

Innovative Subsurface Remediation

**Field Testing of Physical, Chemical,
and Characterization Technologies**

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Field Test of Cyclodextrin for Enhanced In-Situ Flushing of Multiple-Component Immiscible Organic Liquid Contamination: Comparison to Water Flushing

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A pilot-scale field experiment was conducted to compare the remediation effectiveness of an enhanced-solubilization technique to that of water flushing for removal of multicomponent nonaqueous-phase organic liquid (NAPL) contaminants from a phreatic aquifer. This innovative remediation technique uses cyclodextrin, a sugar (glucose)-based molecule, to enhance the apparent aqueous solubility of organic contaminants. The cyclodextrin solution significantly increased not only the apparent solubility for several target contaminants, but also the rate of dissolution. As a result of these effects, the time required for cleanup of NAPL contamination at this field site may be greatly reduced by using cyclodextrin-enhanced flushing. For example, it was estimated that more than 70,000 pore volumes of water flushing would be required to remove the undecane mass that was removed in the 8-pore volume cyclodextrin flush, and for trichloroethene, which exhibited the smallest solubility enhancement, about 350 pore volumes of water flushing would be required.

Pump and treat is currently the conventional method for remediation of subsurface contamination. However, traditional pump-and-treat techniques are considered to be ineffective for removal of nonaqueous phase liquids (NAPLs) from the saturated zone (1,2,3). The aqueous solubilities for many organic compounds are often very small, typically in the order of milligrams per liter. Therefore, large amounts of water must be flushed through the subsurface to remove the contaminant mass, even under conditions of equilibrium mass transfer between the NAPL and aqueous phases.

Contaminant concentrations in extracted water usually decrease rapidly after initiation of pumping and then level off asymptotically to values that are typically well below the equilibrium concentrations (3). Thus, removal of NAPL-phase contamination by dissolution into the aqueous phase occurs much more slowly than is expected because of these apparent mass-transfer limitations. Accordingly, the presence of residual NAPL can serve as a long-term source of ground water contamination, and may severely limit the attainment of remediation goals at many sites (e.g., 1, 3).

Due to the well-documented limitations of pump-and-treat, alternative methods for remediation of NAPL-contaminated sites are a focus of current research (1). Enhanced in-situ flushing is an innovative remediation technique that is currently attracting a great deal of attention. Solubility-enhancement agents increase the apparent solubility of organic pollutants in the flushing fluid, thereby increasing the mass removed per pore volume flushed. Cosolvents (such as alcohols) and surfactants are examples of reagents that have been proposed for this purpose (2). Numerous laboratory studies have been conducted to investigate the effectiveness of surfactants and cosolvents (see 4, 5 for summaries). However, porous media heterogeneity, NAPL distribution, and NAPL composition are likely to be much more complicated at the field scale than in a carefully controlled laboratory study. For this reason, many researchers agree that pilot-scale field experiments are needed to gain the information necessary to design and conduct successful full-scale remediations (6,7,8). However, few field tests of enhanced-solubility, in-situ flushing technologies have been conducted under well-defined and controlled conditions.

The purpose of this paper is to compare the effectiveness of cyclodextrin flushing (i.e., enhanced pump and treat) to that of water flushing (i.e., basic pump and treat) for remediation of NAPL contamination under essentially identical hydrodynamic and hydrogeologic conditions. Cyclodextrin is an oligosaccharide (sugar-based) molecule that complexes organic contaminants, thereby enhancing their apparent solubility.

The cyclodextrin-flushing and water-flushing experiments were conducted between June and August 1996, at a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) site located at Hill Air Force Base (AFB) Utah. This study is one of several treatability studies of innovative remediation technologies that have been conducted at Hill AFB under the Strategic Environmental Research and Development Program (see Bedient et al. (9)). This experiment is the first to use cyclodextrin, a complexing sugar, as an alternative flushing agent for subsurface remediation at the field scale. For an overview of using cyclodextrin as an enhanced-solubility agent for subsurface remediation, as well as for initial results on the mass removal effectiveness of the cyclodextrin flush, see McCray and Brusseau (10), and Brusseau et al. (11).

Site Characterization

Hydrogeology. The aquifer at the site consists of fine-to-coarse sand interbedded with gravel and clay stringers, and has an average thickness of about 8-9 m. The effective porosity within the test cell is approximately 20% (10,12). The saturated portion of the aquifer has a horizontal hydraulic conductivity of about 2.5×10^{-2} cm/sec based on

conservative-tracer test data (12). Underlying the sand-gravel unit is a relatively impermeable clay unit. The average vertical hydraulic conductivity of the clay unit is less than 10^{-7} cm/sec based on constant-head permeability testing of core samples collected from the unit (13).

