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NONIDEAL TRANSPORT OF CONTAMINANTS IN HETEROGENEOUS POROUS MEDIA: CHARACTERIZING AND MODELING ASYMPTOTIC CONTAMINANT ELUTION TAILING FOR SEVERAL SOILS AND AQUIFER SEDIMENTS

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Abstract

Miscible-displacement experiments were conducted to characterize long-term, low-concentration elution tailing associated with sorption/desorption processes. A variety of soils and aquifer sediments, representing a range of particle-size distributions and organic-carbon contents, were employed, and trichloroethene (TCE) was used as the model organic compound. Trichloroethene transport exhibited extensive elution tailing for all media, with several hundred to several thousand pore volumes of water flushing required to reach the detection limit. The elution tailing was more extensive for the media with higher organic-carbon contents and associated retardation factors. However, when normalized by retardation, the extent of tailing did not correlate directly to organic-carbon content. These latter results suggest that differences in the geochemical nature of organic carbon (e.g., composition, structure) among the various media influenced observed behavior. A mathematical model incorporating nonlinear, rate-limited sorption/desorption described by a continuous distribution function was used to successfully simulate trichloroethene transport, including the extensive elution tailing.

Keywords

sorption kinetics; continuous-distribution; transport modeling

INTRODUCTION

Contamination of subsurface environments by organic compounds continues to pose a risk to human health and the environment. Sorption is a critical process influencing the transport and fate of organic contaminants in the subsurface. Contaminant mobility and bioavailability are both mediated in part by sorption. Sorption can also affect the magnitudes and rates of contaminant mass flux at hazardous waste sites. Thus, it is important to understand the impact

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of sorption on retention and transport, including behavior over longer time scales (e.g., ITRC, 2004; SERDP, 2006).

Sorption of organic compounds by natural porous media has been investigated extensively during the past few decades. A prevalent observation from this research is that the desorption of many organic contaminants from soils and sediments is significantly rate-limited, often requiring days or months to attain equilibrium. This phenomenon is of particular relevance in regards to long-term contaminant bioavailability and mass-removal behavior.

One manifestation of rate-limited desorption is a reduced rate of mass removal under advective-diffusive transport conditions, and the concomitant observation of an asymptotic decline in concentrations of contaminant in fluid flowing from a contaminated porous medium (i.e., asymptotic elution tailing). Such tailing behavior has been typically observed for organic compounds when analytical methods with sufficient detection limits have been employed, as shown by the results of both aqueous miscible-displacement experiments (e.g., Pignatello et al., 1993; Piatt and Brusseau, 1998; Ahn et al., 1999; Johnson et al., 2003, 2009; Deng et al., 2008; Kempf and Brusseau, 2009) and gas-purge experiments (e.g., Grathwohl and Reinhard, 1993; Farrell and Reinhard, 1994; Werth et al., 1997; Lorden et al., 1998; Kleinedam et al., 2004; Li and Werth, 2004). The majority of these studies have typically each employed a single porous medium. Thus, the potential impact of tailing phenomena has not been examined contemporaneously to a significant extent for a range of natural porous media. Conducting such studies would help address questions such as what is the impact of the magnitude of retention on the extent of tailing, and if the extent of tailing correlates to soil properties such as organic-carbon content or particle-size distribution.

The objective of this research is to investigate the occurrence of asymptotic elution tailing for a representative organic compound during transport in natural soils and sediments, and to evaluate the influence of soil properties on observed behavior. Several soils and aquifer sediments comprising a range of particle-size distributions, organic-carbon contents, and clay contents are used. Miscible-displacement experiments are conducted wherein trichloroethene elution is monitored over concentration changes spanning six to seven orders of magnitude. Solute transport is simulated using a mathematical model that explicitly accounts for nonlinear, rate-limited sorption/desorption, and pore/grain-scale sorption/desorption heterogeneity with the use of the continuous-distribution approach. The applicability of the model for the diverse porous media employed is evaluated.

