

SUPPORTING INFORMATION

Laboratory Methods.

Detailed descriptions of the laboratory methods, along with all of the measured data can be found in Dai (10); a brief summary follows.

Soils. The soil used in this study was collected from a contaminated site at Hill Air Force Base (AFB), UT. Hill AFB is located approximately 50 km north of Salt Lake City, UT at the western foot of the Wasatch Mountain Range. The University of Florida group conducted two field-scale aquifer remediation studies at this site: one using cosolvents (11) and one using a mixture of cosolvents and surfactants to form a microemulsion precursor (13). The field site was located in a NAPL source zone within a shallow surficial aquifer which is located on the Weber Delta, approximately 100 m above the Weber River valley. The aquifer material consists of sand and gravel (Provo Formation), with a thick (> 60 m) clay aquitard (Alpine Formation) approximately 8 m below ground surface (bgs). The aquifer was contaminated through the use of two chemical disposal pits in the 1940s and 1950s. A variety of liquid wastes such as JP-4 jet fuel, spent degreasing solvents, and waste oils were disposed of in these pits. Migration over the years has caused spreading of the NAPL source zone to an area of approximately 2.8 ha.

The NAPL collected from wells at the site was a very hydrophobic mixture which tended to strongly coat solid surfaces. Contaminated soils collected from the site appeared to be completely coated with the NAPL. Free phase NAPL samples collected at the site were completely miscible with both hexane and methylene chloride. However, methylene chloride extraction did not completely remove the NAPL residue from contaminated soils collected from the site. A 'pitch' coating was left behind. When free-phase NAPL from the site was mixed with uncontaminated soils collected from the site, extraction completely removed the contaminants. These results suggest that

the composition of the free-phase NAPL was different from the NAPL found *in situ* (i.e., coating the soil). The laboratory experiments reported here were conducted with NAPL-coated soils collected from the field site.

Column Experiments. NAPL contaminated soil was well mixed before packing into the columns. The columns were water saturated by pumping water at 0.5 mL/min for 8 hrs. Tracer tests were conducted wherein a nonpartitioning tracer (methanol) was used to estimate the pore volume and a partitioning tracer (2,2-dimethyl-3-pentanol, $K_N = 12.9$) was used to estimate the NAPL saturation. For the SPME column experiment, ethanol was the nonpartitioning tracer, while *n*-heptanol ($K_N = 17.4$) was the partitioning tracer. A pulse of the tracer mixture was displaced through the column using a Gilson piston pump. Effluent samples were analyzed using a GC-FID.

Cosolvency Power. The slope of a log-linear relationship between solubility of organic compounds and the volume fraction of organic solvents yields the cosolvency power. Exact amounts of NAPL-contaminated soil (4.5xx g of moist soil) were weighed into 5-ml HPLC vials, and 1.5 ml of cosolvent mixture solution were transferred to the vials. All measurements were triplicated. These solutions were equilibrated on a rotator for 24 hrs. A 2-ml aliquot of the supernatant was analyzed for target constituents by GC-FID. Ten binary mixtures of ethanol and water were used, with 0, 10, 20, 30, 40, 50, 60, 70, 80, and 90 volume percent ethanol. Nine ternary mixtures were used with 70% ethanol, 2, 4, 6, 8, 10, 12, 15, 20, and 25 volume percent pentanol and the remainder water. The log of the measured concentration of the constituent in the cosolvent mixture was plotted against cosolvent fraction. Based on equation (23) and nonideal considerations, the slope of this line was reported as cosolvency power $\psi = \alpha\beta\sigma$, while the y-intercept was the equilibrium constituent aqueous concentration ($\chi_c C_{c,w}^{sat}$).

The binary solvent mixture log-concentration versus cosolvent fraction plots were linear over

the range $f = 0$ to 0.7 , but tended to level off above this fraction, especially for constituents with high aqueous solubility or low mass fraction in the NAPL (see Figure 2-2 of reference 10), indicating exhaustion of these components from the multicomponent NAPL. Only the linear portions of these curves were used to estimate the slope (cosolvency power), with a minimum of five data points for each regression. Note that the range of measured linear regression coefficients (r^2) for these data was 0.972 to 0.987 .