Contaminant Location and Distribution. The treatment cell used for the remediation experiment was emplaced within a former chemical disposal pit in what is considered to be a source area of water-immiscible organic contaminants (free phase or residual NAPL present). The NAPL mixture is comprised mainly of petroleum hydrocarbons and spent solvents, and is considered to be less dense than water. The NAPL appears to exist as residual saturation within most of the treatment area, and is smeared throughout the saturated, as well as unsaturated, portions of the aquifer as a result of water table fluctuations. The initial NAPL saturation was estimated as approximately 12.6% based on results of a partitioning tracer study (12).

Of the many compounds in the NAPL, 12 "target contaminants" were chosen prior to the experiment for the purpose of evaluating remediation effectiveness. These targets are: trichloroethene (TCE), 1,1,1-trichloroethane (TCA), naphthalene (NAP), o-xylene (o-XYL), m,p-xylene (p-XYL) measured as p-xylene, toluene (TOL), benzene (BENZ), ethylbenzene (EB), 1,2-dichlorobenzene (DCB), 1,2,4-trimethylbenzene (TMB), decane (DEC), and undecane (UND). These compounds were selected to provide a representative subset of the NAPL constituents of concern present within the study area. We estimate that these compounds comprise slightly less than 10% of the total NAPL within the cell (14). The remainder appears to consist primarily of higher molecular weight jet-fuel components, other solvents, and perhaps relatively insoluble, pitch-like components. A more detailed description of the field site hydrogeology and contaminant distribution may be found in Bedient et al. (9).

Methods

Complexing Sugar Flush (CSF) Experiment. The enhanced-remediation technology tested in this study is termed a "Complexing Sugar Flush" (CSF), where cyclodextrin is the complexing sugar. Cyclodextrin is a glucose-based compound that is similar to household corn starch. These lampshade-shaped molecules are unique in that they have a hydrophobic, non-polar interior and a hydrophilic, polar exterior. Relatively non-polar organic contaminants partition to the interior of the molecule (i.e., form inclusion complexes), while the highly polar exterior of cyclodextrin provides the molecule with a large aqueous solubility (approximately 50% by mass). These properties allow cyclodextrin to significantly increase the apparent aqueous-phase concentrations of organic contaminants.

The cyclodextrin derivative used for this experiment was hydroxypropyl- β -cyclodextrin (HPCD), which does not significantly reduce the interfacial tension of the NAPL-water interface and, therefore, is unlikely to mobilize NAPL (14,15). Thus, NAPL removal resulting from cyclodextrin-flushing occurs via an enhanced-solubilization process, and not by mobilization. While mobilization can enhance removal of NAPL from the subsurface, it can be difficult to capture all mobilized

NAPL during remediation. Mobilized DNAPL, for example, could migrate to an uncontaminated region deeper in the aquifer (e.g., 8,16,17). Remediation techniques based on mobilization, therefore, may not be appropriate under certain circumstances.

The cyclodextrin solution was pumped into the contaminated aquifer using a horizontal flow field. The effluent was collected and subjected to selected treatment and disposal operations. An enclosed cell was used for the experiment to minimize migration of normally sparingly-soluble contaminants that could experience enhanced solubilization and transport in the presence of cyclodextrin, and to facilitate mass-balance and performance assessment. The 3-m by 5-m area cell was enclosed by sealed 9.5 mm-thick sheet-pile walls (18), which were driven about 2 m into the low-permeability clay layer. The top of the clay was approximately 8-9 m below ground surface (BGS) in the treatment cell.

A schematic of the cell layout is shown in Figure 1. A line of four injection wells and a line of three extraction wells were used to generate a steady-state flow field that was normal to the lines of wells. The injection and extraction wells (5.1 cm diameter) were fully screened over the saturated thickness. Injection and extraction flow were generated with peristaltic pumps (Master Flex I/P with bench-top controller, Tygon LFL tubing from Cole-Parmer) using a separate pump head for each well. Two piezometers inside the cell were used, along with the injection and extraction wells, to monitor water levels during the test.

Technical-grade cyclodextrin (Cerestar USA Inc., Lot 8028) was used for the experiment. This dehydrated material was comprised of approximately 90% HPCD and 10% production byproducts (mainly hydrated ash). The cyclodextrin was then mixed with potable water to achieve a dissolved HPCD concentration of 10.4wt% using an 80,000-L mixing tank with four top-mounted mixers. About 8 pore volumes of the 10wt% cyclodextrin solution (approximately 65500 L total) were pumped through the cell at a rate of approximately 0.8 pore volumes per day, or 4.54 L/min. Tubing degradation in the peristaltic pump system caused flow rate variations of up to 10%; however, variations of greater than 5% rarely occurred for more than two hours. The flow rate was monitored and adjusted to maintain the water table in the enclosed cell at about 5.5 ± 0.3 m BGS.

