Enhanced Transport of Low-Polarity Organic Compounds through Soil by Cyclodextrin

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The removal of low-polarity organic compounds from soils and aquifers by water flushing is often constrained by sorption interactions. There is great interest in developing systems that can enhance the transport of organic compounds through porous media, thus facilitating remediation. We investigated the potential of hydroxypropyl-β-cyclodextrin (HPCD), a microbially produced compound, to reduce the sorption and to enhance the transport of several low-polarity organic compounds. The results show that cyclodextrin does not interact with the two porous media used in the study. As a result, there is no retardation of cyclodextrin during transport. The retardation of compounds such as anthracene, pyrene, and trichlorobiphenyl was significantly (orders of magnitude) reduced in the presence of cyclodextrin. The enhancement effect of the cyclodextrin was predictable with a simple equation based on three-phase partitioning. The nonreactive nature of cyclodextrin combined with its large affinity for low-polarity organic compounds makes cyclodextrin a possible candidate for use in in-situ remediation efforts.

Introduction

The potential of organic agents such as dissolved organic matter and surfactants to influence the transport of organic compounds in porous media has become a popular research topic. This research has focused on two aspects of the ability of organic materials to facilitate the transport of low-polarity organic compounds that otherwise would be essentially immobile. The first concerns the increased potential for contaminant spreading and the second involves enhancing the removal of contaminants by soil/aquifer flushing. In both cases, the organic agent is usually viewed as a third retention "phase" for contaminants, the existence of which reduces the mass of contaminant associated with the solid phase and concomitantly increases that in the aqueous phase. The solubilization and enhanced-transport properties of dissolved organic matter and surfactants have been investigated in numerous studies and subject to recent review (1, 2). Given the limitations associated with dissolved organic matter and surfactants, especially related to their reactivity with soils, there is interest in examining the ability of other materials to facilitate the transport of organic contaminants for applications in subsurface remediation.

In this work, we examined the potential of hydroxypropyl-β-cyclodextrin (HPCD), a microbially produced compound, to reduce the sorption and to enhance the transport of several low-polarity organic compounds. Cyclodextrins are cyclic oligosaccharides formed from the enzymatic degradation of starch by bacteria. A unique property of these compounds is that they have a hydrophilic shell and a relatively apolar cavity. Cyclodextrins solubilize low-polarity compounds through the formation of water-soluble, 1:1 inclusion complexes. Their ability to increase the apparent aqueous solubilities of several low-polarity organic contaminants was recently demonstrated (3). In this study, we used the miscible displacement technique to investigate the influence of HPCD on the transport of several low-polarity organic compounds through two soils.

Materials and Methods

Materials. The following analytical-grade chemicals (Aldrich Chemical Co., Inc) were employed in the experiments: pentafluorobenzoate (>99% pure), trichloroethene (>99%), 1,2,3-trichlorobenzene (99%), naphthalene (>99%), anthracene (>99%), pyrene (99%), biphenyl (99%), 2-chlorobiphenyl (>98%), and 2,4,4'-trichlorobiphenyl (>98%). Properties of the organic compounds are listed in Table 1. Hydroxypropyl-β-cyclodextrin (HPCD) was also purchased from Aldrich, with no purity reported. Its molecular weight is 1500, and its outer diameter is approximately 1.5 nm.

Two porous materials were used for this study. One (Borden) is a sandy subsoil collected from the Canadian Air Force base in Borden, Ontario. The second (Mt. Lemmon) is a surface soil collected from a site near Tucson, AZ. Measured organic carbon contents and particle-size distributions are reported in Table 2. Both soils were dry sieved (<2 mm) prior to use.

Preparative chromatography columns made of precision-bore borosilicate glass (2.5-cm i.d., 5.0-cm length, Kontes Co.) or precision-bore stainless steel (2.1-cm i.d., 7.0-cm length, Alltech Associated Inc.) were used in the experiments. The columns are designed to have a minimum void volume in the end plates.