MATERIALS AND METHODS

Materials

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. 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. Several natural porous media were used for the experiments. Borden aquifer sediment was collected from the Canadian Air Force Base in Borden, Ontario. Eustis sub-soil was collected from The University of Florida, Gainesville, Florida. Hayhook soil, Mt. Lemmon soil, and AFP 44 aquifer sediment were collected from Pima County, AZ. A mixed medium (Mt. Lemmon Mix) was created by combining 20% of the high organic-carbon Mt. Lemmon soil with 80% of a low organic-carbon sand. Properties of each media are listed in Table 1.

The geochemical composition of the organic-carbon fractions was characterized for selected porous media (Eustis, AFP44, Borden). This characterization was conducted 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 0.1M sodium hydroxide to remove the humic and fulvic acid fraction, and finally, treatment by acid dichromate (0.1M potassium dichromate and 2M sulfuric acid) to remove kerogen.

Methods

The columns were uniformly packed in steps with air-dried porous media. After packing, the columns were saturated with a de-aired electrolyte solution (0.01 N CaCl_2). Complete saturation was assumed once a constant mass was attained for the column. Approximately 10–50 pore volumes of a TCE-saturated solution were injected into the bottom of the vertically positioned column using an ISCO syringe pump (Model 500D). The size of the input pulse was varied between experiments such that it would be several times larger than the expected retardation factor for TCE transport for each porous medium (thereby scaling the volume injected to the magnitude of retardation). After injection of the TCE input pulse, the column was flushed with the electrolyte solution. The experiments were conducted at a flowrate equivalent to a mean pore-water velocity of approximately 20cm/hr, which is within the range of velocities associated with induced-gradient conditions (e.g., pump-and-treat operations). Effluent samples were collected manually in 2-ml or 5-ml glass syringes (Popper & Sons, Inc, New Hyde Park, N.Y.), and analyzed immediately. Replicate experiments (2–4) were conducted for each porous medium. The data for AFP44 were reported previously by Johnson et al. (2009).

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 EC, ramped to 150 EC at a rate of 10 EC per minute, and held for two minutes. The injection port temperature was set at 180 EC, with the detectors at 180 EC and 210 EC 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 0.1 $\mu\text{g L}^{-1}$. Selected samples were also analyzed using UV-Vis spectrophotometry (QDL = 1 mg L^{-1}) to provide confirmation of analytical results.

Data Analysis

The total eluted solute mass was determined through analysis of the area under the concentration versus time curve (zeroth moment). The retardation factor, R ($R = 1 + K_{dp/n}$, where ρ is bulk density and n is porosity), and apparent distribution coefficient, K_d ($\text{L}^3 \text{M}^{-1}$), for trichloroethene were determined through moment analysis of the trichloroethene elution curves.

Rate-limited sorption/desorption has generally been incorporated into mathematical models by use of the two-domain approach, wherein the medium is divided into two sorption domains. However, this approach has been shown to be inadequate for simulating the extensive, low-concentration elution tailing associated with long-term flushing of contaminated porous media. Such observations have led to the use of transport models that incorporate 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). Such a model, hereafter referred to as the continuous-distribution model, was used herein to represent nonlinear, rate-limited sorption/desorption. 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).

RESULTS AND DISCUSSION

General Transport Behavior

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. Dispersivity values obtained from calibration of an ideal advective-dispersive transport model to the PFBA data are reported in Table 1. Larger values are obtained for the media with larger particle-size distributions (larger uniformity coefficients), as would be expected.

Mass recoveries for the TCE experiments ranged from 97–103%, 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 and K_d values for TCE determined from moment analysis of the breakthrough curves are presented in Table 2. The values are observed to range considerably, with larger values obtained for the porous media with larger organic-carbon contents.

Trichloroethene transport exhibited extensive elution tailing for all media (Figure 1). Several hundred to several thousand pore volumes of water flushing were required to reach the quantifiable detection limit, despite the relatively low retardation factors. The elution tailing is generally more extensive for the media with higher organic-carbon contents. For example, approximately 500 pore volumes were required to reach the detection limit for the Hayhook soil ($f_{oc} = 0.08\%$), while approximately 4000 pore volumes were required for the Eustis ($f_{oc} = 0.38\%$) soil (Figure 2). The results of replicate experiments indicate that the transport behavior was reproducible, as illustrated in Figure 2.

