

**SUPPORTING INFORMATION**  
**ENVIRONMENTAL SCIENCE & TECHNOLOGY**

**Liquid-Liquid Mass Transfer of Partitioning Electron Donors in Chlorinated Solvent Source Zones**

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## **Supporting Information: Materials and Methods**

### **Materials and Solution Preparation**

High-performance liquid chromatography (HPLC)-grade (99.5% purity) TCE was obtained from Fisher Scientific (Fair Lawn, NJ) and dyed with the hydrophobic dye Oil-Red-O (Fisher Scientific) at a concentration of  $4 \times 10^{-4}$  M to visualize the TCE-DNAPL. Two partitioning electron donors, nHex (HPLC grade, 99+% purity) and nBA (HPLC grade, 99.7% purity), were purchased from Sigma-Aldrich (Saint Louis, MO). Relevant physical properties of nHex and nBA are: densities of 0.82 and 0.88 g/cm<sup>3</sup>, molecular weights of 102.7 and 116.2 g/mol, and aqueous solubilities of 5,900 and 7,000 mg/L, respectively. Federal Fine Ottawa sand (30-140 mesh), obtained from the US Silica Company (Berkeley Spring, WV), was used in the column studies due to its low organic carbon content ( $< 0.01$  mg/g) and translucent color. The mean grain size ( $d_{50}$ ) of Federal Fine Ottawa sand is 0.32mm, while the intrinsic permeability is  $4.2 \times 10^{-11}$  m<sup>2</sup> [1]. Aqueous solutions containing nHex or nBA (4,100-5,300 mg/L), sodium bromide (1,000 mg/L, 10 mM ionic strength; Fisher Scientific) and calcium chloride (500 mg/L, 10 mM ionic strength; Fisher Scientific) were prepared in deionized and degassed water (Nanopure; Barnstead/Thermolyne Corp., Dubuque, IA).

### **Column preparation**

Borosilicate glass columns (Kontes Glass Company, Vineland, NJ) equipped with Teflon endplates fitted with 40-mesh and 70  $\mu$ m nylon screens (Spectrum Laboratories Inc., Rancho Dominguez, CA). Whatman No. 42 filter paper, which is water-wetting, was inserted in the top endplate to inhibit breakthrough of TCE-DNAPL during imbibition and cause NAPL to flow back into the porous media, facilitating a uniform distribution of NAPL near the column outlet. The columns were dry packed in approximately 2-cm increments with gentle vibration and

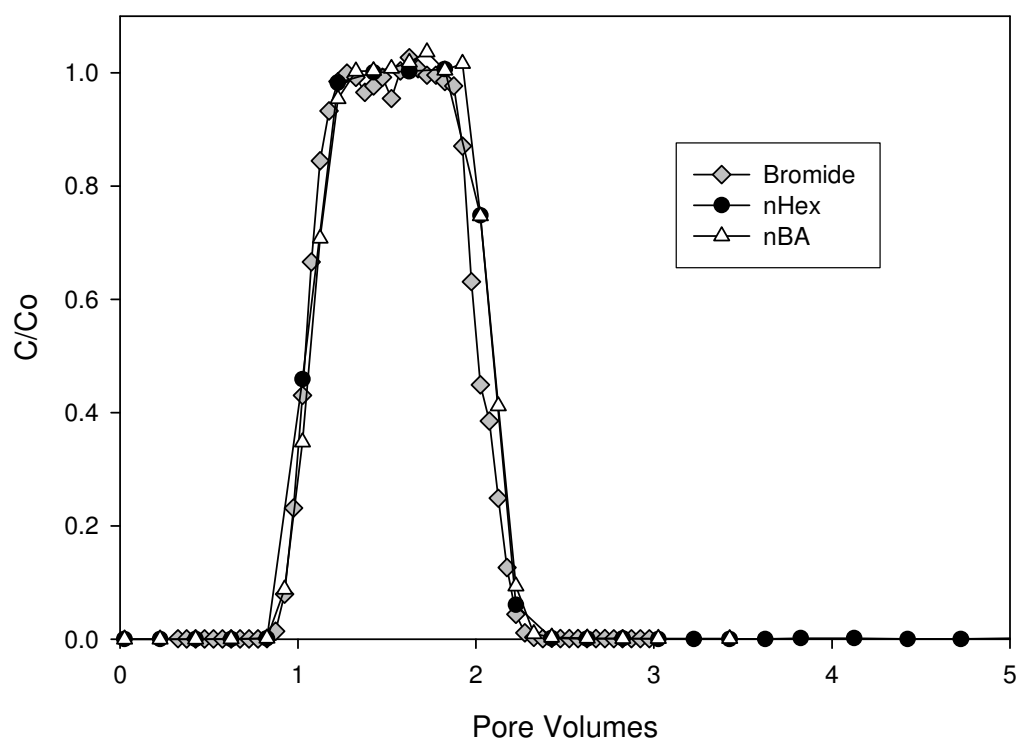
spatula mixing to minimize layering. When packing was complete, the columns were purged with CO<sub>2</sub> gas for at least 30 minutes to facilitate the dissolution of entrapped gas during the initial saturation with a background electrolyte solution (500 mg/L CaCl<sub>2</sub>) for a minimum 10 pore volumes (PVs). The PV of each column was determined from the change in column weight following complete water saturation, and ranged from 98 to 100 mL. A non-reactive tracer (Br<sup>-</sup>) test was conducted prior to NAPL imbibition to confirm the aqueous PV, to ensure the absence of low-flow or immobile zones of water, and to assess hydrodynamic dispersion and flow properties of each column.