After the eighth day, flow was interrupted for one day to investigate the potential for rate-limited dissolution. Brief results of this flow-interruption experiment will be discussed in a forthcoming section (detailed results may be found in McCray (14)). Two more days of cyclodextrin flushing was conducted after the flow-interruption period. At the end of the experiment, about 12 pore volumes of cyclodextrin-free water were flushed through the cell to remove the cyclodextrin. Aqueous samples were collected at each extraction well (E51, E52, E53 on Figure 1) to monitor for target-contaminant and cyclodextrin concentrations. Samples were collected hourly for the first 36 hours of the experiment, and every 3 to 4 hours thereafter.

Core samples, which were collected at various depths throughout the treatment cell before and after the experiment, were analyzed for the total resident concentrations of each target contaminant. The pre-remediation cores were collected while drilling injection and extraction wells, and from other boreholes. The post-remediation cores were collected at locations as close as possible to the pre-

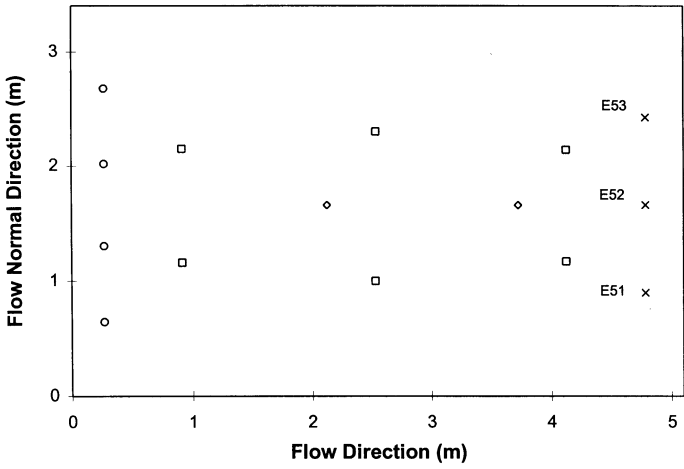


FIGURE 1. Schematic (plan view) of treatment cell, well locations, and soil core sampling locations (O = injection wells, x = extraction wells, ◇ = other pre-remediation soil samples, □ = post-remediation soil samples).

remediation cores (see Figure 1), within the limitations of the drilling equipment. The cores were collected in sections using a hollow-stem auger with 120 cm-long sample cylinders (USAF, 1995). Only those samples that were collected from the treatment zone were used for this analysis.

Water-Flush Experiment. A water-flush (WF) experiment was performed prior to the cyclodextrin experiment to simulate pump-and-treat remediation for comparison with the CSF. Approximately 19.5 pore volumes of water were flushed through the cell during the water flush at a rate of 0.8 pore volumes per day (4.54 L/min). This pumping period was not continuous; flow was interrupted twice. The first interruption (no-flow) period was imposed after about 17 days of pumping and lasted for 21 days. Pumping was then reinitiated and continued for about 5 days, after which a 4-day no-flow period was imposed. Pumping was then resumed and continued for 3 days, after which the CSF was initiated without interrupting flow.

Aqueous samples were collected from the extraction wells during the experiment and analyzed for concentrations of the target contaminants. It is well known that water-flushing typically results in a rapid decrease in extracted contaminant concentrations as the first pore volume, which may contain relatively high concentrations associated with near-equilibrium conditions, is removed from the subsurface. Concentrations will then typically exhibit (within sample variance) some asymptotic profile wherein concentrations are smaller than the equilibrium values. The concentrations at the end of the water flush (and just prior to the CSF) are thus assumed to be a conservative estimate of the concentrations that would be observed during a long-term pump-and-treat operation.

The CSF was initiated during the asymptotic-concentration period such that steady flow conditions, including a constant water-table elevation, were maintained during the transition between the WF and CSF. Using this procedure, direct comparisons of contaminant mass-removal effectiveness can be made for the two technologies under nearly identical hydrogeological conditions and contaminant distributions. This type of comparison is desirable because it provides direct evidence of the improvement in remediation performance achieved by the CSF compared to pump and treat. It is evident that optimal pump-and-treat remediation design, as well as optimal enhanced-solubility flushing techniques, may not always use the continuous, constant flow-rate design used in this experiment. However, for the purposes of comparison, both remediation technologies must have a common basis.