Influence of Soil Properties on Nonideal Transport

As noted above, extensive asymptotic elution tailing was observed for trichloroethene for all media. This is consistent with the results of prior studies (e.g., Pignatello et al., 1993; Piatt and Brusseau, 1998; Ahn et al., 1999; Johnson et al., 2003, 2009; Deng et al., 2008; Kempf and Brusseau, 2009). In contrast to the prior work, the use of several media in this current study allows for an examination of the impact of soil properties on the observed tailing phenomenon.

To compare elution behavior among the various media, eluted pore volumes were normalized by the retardation factor of trichloroethene for each particular porous medium (Figure 3). Given that the magnitude of sorption (R value) corresponds directly to organic-carbon content, this normalization in essence addresses the impact of organic-carbon content on elution behavior. Interestingly, the extents of the normalized elution tailing do not correspond directly to the magnitudes of the retardation factor (or organic-carbon content). For example, the greatest normalized tailing is observed for Eustis, despite the fact that its retardation factor is more than 3-times smaller (and its organic-carbon content is more than 10-times smaller) than that of the Mt. Lemmon soil. Additionally, the normalized tailing behavior for the Mt. Lemmon mix is similar to that observed for the Mt. Lemmon soil, despite the large difference in organic-carbon contents. This latter result indicates that mixing a large fraction of sand with the Mt. Lemmon

soil did not affect the inherent TCE tailing behavior. The extent of normalized tailing also did not correlate with clay content or particle-size distribution. All of these results suggest that differences in the geochemical nature of the organic carbon (e.g., composition, structure) among the various media may be influencing observed behavior.

Mechanisms potentially responsible for nonideal sorption of hydrophobic organic compounds by natural porous media are generally considered to involve primarily interactions with organic-carbon components of the sorbents (e.g., Brusseau et al., 1991; Luthy et al., 1997; Xing and Pignatello, 1997; Weber and Young, 1997; Cornelissen et al., 2005; Abu and Smith, 2006; Koelmans et al., 2006; Morelis and van Noort, 2008; Prevedouros et al., 2008). Attention has recently focused on so-call hard-carbon components such as black carbon and kerogen as potential sources of recalcitrant behavior for organic contaminants. Experiments conducted to characterize the organic carbon of selected porous media showed a diversity in composition for all three media tested. For example, the organic carbon for the Eustis soil was found to be composed of approximately 37% hard carbon (kerogen and black carbon) and 63% soft carbon (humic/fulvic acids, lipids), while the organic carbon for AFP 44 aquifer material is composed of approximately 61% hard carbon and 39% soft carbon. The organic carbon for Borden aquifer material comprised a high percentage of kerogen and black carbon, consistent with the results of Ran et al. (2007). Interestingly, the porous medium (Eustis) for which the most extensive TCE elution tailing was observed has the smallest fraction of hard carbon among those analyzed. It is likely that the geochemical properties of the organic-carbon components vary among the soils and sediments, given differences in environmental conditions under which the media were formed and weathered. Thus, it is to be expected that differences in component composition and structure, as well as content, may influence sorption/desorption behavior.

Transport Modeling

As discussed above, the continuous-distribution approach has become a popular means by which to represent rate-limited sorption/desorption in transport models. Despite its popularity, the applicability of the approach has not been tested for a wide range of natural soils and sediments. The transport model incorporating a continuous-distribution function for sorption/desorption produced generally good simulations of the measured data, as illustrated in Figure 1. 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. For Mt. Lemmon soil, however, the model was less able to approximate the shape of the observed curve.

Calibrated parameters comprised the mean desorption rate coefficient (k_2), the variance of k_2 , and the fraction of instantaneous desorption (F). Values for the three parameters are presented in Table 2. Sensitivity analyses were conducted to evaluate the robustness of the fitted parameters. The results of those conducted for a Hayhook soil experiment are shown in Figure 4. The results illustrate the sensitivity of the model to these parameters, wherein it is observed that relatively small changes in the parameter values result 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 (data not shown). 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).