TCE-DNAPL was introduced through the bottom of each column at a flow rate of 2 mL/min using a Model 22 Harvard Apparatus syringe pump (Holliston, MA). When TCE-DNAPL reached the top of the column, injection was ceased, and the background electrolyte solution was then introduced through the top of the column in a down flow mode at a flow rate of 2 mL/min to displace mobile TCE-DNAPL. Following the entrapment of TCE-DNAPL, the residual NAPL saturation ( $S_n$ ) was computed based on the change in column weight and fluid contrast difference as previously described [2]. The absence of immobile water and low-flow zones within the column was reconfirmed by a second non-reactive tracer test conducted after the establishment of residual NAPL (representative BTCs are shown in Figure 3).

## **Analytical Methods**

Aqueous samples obtained from the column and batch studies were analyzed for PEDs and TCE using a Hewlett-Packard (HP) model 6890 gas chromatograph (GC) equipped with a liquid autosampler (HP 7683), a flame ionization detector (FID), and an electron capture detector (ECD). Br<sup>-</sup> concentrations were measured using an ion-selective probe (Cole Parmer, Vernon Hills, IL) connected to an Accumet Model 50 pH/ion/conductivity meter (Fisher Scientific). For

94 each GC and probe analyses, a minimum of six standards were used to generate calibration  
95 curves.



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97 Figure S-1: Bromide, nHex and nBA effluent breakthrough curves for Federal Fine Ottawa sand  
98 in the absence of TCE-NAPL.  
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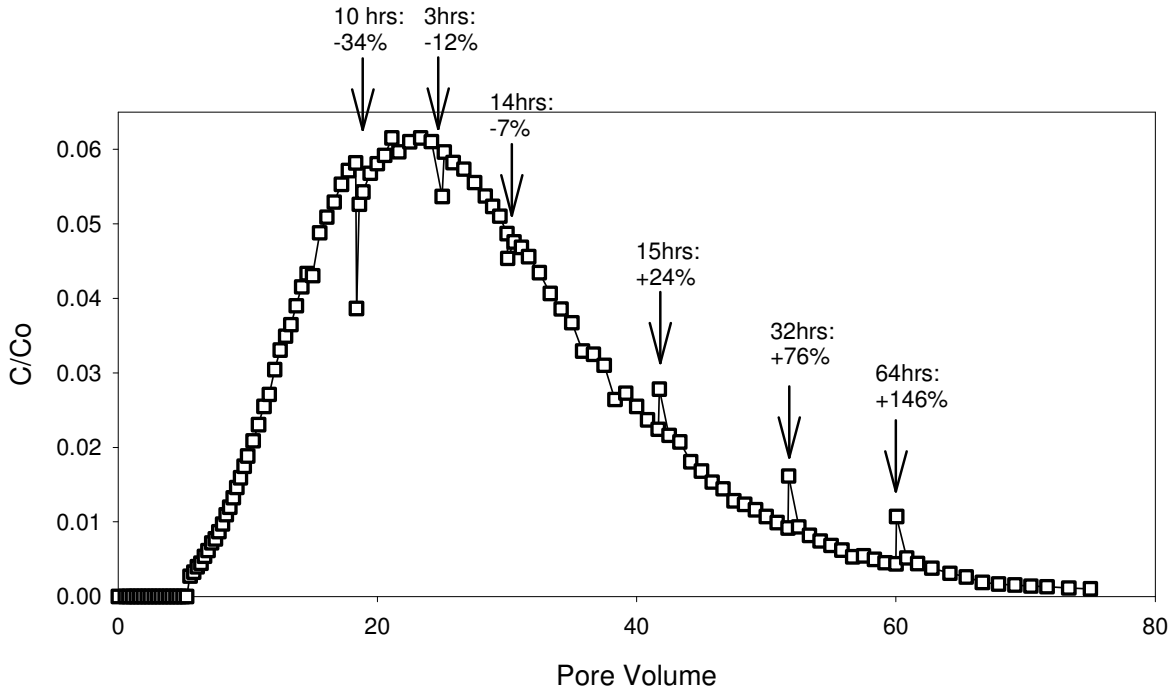