Analytical Methods. All aqueous-phase extraction-well samples were collected with no head space in 40-mL glass vials with teflon-lined caps. Five-mL portions of the samples were then transferred to 20-mL glass head-space vials (Teflon-lined septum and crimp cap) and analyzed by gas chromatography with a flame ionization detector (GC-FID) (Shimadzu, GC-17A) fitted with a capillary column and a head-space autosampler (Tekmar, 7000). When storage was necessary, samples were stored in the dark at 4°C for periods up to several months. Results from several analyses indicate that volatilization and biodegradation (or other means of mass loss) were not significant during the storage period. With the method described above, quality

assurance-quality control standards were met for 10 of the 12 compounds for the CSF samples.

Benzene exhibited soil-phase concentrations several orders of magnitude less than the other target compounds, and presented analytical difficulties for samples containing cyclodextrin due to a coeluting compound. Similar analytical difficulties related to coelution also occurred for TCA in samples containing cyclodextrin. Thus, CSF results for BENZ and TCA are not reported in this research. The compounds BENZ, DEC and UND could not be consistently detected in water-flush samples, and are thus not reported for the water-flush analysis.

During coring, soil samples were placed into vials containing methylene chloride (extractant) and acid, and delivered to the Environmental Laboratory at Michigan Technological University for analysis. Samples were stored at 4 °C until analysis. Prior to analysis, the samples were allowed to equilibrate to room temperature and then were sonicated for 15 minutes. After sonication, the samples were centrifuged at 2300 revolutions per minutes for 15 minutes to separate the phases. A 1.0 ml aliquot of the methylene chloride phase was added to a 1.8 mL auto-sampler vial with a Teflon-lined septum and crimp cap. Then, 2 μ L portions of the samples were analyzed by a gas chromatograph (GC) (Hewlett Packard 5890 with capillary column)-mass spectrometer (Hewlett Packard 5970), equipped with an automatic sampler (Hewlett Packard ALS 7673). Using this method, quality-assurance-and-control (QA-QC) standards were met for all 12 compounds.

Results And Discussion

Contaminant Elution. As expected, the concentrations for most contaminants decrease by a factor of about 10 to more than 100 within the first few days of the water flush (e.g., see Figure 2), and maintain relatively asymptotic levels thereafter. Slight increases in concentration appear to have occurred after each flow interruption period (this will be discussed in a forthcoming section). The amount of pumping required to reach asymptotic concentration levels varies among the contaminants, but is generally one to four pore volumes. Thus, the equivalent of between 15-18 pore volumes were flushed during the asymptotic-concentration period.

The initial contaminant concentrations are relatively high, probably because the system was static for several weeks prior to the experiment, which provided sufficient time to achieve equilibrium between the NAPL and water phases. The subsequent small, asymptotic concentrations are typical for pump-and-treat operations (2,3) and, as will be discussed in a forthcoming section, probably result from rate-limited dissolution between the NAPL and aqueous phases. The mass removed during the WF was relatively small for the targets; thus, concentration reductions due to decreasing mole fractions are not of significance. Decreasing concentrations may also result if the flushing fluid, due to porous-media heterogeneities or NAPL relative-permeability effects, experiences limited contact with the NAPL (bypass flow). However, as will be discussed later in this chapter, bypass flow is not thought to be the primary constraint on dissolution for this experiment. Generally, an enhanced flushing technique would not be used until asymptotic-concentration levels are reached with conventional water flushing because pump-and-treat remediation may be nearly as

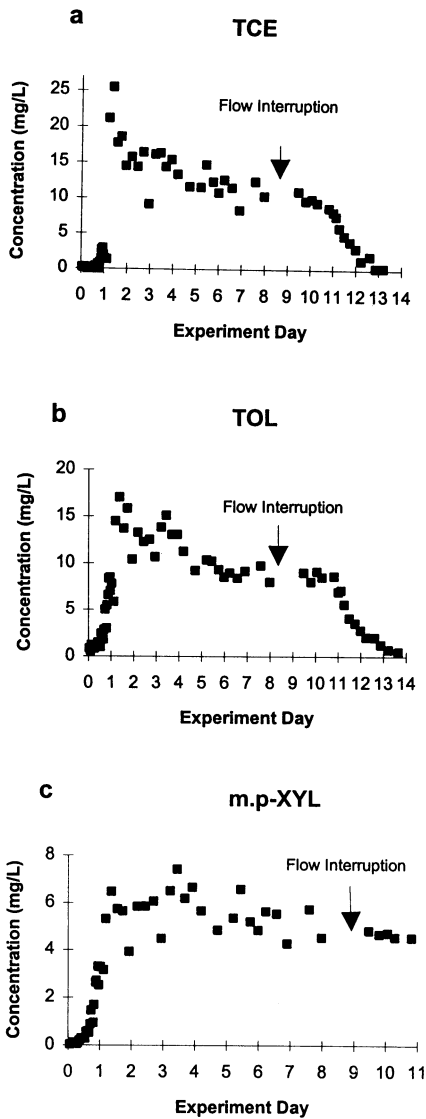


FIGURE 2. Flux-averaged extraction-well concentrations for selected contaminants during the water flush. The horizontal axis represents the number of days for which pumping was conducted. Flow interruption 1 consisted of a 21-day no-flow period, flow interruption 2 consisted of a 4-day no-flow period.

effective as (and less costly than) enhanced-solubility remediation schemes in the early stages of pumping.