SUMMARY

A series of miscible-displacement experiments was conducted to characterize the sorption and transport of trichloroethene in several natural porous media comprising a range of geochemical properties. Effluent samples were monitored over concentrations of six to seven orders of magnitude, allowing characterization of asymptotic tailing phenomenon. The results of the column experiments showed that trichloroethene exhibited extensive elution tailing for all of the media employed. The extent of retardation-normalized tailing did not correlate with basic porous-medium properties such as organic-carbon content, clay content, or particle-size distribution. It is suggested that trichloroethene desorption and concomitant elution tailing is influenced by differences in the geochemical nature of organic-carbon components of the porous media. 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 extensive tailing was due primarily to rate-limited desorption, with a minor contribution from nonlinear sorption. Such behavior is expected to have an impact on contaminant persistence and long-term bioavailability in soils and sediments, and to affect long-term mass flux at hazardous waste sites.

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REFERENCES

- Ahn I, Lion LW, Shuler MW. Validation of a hybrid “two-site gamma” model for naphthalene desorption kinetics. *Environ. Sci. Technol* 1999;33:3241–3248.
- Brusseau ML, Jessup RE, Rao PSC. Nonequilibrium sorption of organic chemicals: Elucidation of rate-limiting processes. *Environ. Sci. Technol* 1991;25:134–142.
- Chen W, Wagenet RJ. Solute transport in porous media with sorption-site heterogeneity. *Environ. Sci. Technol* 1995;29:2725–2734.
- Connaughton DF, Stedinger JR, Lion LW, Shuler ML. Description of time-varying desorption kinetics: release of naphthalene from contaminated soils. *Environ. Sci. Technol* 1993;27:2397–2403.
- Culver TB, Hallisey SP, Sahoo D, Deitsch JJ, Smith JA. Modeling the desorption of organic contaminants from long-term contaminated soil using distributed mass transfer rates. *Environ. Sci. Technol* 1997;31:1581–1588.
- Deng J, Jiang X, Zhang X, Hua W, Crawford JW. Continuous time random walk model better describes the tailing of atrazine transport in soil. *Chemosphere* 2008;2150–2157. [PubMed: 18289634]
- Farrell J, Reinhard M. Desorption of halogenated organics from model solids, sediments, and soil under unsaturated conditions. 2. Kinetics. *Environ. Sci. Technol* 1994;28:63–72.
- Grathwohl P, Reinhard V. Desorption of trichloroethylene in aquifer material: Rate limitation at the grain scale. *Environ. Sci. Technol* 1993;27:2360–2366.
- Haggerty R, Gorelick SM. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. *Water Resour. Res* 1995;31:2383–2400.
- Haggerty R, Gorelick SM. Modeling mass transfer processes in soil columns with pore-scale heterogeneity. *Soil Sci. Soc. of Amer. J* 1998;62:62–74.
- Interstate Technology and Regulatory Council Dense Nonaqueous Phase Liquids Team. Regulatory overview: DNAPL source zone reduction: Facing the challenge. 2002 April;
- Jeong S, Werth CJ. Evaluation of methods to obtain geosorbent fractions enriched in carbonaceous materials that affect hydrophobic organic chemical sorption. *Environ. Sci. Technol* 2005;39:3279–3288. [PubMed: 15926579]
- Johnson GR, Norris DK, Brusseau ML. Mass removal and low-concentration tailing of trichloroethene in freshly-amended, synthetically-aged, and field-contaminated aquifer material. *Chemosphere* 2009;75:542–548. [PubMed: 19157496]

