



Nonideal transport of contaminants in heterogeneous porous media: 10. Impact of co-solutes on sorption by porous media with low organic-carbon contents

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HIGHLIGHTS

- The impact of co-solutes on sorption of PCE by media with low organic-carbon contents was examined.
- No competitive sorption was observed for the medium with lower hard-carbon content.
- Competitive sorption was observed for the medium with higher hard-carbon content.

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ABSTRACT

The impact of co-solutes on sorption of tetrachloroethene (PCE) by two porous media with low organic-carbon contents was examined by conducting batch experiments. The two media (Borden and Eustis) have similar physical properties, but significantly different organic-carbon (OC) contents. Sorption of PCE was nonlinear for both media, and well-described by the Freundlich equation. For the Borden aquifer material (OC = 0.03%), the isotherms measured with a suite of co-solutes present (1,2-dichlorobenzene, bromoform, carbon tetrachloride, and hexachloroethane) were identical to the isotherms measured for PCE alone. These results indicate that there was no measurable impact of the co-solutes on PCE sorption for this system. In contrast to the Borden results, there was a measurable reduction in sorption of PCE by the Eustis soil (OC = 0.38%) in the presence of the co-solutes. The organic-carbon fractions of both media contain hard-carbon components, which have been associated with the manifestation of nonideal sorption phenomena. The disparity in results observed for the two media may relate to relative differences in the magnitude and geochemical nature of these hard-carbon components.

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1. Introduction

Sorption is one of the primary processes influencing the transport and fate behavior of organic compounds in the environment. An accurate understanding of sorption mechanisms and their impact can often be critical for assessing risk, evaluating bioavailability, and implementing remediation efforts. One key aspect of characterizing sorption processes is determining the potential significance of rate-limited, nonlinear, and hysteretic sorption (e.g., Brusseau and Rao, 1989; Pignatello and Xing, 1996; Luthy et al., 1997), which may be considered nonideal behavior in contrast to the ideal case of instantaneous, linear, non-hysteretic sorption. Over the past

two decades, a large body of research has been developed focusing on nonideal sorption and potential causative mechanisms. Attention has recently focused on the condensed or hard-carbon components of soil organic carbon, such as black carbon and kerogen, as potential sources of nonideal sorption behavior (e.g., Luthy et al., 1997; Weber and Young, 1997; Xing and Pignatello, 1997; Bucheli and Gustafsson, 2000; Jonker and Koelmans, 2002; Ran et al., 2003; Xiao et al., 2004; Cornelissen et al., 2005; Chai et al., 2007; Prevedouros et al., 2008; Johnson et al., 2009; Russo et al., 2010).

Competitive sorption is another potential nonideal sorption phenomenon that may have significant impacts on transport and fate behavior. Several studies have been conducted to examine the impact of co-solutes on sorption of lower-polarity organic compounds by natural soils and sediments (e.g., Lee et al., 1988; McGinley et al., 1993; Xing et al., 1996; Xing and Pignatello, 1997; White and Pignatello, 1999; White et al., 1999; Li and Werth, 2001; Rivett and Allen-King, 2003; Ju and Young, 2004; Zhang et al., 2010; Xiao and Huang, 2011). The majority of such

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experiments have used porous media with total organic-carbon contents of 1% or greater. Conversely, few have been conducted using media with organic-carbon contents between 0.1% and 1% (McGinley et al., 1993; Li and Werth, 2001; Zhang et al., 2010), and fewer still with values less than 0.1% (Lee et al., 1988; Rivett and Allen-King, 2003).

The objective of this research was to examine the impact of co-solutes on sorption of tetrachloroethene by two porous media with low organic-carbon contents. One medium employed is the Borden aquifer material, collected from the site at which a well-known field study was conducted to examine the impact of sorption phenomena on transport of organic compounds in groundwater (Mackay et al., 1986). The second medium is a sandy soil that has similar physical properties as the Borden material, but a significantly larger organic-carbon content.

2. Materials and methods

2.1. Materials

Tetrachloroethene (PCE) was used as the model organic compound. In addition, 1,2-dichlorobenzene, bromoform, carbon tetrachloride, and hexachloroethane were used as the co-solutes. Dichloromethane was used to extract sorbed-phase PCE for selected batch-reactors, as discussed below. All chemicals (Aldrich Chemical Co., Inc., Milwaukee, WI) were reagent grade. Relevant properties of the chemicals are presented in Table 1.