Experimental Procedures. The columns were packed in incremental steps with the dry porous medium to establish uniform bulk density. After packing, the columns were slowly wetted from the bottom with electrolyte solution (0.01 N CaCl₂). After saturation was achieved, about 100 pore volumes of solution were pumped through the columns to condition them to the electrolyte solution. Bulk densities and porosities for the columns are reported in Table 2. The unusually small bulk density and large porosity associated with the Mt. Lemmon soil results from its large organic carbon content.

The apparatus and methods employed for the miscible displacement studies were similar to those used by Brusseau et al. (4). One single-piston HPLC pump (Gilson Medical Electronics, Model 305) was connected to the column, with a three-way switching valve placed in-line to facilitate switching between solutions with and without the solute(s) of interest. The system was designed so that the solute contacted only stainless steel, glass, or Teflon.

A flow-through, variable-wavelength UV detector (Gilson, Model 115) was used to continuously monitor concentrations of pentafluorobenzoate (235 nm), trichloroethene (225 nm), naphthalene (225 nm), biphenyl (250

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compound	solubility (mg/L)	log K_{ow}	C_0 (mg/L)[a]
trichloroethene	1155[b]	2.61[c]	37
naphthalene	30.0[b]	3.36[d]	16
biphenyl	7.5[b]	4.09[d]	saturated[e]
trichlorobenzene	18.0[f]	4.14[f]	saturated
2-chlorobiphenyl	3.76[g]	4.51[g]	saturated
anthracene	0.075[b]	4.54[d]	saturated
pyrene	0.16[b]	4.88[d]	saturated
2,4,4'-trichlorobiphenyl	0.115[g]	5.62[g]	saturated[h]

[a] C_0 is the concentration of solute in the solutions used for the transport experiments. [b] From ref 19. [c] From ref 20. [d] From ref 21. [e] Denotes solution saturated to aqueous solubility limit. [f] From ref 22. [g] From ref 17. [h] The concentration of trichlorobiphenyl in the trichlorobiphenyl/HPCD experiment was 1 mg/L, which was achieved by the presence of the HPCD. This concentration was used to allow analysis by the flow-through UV detector.

Table 2. Properties of Soils

soil	organic carbon (%)	sand (%)	slit (%)	clay (%)	bulk density (g/cm³)	porosity
Borden	0.29	98	1	1	1.65	0.44
Mt. Lemmon	12.6	60.3	24.0	15.7	0.8	0.7

nm), trichlorobenzene (225 nm), chlorobiphenyl (220 nm), and trichlorobiphenyl with HPCD (210 nm) in the column effluent. The values in parentheses denote the wavelengths used for each compound. A flow-through fluorometer (Gilson, Model 121) was used for the anthracene, pyrene, and HPCD experiments (excitation filter, 265 nm; emission filter, 305 nm). The transport of HPCD was analyzed by measuring the fluorescence of HPCD complexed with TNS, 2-p-toluidinnaphthalene-6-sulfonate (5). Since TNS was sorbed by the soils, the columns were preconditioned to TNS prior to injecting the solution containing the TNS–cyclodextrin complex. Output for all experiments was recorded on a strip-chart recorder (Fisher, Recordall Series 5000).

A flow rate of 1.6 mL/min was used for all miscible displacement experiments. This corresponds to pore-water velocities of approximately 60 and 27 cm/h for the Borden and Mt. Lemmon columns, respectively. Pentafluorobenzoate, which was not sorbed by either of the two soils, was used to characterize the hydrodynamic conditions of the columns. A HPCD concentration of 10 g/L was used for all transport experiments except where noted. The concentrations of organic compounds used in the experiments are listed in Table 1.

Data Analysis. The equation used to describe one-dimensional advective–dispersive transport of solute in a homogeneous porous medium under conditions of saturated, steady-state water flow is

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{1}$$

where C is concentration of compound in solution (M/L), x is distance (L), v is average pore-water velocity ($v = q/n$, where q is Darcy flux and n is porosity, L/T), t is time (T), R is the retardation factor [$1 + (\rho/n)K_d$], K_d is the equilibrium sorption constant (L^3/M), ρ is the bulk density of the soil (M/L^3), and D is the longitudinal dispersion coefficient (L^2/T).