- 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.
- Kempf A, Brusseau ML. Impact of non-ideal sorption on low-concentration tailing behavior for atrazine transport in two natural porous media. *Chemosphere* 2009;77:877–882. [PubMed: 19699507]
- Kleineidam S, Rugner H, Grathwohl P. Desorption kinetics of phenanthrene in aquifer material lacks hysteresis. *Environ. Sci. Technol* 2004;38:4169–4175. [PubMed: 15352457]
- Li J, Werth CJ. Slow desorption mechanisms of volatile organic chemical mixtures in soil and sediment micropores. *Environ. Sci. Technol* 2004;38:440–448. [PubMed: 14750718]
- Li Z, Brusseau ML. Nonideal transport of reactive solutes in heterogeneous porous media. 6. Microscopic and macroscopic approaches for incorporating heterogeneous rate-limited mass transfer. *Water Resour. Res* 2000;36:2853–2867.
- Lorden SW, Chen WL, Lion LW. Experiments and modeling of the transport of trichloroethene vapor in unsaturated aquifer material. *Environ Sci. Technol* 1998;32:2009–2017.
- Pedit JA, Miller CT. Heterogeneous sorption processes in subsurface systems. 1. Model formulations and applications. *Environ. Sci. Technol* 1994;28:2094–2104.
- Piatt JJ, Brusseau ML. Rate-limited sorption of hydrophobic organic compounds by soils with well-characterized organic matter. *Environ. Sci. Technol* 1998;32:1604–1608.
- Pignatello JJ, Ferrandino FJ, Huang LQ. Elution of aged and freshly added herbicides from a soil. *Environ. Sci. Technol* 1993;27:1563–1571.
- Ran Y, Baohua X, Fu J, Sheng G. Sorption and desorption hysteresis of organic contaminants by kerogen in a sandy aquifer material. *Chemosphere* 2003;50:1365–1376. [PubMed: 12586168]
- Saiers JE, Tao G. Evaluation of continuous distribution models for rate-limited solute adsorption to geologic media. *Water Resour. Res* 2000;36:1627–1639.
- Strategic Environmental Research and Development Program (SERDP). Final report : SERDP and ESTCP expert panel workshop on reducing the uncertainty of DNAPL source zone remediation. 2006 September; 2006.
- Werth CJ, Cunningham JA, Roberts PV, Reinhard M. Effects of grain-scale mass transfer on the transport of volatile organics through sediments. 2. Column results. *Water Resour. Res* 1997;33:2727–2740.
- Zhang Z, Brusseau ML. Nonideal transport of reactive porous media: 7. Distributed-domain model incorporating immiscible-liquid dissolution and rate-limited sorption/desorption. *J. Contam. Hydrol* 2004;74:83–103. [PubMed: 15358488]

Figure 1.
Elution curves and mathematical-model simulations for miscible-displacement experiments.

Figure 2.
Measured and simulated elution curves for three replicate experiments with Eustis soil.

Figure 3.
Normalized elution curves, with pore volumes divided by respective retardation factor (PV/
R).

Figure 4. Sensitivity analysis for mathematical model (experiment conducted with Hayhook soil): a. mean desorption rate coefficient (k_2), b. variance of k_2 , c. F value. The F value represents the fraction of instantaneous desorption.

Table 1

Porous Medium Properties

Porous Medium	Sand %	Silt %	Clay %	Organic Carbon Content %	Bulk Density (g/cm ³)	Porosity	Median Grain Diameter d ₅₀ (mm)	Uniformity Coefficient (d ₆₀ /d ₁₀)	Dispersivity a _L (cm)
Borden	96.2	2.0	1.8	0.03	1.74	0.34	0.21	1.9	0.13
Eustis	96	1.0	3.0	0.38	1.69	0.36	0.27	2.3	0.10
AFP 44	97.5	1.3	1.2	0.06	1.81	0.32	0.33	4.6	0.64
Hayhook	85.5	4.3	10.2	0.08	1.64	0.38	0.26	16	1.75
Mt. Lemmon Mix	89	7.8	3.2	2.7	1.45	0.44	0.17	3.1	0.20
Mt. Lemmon soil	60	24	16	10	1.17	0.56	0.11	23	0.44

Table 2

Transport Parameters

	Mean k_2	Variance k_2	F	Retardation Factor	K_d
Borden	0.5	9.0	0.25	1.5	0.10
Eustis	1.7	9.2	0.1	2.4	0.30
AFP 44	3.4	9.8	0	1.1	0.02
Hayhook	3.0	8.0	0.7	1.3	0.07
Mt. Lemmon Soil	0.05	15	0.3	8.2	3.4
Mt. Lemmon Mix	10.9	5.0	0	3.4	0.73