Similar solubilization experiments were also conducted with free-phase NAPL collected from the site. These experiments remove the effect of solvent-sorbent interactions (characterized by the empirical parameter α) such that the slope of the log-linear plot of concentration of the constituent in the cosolvent mixture versus cosolvent fraction is equivalent to $\beta\sigma$. Thus, comparison of the slopes from the free-phase NAPL and NAPL-contaminated soil dissolution experiments allows calculation of α for each constituent. These values for ethanol-water mixtures were determined to be 1.07 , 1.12 , and 1.25 for 1,2-DCB, 1,3,5-TMB, and *n*-undecane, respectively (see Table 2-6 of reference 10). However, for the ternary solvent mixture, the NAPL-contaminated soil and free-phase NAPL dissolution experiments were conducted with different ethanol fractions, precluding direct comparison (and thus direct estimation of α).

Numerical Model.

The simulation model developed by Augustijn et al. (9) for cosolvent-enhanced desorption of contaminants was adapted to simulate cosolvent-enhanced dissolution of NAPLs. The one-dimensional flow model is based on the continuum approach, where desorption is assumed to occur instantaneously at only a fraction of sorption sites, and is described by a first-order mass transfer model at all other sites. For the work presented here, this bicontinuum approach was also assumed

to be appropriate for NAPL dissolution.

The model assumes a water-saturated soil initially in equilibrium with NAPL contaminants that is then flushed with a solvent mixture. Contaminant dissolution and transport in the soil are modified as the mixed solvent front advances through the soil, displacing the resident pore water. Equations (8) and (9) were solved using a Crank-Nicolson central finite difference method. An analytical solution to the advection-dispersion equation was used to describe cosolvent composition in the column. As the mixed solvent front progresses through the soil column, cosolvent effects on sorption are reflected by changes in the model parameters: R , F , and ω .

Laboratory Column Experiment Results.

Cosolvent. While replicate column experiments were not conducted as part of this study, the results presented here are consistent with similar experiments conducted earlier (33). These dissolution experiments were conducted with similarly homogenized aquifer material from the contaminated site and involved flushing of the same cosolvent mixtures as reported above. The GC analyses for the preliminary experiments suffered from poor chromatographic separation of the individual NAPL constituents, limiting our ability to make a universal comparison. However, the dissolution data for *o*-xylene were well-resolved and these data are compared to the *o*-xylene data for the present study (not shown above) in Figure S-3. The nonequilibrium model fits are also shown for both sets of experiments. Note that while the total mass of *o*-xylene differed in the two sets of experiments, the overall BTC shapes, including peak height and extent of tailing, were similar. The ethanol/pentanol/water mixture solubilized the NAPL more quickly and with less rate-limited tailing than the ethanol/water mixture in both sets of experiments. The model parameters required to fit these data are shown in Table S-1. Note that identical values of the nonequilibrium parameter F

were obtained for both sets of experiments, and the ω_w values varied by approximately 33% (recall from Figure 3 that for the constituents considered here, $k_{2,w}$ values varied over three orders of magnitude). These data suggest the repeatability of the observed phenomena.

Supplemental References

(33) Johnson, G.R., M.E. Thesis, University of Florida, Gainesville, FL, 1996.

Table S-1. Nonequilibrium model input parameters for laboratory column cosolvent flushing experiments for *o*-xylene dissolution.

Data Source	P	f	R_w	ψ	F	ω_w
<u>Reference (33)</u>						
ethanol/water	38	0.7	350	3.85	0.05	8.0E-2
ethanol/pentanol/water	38	0.8	350	4.18	0.05	8.0E-2
<u>Reference (10)</u>						
ethanol/water	15	0.7	340	3.85	0.05	6.0E-2
ethanol/pentanol/water	20	0.8	340	4.18	0.05	6.0E-2