The effect of cyclodextrin on the transport of organic compounds is accounted for by modifying the retardation

factor in the following manner. The concentration of solute in the aqueous phase (C) consists of both dissolved and complexed (associated with the cyclodextrin) species. Thus, C is defined as

$$C = C_d(1 + XK_c) \tag{2}$$

where C_d is the concentration of dissolved compound (mg/L), X is the concentration of cyclodextrin in solution (kg/L), and K_c is the equilibrium constant describing distribution of organic compound between cyclodextrin and the aqueous phase (L^3/M).

The modified sorption equation is obtained by substituting eq 2 into an isotherm equation of the form $S = K_d C_d$:

$$S = \frac{K_d C}{1 + XK_c} \tag{3}$$

With the assumption that the organic compound–cyclodextrin complex is not sorbed by the soil, the modified retardation factor is given by

$$R = 1 + \frac{\rho}{n}\frac{K_d}{1 + XK_c} \tag{4}$$

The validity of the assumption that complexed solute is not sorbed will be evaluated in the Results and Discussion section. The modified retardation factor given by eq 4 is of the same form as those developed to account for facilitated transport by dissolved organic matter and surfactants (cf., refs 6–8).

The results of the miscible displacement experiments with cyclodextrin were analyzed by using a nonlinear, least-squares optimization program (9) to solve eq 1. Due to the low retardation factors obtained in the presence of HPCD, an assumption of local equilibrium could be used for sorption (cf., ref 10). For the experiments wherein cyclodextrin was not in the solution, we used a transport model employing the well-known two-domain representation of rate-limited sorption (cf., ref 10) coupled to the optimization program (9).

Results and Discussion

Sorption and Transport of Cyclodextrin. The breakthrough curves obtained for transport of pentafluorobenzoate (PFBA) and hydroxypropyl-β-cyclodextrin (HPCD) through the two porous media are presented in Figure 1. For both media, the optimized retardation factors obtained by nonlinear, least-squares analysis are 1.0 for PFBA and HPCD. From this result, it follows that there is no measurable sorption of HPCD by either the Borden or the Mt. Lemmon media. This is substantiated by the results of batch sorption experiments, which showed no sorption of HPCD by the Borden or the Mt. Lemmon material (data not shown).

The pore volumes of the columns were calculated by measuring the mass of water retained in each column after complete saturation. A comparison of these independent measurements to R values obtained from mathematical analysis of tracer breakthrough curves can elucidate the presence of porosity that does not participate in flow and transport. The fact that retardation factors of 1.0 were obtained for PFBA indicates that there was no measurable nonconducting porosity in either column. Furthermore,
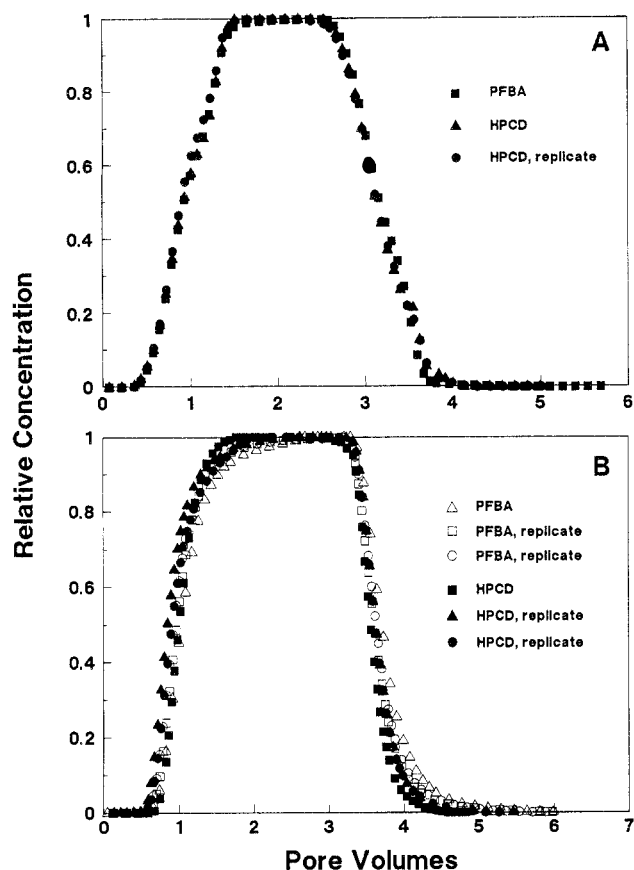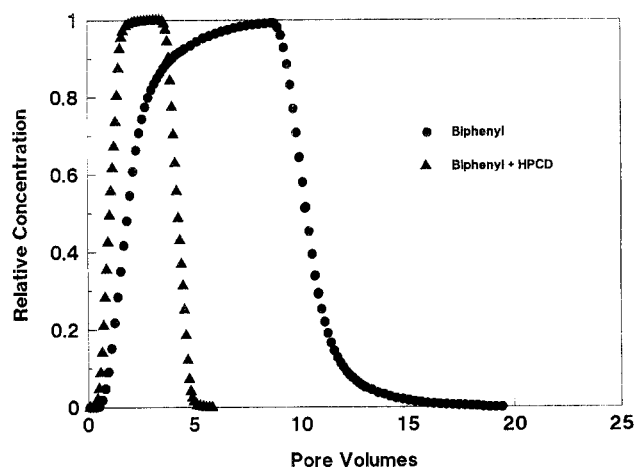
Figure 1. Breakthrough curves for transport of pentafluorobenzoate (PFBA), C_0 = 0.1 g/L, and hydroxypropyl-β-cyclodextrin (HPCD), C_0 = 2 g/L, through porous media; (A) Borden soil, (B) Mt. Lemmon soil. C_0 is the concentration of solute in the influent solution.