Figure S-2: A detailed illustration of the influence of flow interruptions on nBA mass transfer during the 2.5 mL/min pulse effluent BTC.

A summary of the impacts on the nBA BTC shown in Figure S-2 due to flow interruptions: a drop in aqueous effluent concentrations of 34% after a 10-hrs interruption near the plateau (PV 18), 12% drop after at PV 25 after 3 hrs, 7% drop at PV 30 after 14-hrs, 24% increase at PV 42 after 15-hrs, 76% increase at PV 52 after 32 hrs, and a 145% increase at PV 60 after 64 hrs. Injection of nBA at slower flow rates of 0.5 and 1.5 mL/min, the concentration drop never exceed 10 to 15%, respectively, even with the incorporation of significantly longer periods of flow interruption (up to 355 hrs), consistent with the diminished importance of rate limited mass transfer at slower flow velocities.

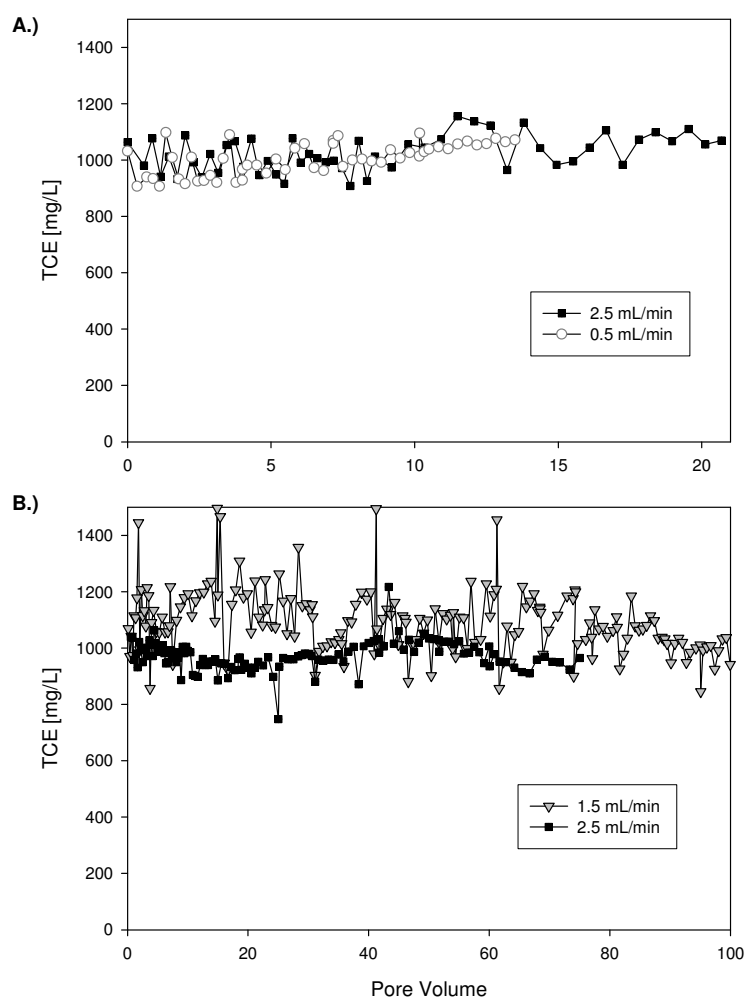


Figure S-3: Additional TCE effluent data not represented in Figure 3 for A.) nHex and B.) nBA.

#### References:

1. Suchomel, E. J.; C.A., R.; Pennell, K. D., Evaluation of trichloroethene recovery processes in heterogeneous aquifer cells flushed with biodegradable surfactants. *Journal of Contaminant Hydrology* **2007**, *94*, 195-214.
2. Pennell, K. D.; Jin, M.; Abriola, L. M.; Pope, G. A., Surfactant enhanced remediation of soil columns contaminated by residual tetrachloroethylene. *Journal of Contaminant Hydrology* **1994**, *16*, (1), 35-53.