed water-saturated column using a gas-tight syringe attached to a syringe pump (Sage Model 355). The volume and flowrate of injection was selected to achieve the targeted saturation. Following the injection, the mobile-phase TCE was removed via injection of two pore volumes of a saturated TCE solution into the top of the column at approximately 5 cm/h, followed by ten pore volumes at a pore-water velocity of approximately 60 cm/h. The capillary number for this displacement process was approximately 10^{-6}, consistent with previously published studies and which has been shown to produce stable, discontinuous (residual) distributions of nonwetting liquids [21,22]. Final values for TCE fluid saturation were determined by moment analysis using the effluent data collected during the dissolution experiments.

The dissolution experiments were conducted in duplicate or triplicate for each porous medium. An additional set of experiments was conducted with the Hayhook medium to evaluate the impacts of organic-liquid saturation level and representative elementary volume (REV) on mass-removal behavior. Dissolution was initiated by flushing the column with de-aired aqueous solution at a flowrate equivalent to a mean pore-water velocity of approximately 20 cm/h. The solution was pumped into the column from the bottom (the same direction in which organic liquid was injected into the column) using an HPLC pump. The original endplates (distribution plate and porous frits) were replaced with clean endplates while dissolution remained in the steady-state stage, approximately 20 pore volumes after dissolution began, to reduce the impact of TCE entrapped in the endplates on mass flux. Effluent samples were collected with 2-ml or 5-ml glass syringes (Popper & Sons, Inc., New Hyde Park, NY) and diluted as needed.

Multiple approaches were used to ensure that the observed behavior was not an artifact of the system or methods. As noted above, the porous endplates were replaced during the initial steady-state stage for all experiments so that organic liquid trapped in the endplates during column preparation would not influence long-term mass removal. For selected experiments, the endplates were replaced a second time, prior to the start of the secondary steady-state stage. In addition, selected experiments were conducted wherein a stainless steel screen was used in place of the porous endplates. Finally, to confirm whether or not organic liquid was still present in the porous medium at the start of a secondary steady-state stage, an in situ ethanol flush was performed for selected experiments. For these experiments, the columns were flushed continuously with water, in identical fashion to the aqueous flushing experiments, up to the point where the first secondary steady-state region was observed in the corresponding aqueous flushing experiment. At this point, the column was flushed with ethanol, and the effluent was sampled to determine the mass removed. The mass extracted was compared to the mass calculated to be present in the column in the aqueous and sorbed phases. The latter quantity was determined using the K_d value obtained from the miscible-displacement experiments and the measured aqueous concentration (prior to the ethanol flush).

2.3. Chemical analysis

PFBA samples were analyzed using a UV–vis spectrophotometer (SPD-10A Shimadzu) at a wavelength of 262 nm. Aqueous TCE samples, ranging in concentrations from saturation (1300–1400 mg/L) to approximately 10 mg/L were analyzed using a UV–vis spectrophotometer at a wavelength of 232 nm. A GC-ECD (Electron Capture Detector) with headspace autosampler and a Supelco SPB-624 capillary column was used to analyze TCE samples for concentrations below 10 mg/L. GC analysis was also used for samples containing ethanol. The oven temperature was held at 40 °C for 2 min and then increased at a rate of 10 °C/min to a final temperature of 170 °C. The injector temperature was set at 180 °C, and the detector temperature was set at 200 °C. The quantifiable detection limit for this method was approximately 0.5 μg/L.

3. Results

Aqueous miscible-displacement experiments (no organic liquid present) were conducted to determine the impact of sorption/desorption on TCE transport and elution behavior (see Fig. 1a). TCE exhibited different magnitudes of sorption to the porous media (see retardation factors in Table 1). Extended elution tailing was observed starting at concentrations approximately five