Borden aquifer material was collected from the site at which the well-documented natural-gradient organic tracer experiment was conducted (Mackay et al., 1986). The samples were collected from an interval approximately 1.5–3 m below ground surface (and below the water table), coincident with the injection interval for the field experiment. Two samples were collected from different locations, with one (used for experiments 1 and 2 in Fig. 1) collected adjacent to the injection zone. The properties of the Borden sediment, and its sorption of organic compounds, have been characterized in several studies (e.g., Curtis et al., 1986; Lee et al., 1988; Ball and Roberts, 1991; Ran et al., 2003; Rivett and Allen-King, 2003). Eustis sandy surface soil was collected from the University of Florida campus. The properties and sorption behavior of the Eustis soil have also been characterized in several studies (Brusseau et al., 1989, 1991, 2012; Nkedi-Kizza et al., 1989; Brusseau, 1993; Russo et al., 2010). Both media were air dried after collection and stored for future use.

Pertinent properties of the media are presented in Table 2. The physical properties of the two media are similar. Conversely, the organic-carbon content for the Eustis soil is approximately ten times larger than that of the Borden material. The geochemical compositions of the organic-carbon fractions of the two media were characterized previously (Russo et al., 2010). The organic carbon for Borden aquifer material comprises a high percentage (~65%) of kerogen and black carbon, consistent with the results of Ran et al. (2003). The organic carbon in the Eustis media is composed of approximately 37% hard carbon (kerogen and black carbon) and 63% soft carbon (humic/fulvic acids, lipids).

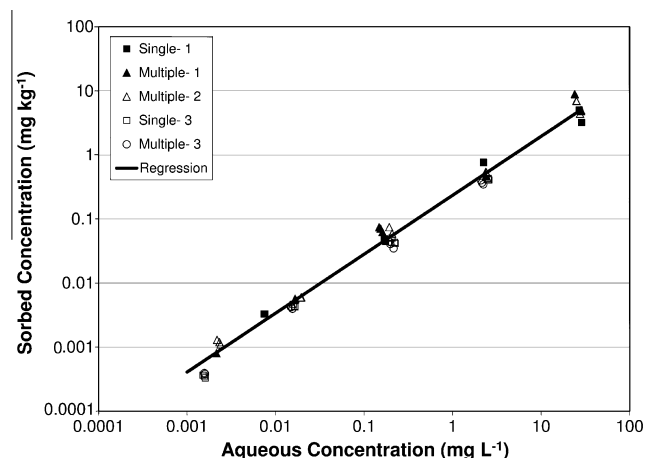


Fig. 1. Isotherm data for sorption of tetrachloroethene by the Borden aquifer material. Single and multiple refer to the absence or presence of co-solutes (1,2-dichlorobenzene, bromoform, carbon tetrachloride, and hexachloroethane). Regression obtained with Freundlich equation ($S = 0.23C^{0.9}$, $r^2 = 0.991$, where S is sorbed-phase concentration and C is aqueous-phase concentration).

For the Borden experiments, an electrolyte solution was prepared to be representative of the groundwater at the Borden field site, as described by Ball and Roberts (1991). The solution comprised CaCO_3 (100 mg L^{-1}), MgSO_4 (25 mg L^{-1}), NaCl (3.8 mg L^{-1}), and KCl (1.1 mg L^{-1}). An electrolyte solution containing 0.01 N CaCl_2 was used for all Eustis experiments. Aqueous solutions of PCE and the other solutes were made by dilution of pre-prepared stock solutions saturated with the target compounds. The stock solutions were prepared without the use of methanol or other solubilizers.

2.2. Experiment setup

Three sets of experiments were conducted. The first comprised preliminary batch rate experiments to determine the time required for sorption to attain equilibrium, which was less than approximately 2 d for samples prepared with pulverized media, consistent with prior results (Ball and Roberts, 1991). Equilibration times of 3–5 d were used for all experiments employing pulverized samples, with longer times for those employing unpulverized samples.

The second set of experiments was conducted to examine the impact of a suite of co-solutes on the sorption of PCE for Borden and Eustis media. The concentrations used for the co-solutes were matched to the values used in the Borden natural-gradient field study, as follows: 1,2-dichlorobenzene ($332 \mu\text{g L}^{-1}$), bromoform ($32 \mu\text{g L}^{-1}$), carbon tetrachloride ($31 \mu\text{g L}^{-1}$), and hexachloroethane ($20 \mu\text{g L}^{-1}$). Three sets of triplicate samples were prepared, one set with PCE solution only and no sediment (control), one set with sediment and PCE solution (no co-solutes), and one set with sediment, PCE solution, and the co-solutes.

Table 1
Properties of the chemicals.

Compound	Aqueous solubility ^a (mg L^{-1})	$\text{Log } K_{ow}$ ^b	Henry's constant ^b
Tetrachloroethene	150	2.6	0.59
Bromoform	3190	2.3	0.02
Carbon tetrachloride	1160	2.7	0.98
1,2-Dichlorobenzene	145	3.4	0.08
Hexachloroethane	50	3.6	0.12

^a From Verschuere (1996).

^b From Curtis et al. (1986).

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