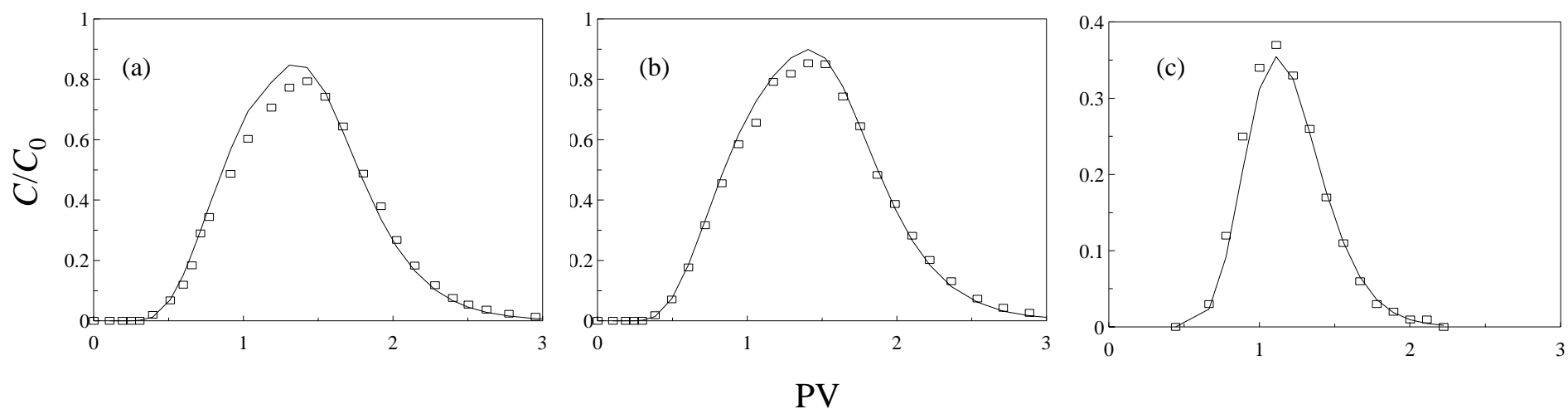


Figure S-1. Preflushing nonpartitioning tracer BTCs with one-dimensional solute transport model fits for laboratory columns flushed with (a) 70% ethanol/30% water, (b) 70% ethanol/10% *n*-pentanol/20% water, and (c) SPME precursor solution. Squares are methanol data and solid lines are advection-dispersion model fits.