The elution curves for selected contaminants obtained during the CSF are presented in Figure 3. The concentrations are flux-averaged values obtained from the concentrations of all three extraction wells. As will be discussed in a forthcoming section, cyclodextrin induced very large increases in the aqueous concentrations of all the target contaminants, ranging from about 100 to more than 10,000 times the concentrations achieved in the water flush conducted immediately prior to the CSF. The effluent concentrations experience a large, initial increase followed by a decrease to a somewhat constant value for most contaminants. The initial increase occurs simultaneously with the increase in HPCD concentration to 10%. The subsequent decrease in concentrations for most contaminants are believed to be due, in part, to the effect of a decreasing mole fraction (10,14)

Remediation Performance. As a direct measure of the effectiveness of the CSF, the concentrations and mass removed of the target contaminants during the CSF are compared to the average concentrations and mass removed during the water flush conducted before the CSF. This comparison allows for analysis of the relative magnitudes and rates of mass removal for the two remediation methods. As stated previously, steady flow conditions, including a constant water table elevation, were maintained during the transition from the water flush to the CSF. Therefore, any concentration enhancement in the extraction well effluent during the CSF was due solely to the effects of the cyclodextrin on the apparent solubility of the contaminants.

The amount of contaminant mass removed from the subsurface during water- and sugar-flushing can be calculated for each contaminant by integrating under the elution curves (Figures 2 and 3). The total amount of mass of each target contaminant removed from the treatment cell during flushing, as well as the percentages of total mass removed by the water flush and by the CSF, are reported in Table 1. The water flush removed significant amounts of mass for some of the more soluble components (e.g., the ones shown in Figure 2). However, most of the mass removal for the water flush occurred during the first several pore volumes. As is apparent from the results in the table, the CSF removed significant amounts of mass for these compounds after the mass removal became negligible during the water flush.

The CSF-induced solubility enhancements for the target contaminants are shown in Table 2. The aqueous concentrations for all compounds listed in the table except TCE were below GC detection limits in the effluents of one or more extraction wells, typically E53 or E51, for the latter part of the water flush. In these cases, the lesser of the GC-method detection limit or the calculated equilibrium concentrations (solubility times calculated mole fraction) was used as a conservative estimate of the maximum water-flush concentrations. Thus, the actual concentration enhancements for these contaminants may have been greater than those reported here due to an overestimation of the water-flush concentrations in the effluents of one or more wells. Mass removal may be inferred from the solubility enhancement. That is, for constant water-flush and CSF concentrations, and when equal volumes are flushed, the ratio of mass removed for the two flushing techniques should approximately equal the solubility enhancement.

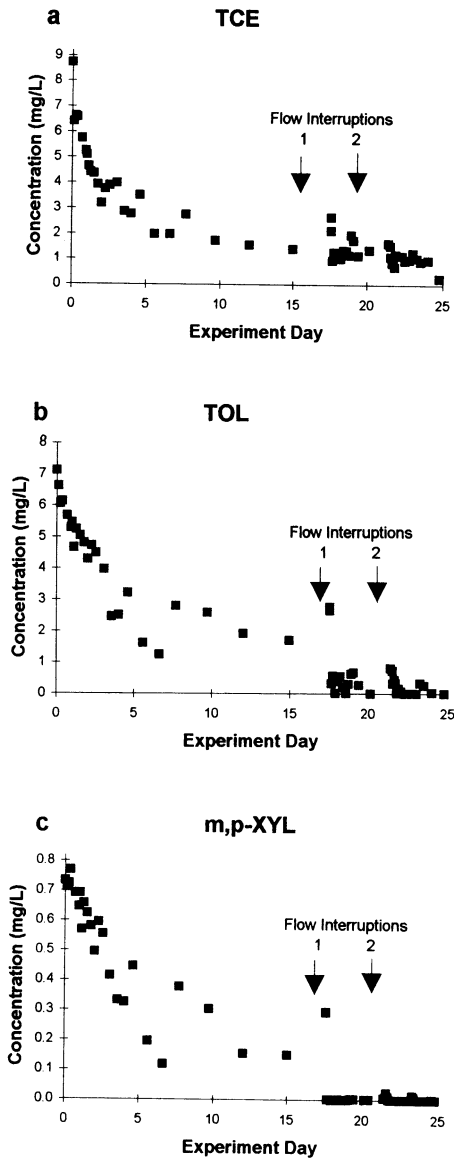


FIGURE 3. Flux-averaged extraction-well concentrations for selected contaminants during the CSF.

TABLE 1. Relative Amounts of Mass Removed by Water Flush (WF) and Complexing Sugar Flush (CSF)

Compound	Total Mass Removed WF + CSF (g)	% Removed by Water Flush: (First 11 PV) ^a	% Removed by Water Flush: (Last 8 PV) ^a	% Removed by CSF (8 PV) ^a
TOL	994	31.3	0.8	67.9
TCE	919	19.2	1.1	79.8
o-Xyl	131	19.0	< 0.1	81.0
m,p-Xyl	369	8.8	0.1	91.1
EB	103	7.3	0.1	92.6
DCB	5273	4.2	0.1	95.7
NAP	385	2.3	0.2	97.5
TMB	193	2.8	< 0.1	97.6
DEC	54	< 0.01	< 0.01	>99.9
UND	288	< 0.01	< 0.01	>99.9

PV = pore volumes

a. Calculated from total mass removed via extraction wells from aqueous concentration data

The apparent solubilities for the target compounds are greatly enhanced by the cyclodextrin solution. The initial solubility enhancements range from 85 for TCE, to greater than 12,000 for UND. Because solubility enhancements for many of the compounds are minimum values, trends in the enhancements based on contaminant properties are not easily discerned. However, it is apparent from the data in Table 2 that the more-hydrophobic compounds experience a larger solubility enhancement. These results are consistent with those obtained in laboratory studies (14,19). The absolute amount of mass removed for a contaminant depends on the contaminant's aqueous concentration in the extracted cyclodextrin solution (which is a function of the solubility enhancement, the water solubility of the contaminant, and the NAPL-phase mole fraction of the contaminant) and the number of pore volumes flushed (10). For the target contaminants in this study, larger mass removal was generally achieved for the less-hydrophobic compounds due to their higher initial CSF concentrations in the extraction-well effluent and to the relatively short duration of pumping (10).

The contaminant concentrations in the CSF flushing fluid, and thus, the concentration enhancements, generally decline with time and achieve a relatively constant level. Based on partitioning-tracer test analysis (12), a significant portion of the mass (about 44%) was removed prior to reaching the final CSF concentrations shown in Figure 3. The final concentrations are indicative of the long-term mass removal of the remaining NAPL that would be achieved by the CSF. The long-term

water-flushing concentrations that would be expected for the conditions of this experiment are the asymptotic values (Figure 2) listed in Table 2. Once effluent concentrations reach an asymptotic level during water flushing, one would expect these levels to remain constant, or to slightly decrease, for a very long time. The long-term mass-removal improvement achieved by the CSF, therefore, can be estimated by comparing the final CSF concentrations to the final water-flush concentrations. This ratio is expressed as the final enhancement value in Table 2. For the target compounds, the advantage of using cyclodextrin as a flushing-solution agent is apparent.

TABLE 2. Aqueous Concentrations and Concentration Enhancements for Water Flush (WF) and Complexing Sugar Flush (CSF)

Compound	WF Final Conc. ^a (mg/L)	CSF Initial Conc. ^b (mg/L)	^c Initial Solubility Enhancement	^d CSF Final Conc. (mg/L)	^e Final Solubility Enhancement
UND	0.0005 ^e	6.0	>12000	5.0	>10,000
DEC	0.0002 ^e	1.3	>6500	1.3	>6500
m,p-Xyl	0.0029 ^f	6.5	>2241	4.6	>1586
TMB	0.0017 ^f	3.7	>2128	2.8	>1610
DCB	0.1162 ^f	144	>1240	48	>413
EB	0.0033 ^f	2.4	>735	0.8	>245
o-Xyl	0.0067 ^f	2.4	>359	1.2	>180
NAP	0.0292 ^f	9.2	>315	4.5	>154
TOL	0.0828 ^f	17	>205	8.7	>105
TCE	0.2346	20	85	9.1	39

a. Flux-averaged concentration of all 3 extraction wells (during last 3 days of water flush)

b. Initial maximum extraction-well concentration (flux-averaged concentration for all 3 extraction wells) after [HPCD] reached 10%.

c. Solubility enhancement = avg. extraction-well concentration for CSF / avg. extraction-well concentration for WF.

d. Average extraction-well concentration during last day of CSF.

e. Below analytical detection limits in all extraction wells. The aqueous conc. was approximated using the mole fractions times aqueous solubility as a conservative estimate of the steady-state water flush concentration.

f. Below analytical detection limits in one or two extraction wells. The aqueous conc. for these wells was approximated as in e. The actual concentrations for the remaining well(s) are used.