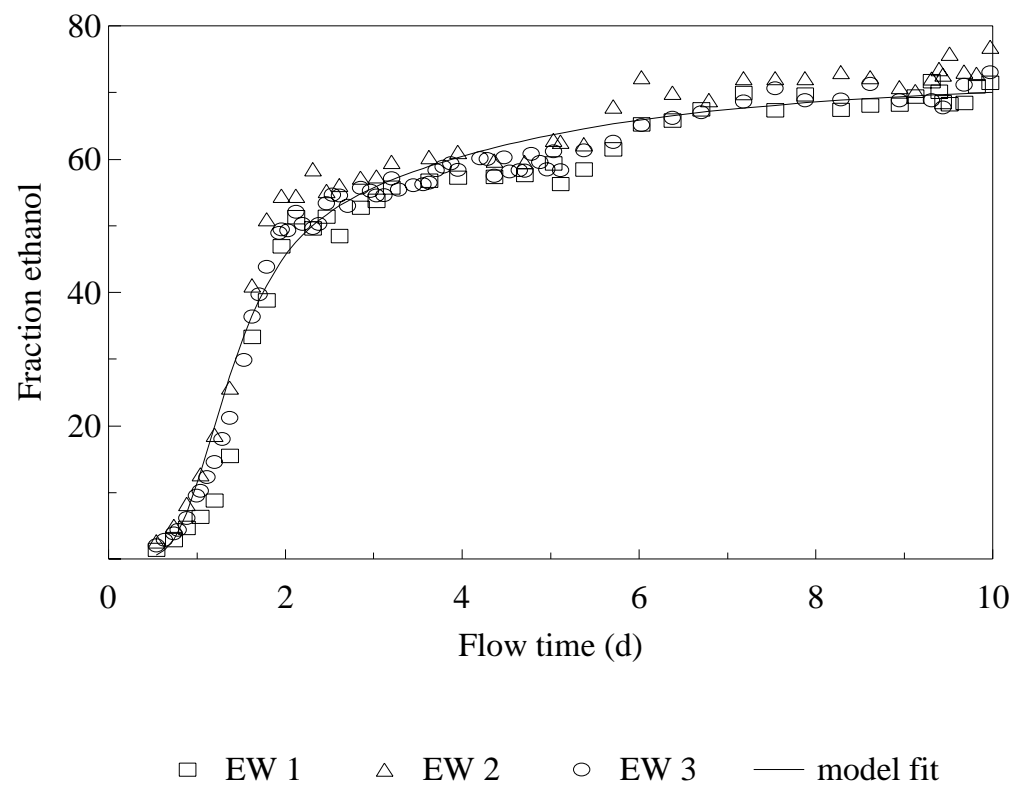


Figure S-2. Ethanol elution profile at all three extraction wells from the cosolvent field study, with a model fit from the superposition of two advection-dispersion equations.

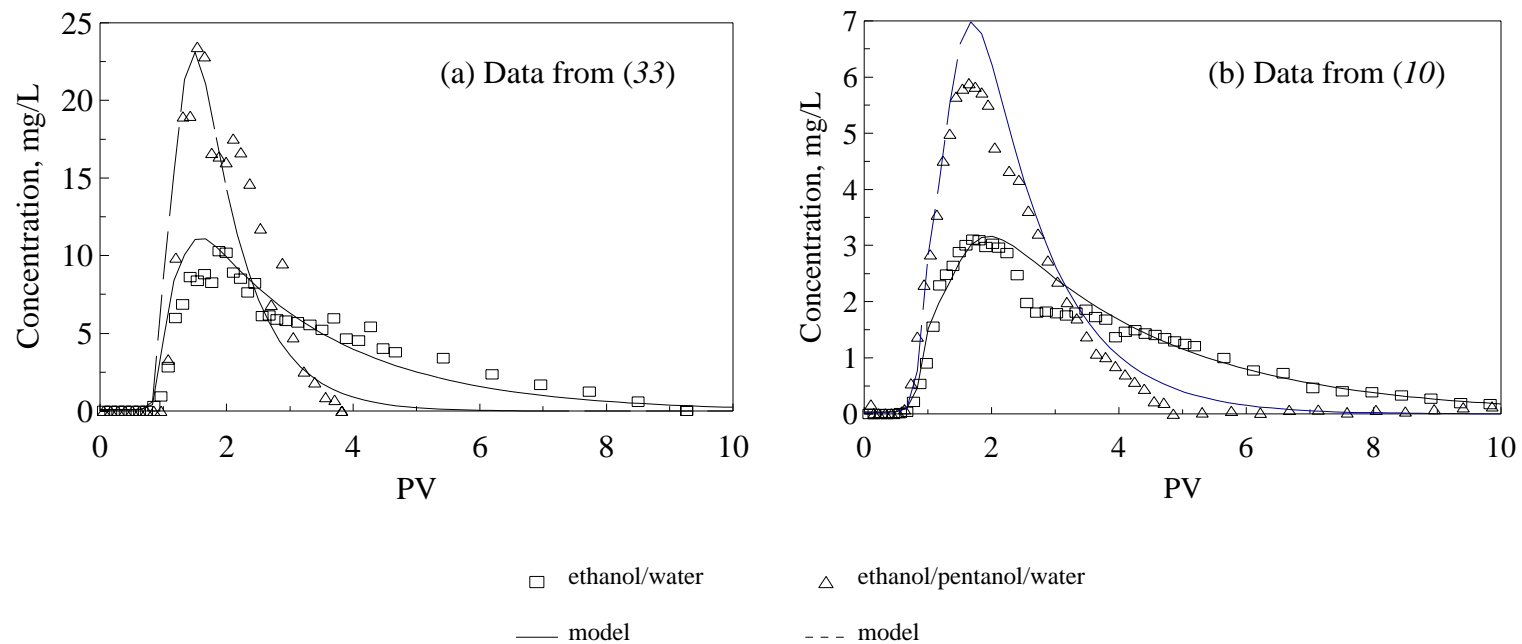


Figure S-3. Comparison of dissolution data for *o*-xylene from two independent column studies. Both data sets show measured and simulated BTCs from laboratory columns packed with contaminated soil from the Hill AFB cosolvent field site and flushed with either 70% ethanol/30% water or 70% ethanol/10% n-pentanol/20% water.