As the NAPL saturations become very small, it is possible that the CSF concentrations may decrease below the final concentrations shown in Figure 3. Nonetheless, compared to water flushing, the amount of mass removed during the 8-pore volume (10-day) CSF alone is substantial (Table 1). For example, assuming that the water-flush concentrations for UND would be maintained indefinitely, more than 70,000 PV (240 years) of water-flushing would be required to remove the amount of UND mass removed during the 8-pore volume CSF. Similar calculations for DCB indicate that more than 5300 PV (18 years) of water flushing would be required after the asymptotic concentration levels are reached. The improvement is significant even for TCE, which has the smallest enhancement, for which about 350 PV (more than one year) of water flushing would be required to remove the mass that was removed in ten days by the CSF. These results clearly indicate that the time required for NAPL cleanup at this field site may be greatly reduced by cyclodextrin-enhanced flushing.

Flow Interruption Experiments. The potential for rate-limited dissolution during the CSF was investigated by interrupting flow for one day after 8 days of flushing. Two flow interruption periods were induced during the water flush (as described previously). During flow periods, less time is available to achieve chemical equilibrium between the NAPL and the flowing aqueous phase than for when flow is stopped. If mass transfer between the NAPL and aqueous phases is rate-limited rather than instantaneous, then an increase in the effluent concentration should be observed once flow is restarted. Figure 3 illustrates that there is not a significant increase in the effluent concentrations of the selected target contaminants after restarting flow (on day 9). Generally, these results indicate that the NAPL dissolution in the presence of the cyclodextrin solution was near equilibrium during the latter stages of the CSF. However, the duration of the no-flow period may not have been sufficient to detect changes in local mass-transfer processes. Thus, these results should not be interpreted to mean that NAPL dissolution was instantaneous everywhere within the cell.

During the water flush there appears to have been a slight increase in concentrations for the most of the target contaminants following the no-flow periods (at about 17 and 22 days in Figure 2, for which the no-flow periods are omitted from the time axis). This result indicates that non-equilibrium dissolution conditions may have existed during the water flush, which was hypothesized earlier. The durations of these no-flow periods were considerably longer than the one for the CSF; but do not appear to have been of sufficient duration to attain the equilibrium concentration values exhibited at the start of the water flush. Another method for determining whether the global NAPL-aqueous phase mass-transfer processes were at equilibrium is described in the following section.

Analysis of Equilibrium Dissolution Behavior. Ideal equilibrium dissolution of NAPL constituents into water may be represented by Raoult's Law:

$$C_i^{w*} = X_i^N S_i^w \quad (1)$$

where C_i^{w*} is the equilibrium aqueous concentration of NAPL constituent i in water, X_i^N is the mole fraction of i in the NAPL phase, and S_i^w is the single-component aqueous

solubility of component i in water. For ideal NAPL dissolution into a solution containing an enhanced-solubility agent, a simple modification of Raoult's Law may be used (14):

$$C_i^{A*} = X_i^N E_i S_i^w \quad (2)$$

where C_i^{A*} is the equilibrium aqueous concentration of NAPL constituent i in a solution containing cyclodextrin (the superscript A denotes the aqueous phase), the parameter E_i is the solubility enhancement induced by the cyclodextrin solution (which may be determined in the laboratory from batch solubility experiments). The magnitude of E_i depends linearly on the cyclodextrin concentration and the partition coefficient of the cyclodextrin-organic molecule complex (19).

To determine whether the global NAPL-aqueous phase mass-transfer processes within the treatment cell were at equilibrium for various constituents during the water flush and CSF, the aqueous concentrations predicted by equation 1 for water, and by equation 2 for the cyclodextrin solution, can be compared to the measured concentrations. This comparison requires an estimate of the NAPL-phase mole fractions. These mole fractions may be calculated from: measured values for soil-core concentrations, NAPL saturations (10, 12), porosity, and soil bulk density (2 g/cm^3); an estimated value for the average molecular weight of the bulk NAPL (180 g/mole); and tabulated molecular properties of the target contaminants. For details of the mole-fraction calculation, the reader is referred to McCray and Brusseau (10).

The use of soil-core concentrations, which represent the total contaminant mass in all phases (NAPL, water, and soil), to calculate NAPL-phase mole fractions requires the assumption that all of the contaminant mass resides in the NAPL phase. Total contaminant mass in the cell before and after remediation was calculated from the soil-core concentrations, cell volume, and estimated bulk density (2 g/cm^3). Total aqueous-phase contaminant mass present in the cell before and after remediation was calculated from static-groundwater-sample concentrations (10,11). Sorbed (soil-phase) mass was estimated from the static groundwater concentrations and literature values for sorption coefficients (14). For this study, it was estimated that more than 98.5% of the mass of each target contaminant resided in the NAPL phase.

Using the calculated mole fractions, theoretical equilibrium aqueous concentrations are calculated for the start of the water flush, the end of the water flush, and the initial phase of the CSF (Table 3). The analysis indicates that the predicted concentrations are generally within a factor of about three to four of the measured ones at the start of the water flush and within a factor of three of the measured concentrations during the initial phase of the CSF. Several researchers (20,21) have used a factor of two as the arbitrary standard for ideal, equilibrium dissolution behavior. Given the complexity of this field experiment, a factor of three between measured and expected concentrations would support the assumption of equilibrium dissolution. During the latter phase of the water flush, however, the measured concentrations are significantly below the theoretical predictions based on Raoult's Law. Because the mole fractions at the beginning and end of the water flush are nearly identical, the equilibrium concentrations should also be nearly identical. Thus,

this difference is attributed to the effect of rate-limited dissolution during the latter stages of the water flush, as discussed below.

TABLE 3. Measured (C_m) vs. Theoretical (C_{ideal}) Aqueous Concentrations for Water Flush (WF) and Complexing Sugar Flush (CSF)

Compound	E_i	Solubility ^d	Initial WF	End WF	Initial CSF
			C_m/C_{ideal}	C_m/C_{ideal}	C_m/C_{ideal}
TCE	6.5 ^a	1100	2.3	0.14	2.4
DCB	27 ^a	137	0.8	0.05	2.0
NAP	30 ^a	110	1.5	0.20	2.1
TMB	17 ^a	57	1.5	0.02	2.9
mp-XYL	24 ^{b,c}	170	3.7	0.02	1.6
o-XYL	16 ^a	152	1.0	0.02	0.4
EB	25 ^a	150	1.7	0.04	1.1
TOL	10 ^a	550	1.7	0.03	0.7
TCA	5.8 ^b	4500	3.6	0.68	g
BENZ	3.5 ^b	1790	f	f	g
DEC	8650 ^a	0.02	f	f	0.9
UND	6300 ^a	0.015 ^e	f	f	1.8

a. Measured for this work

b. Obtained from K_{ow} vs. K_{cw} correlation (10), updated using recent measurements (14).

c. Average properties for m- and p-xylene assumed for solubility.

d. Representative solubility from values listed in (22,23).

e. Values for UND are average of values for DEC and Dodecane from (23).

f. Not reported; below analytical detection limits.

g. Not reported due to analytical difficulties for samples containing cyclodextrin.

Dissolution Rate Differences Between the Water Flush and CSF and Implications for Remediation. The hydrodynamic conditions and NAPL distributions at the end of the water flush were essentially identical to those at the start of the CSF. Thus, given that dissolution was rate limited at the end of the water flush and near equilibrium during the initial stage of the CSF, it appears that the cyclodextrin solution caused an increase in the rate of NAPL dissolution. This phenomenon may also be illustrated by comparing the solubility enhancements measured in the field (Table 2) to the solubility enhancements measured with batch equilibrium studies (Table 3). The values measured for the batch experiments reflect equilibrium concentrations.

However, under the field conditions, dissolution is an equilibrium process during the CSF, and is rate limited during the water flush. Thus, the field-measured solubility enhancements are generally an order of magnitude larger than those measured from the batch experiments. These results are strong evidence the CSF caused an increase in the dissolution rates for the target contaminants.

Bypass flow (described earlier) may often limit NAPL-water contact during pump-and-treat remediation, and thus result in sub-equilibrium aqueous concentrations. However, if the effects of bypass flow had been significant, then it would be expected that aqueous concentrations measured during the CSF would also have been below equilibrium values. Thus, bypass flow is not thought to have caused significant dissolution limitations during the water flush or the CSF. The cyclodextrin flushing solution did not cause a measurable change in the hydrodynamic conditions at the site, and mobilized NAPL (droplets or emulsions) were not present in extraction-well samples (10, 14). Thus, the apparent increase in the dissolution rate is attributed to the impact of the cyclodextrin on the rate of mass transfer between the NAPL and aqueous phases. The mechanisms potentially responsible for this are currently under investigation.

Conclusions

These pilot-scale field experiments were intended to mimic one-pore-volume-per-day remediation scenarios while maintaining strict hydrodynamic conditions that may not be possible in some large-scale remediation efforts. For the conditions under which these experiments were conducted, the CSF is significantly more efficient than water flushing for removing NAPL contaminants from the subsurface. The CSF appears to increase not only the magnitude of the apparent solubility for the target contaminants, but also the rate of dissolution. Thus, cyclodextrin flushing may be useful at sites where dissolution of NAPL into a flushing solution is significantly inhibited due to mass-transfer rate limitations.

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