Figure 2. Breakthrough curves for transport of biphenyl with and without HPCD through Borden soil.

Figure 3. Breakthrough curves for transport of 2-chlorobiphenyl with and without HPCD through Borden soil.

Figure 4. Breakthrough curves for transport of pyrene with and without HPCD through Borden soil.

the fact that retardation factors were the same for HPCD and PFBA indicates that there was no "pore exclusion" of HPCD. In other words, the HPCD molecules can enter (and leave) the entire water-saturated domain.
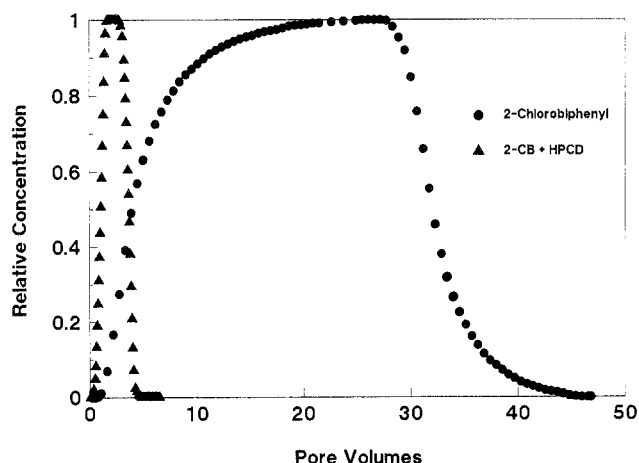
The observation of no sorption, retardation, or pore exclusion of HPCD during transport is in contrast to results reported for other organic materials. For example, the transport of dissolved organic matter (8, 11, 12) and surfactants (7, 13-15) through soil has been shown to be significantly retarded by sorption interactions. In addition, data have been reported showing pore exclusion of large organic materials during transport in soil (7, 16).

The use of organic materials such as surfactants is being discussed as a means by which to enhance the desorption and removal of contaminants, thereby increasing the effectiveness of subsurface remediation. Sorption, retardation, and pore exclusion reduce the effectiveness of the enhancement agent in this regard. Sorption by the solid phase will necessitate using additional mass of the agent. Sorption and retardation of the agent means that additional time is required for the agent to encompass the contaminated zone. Sorption of the agent may also lead to enhanced sorption and retardation of the contaminant. The exclusion of the agent from a fraction of the porosity limits the mass of contaminant that can be directly affected by the agent. The absence of sorption, retardation, and pore exclusion during HPCD transport means that the maximum enhancement effect can be realized with this compound.
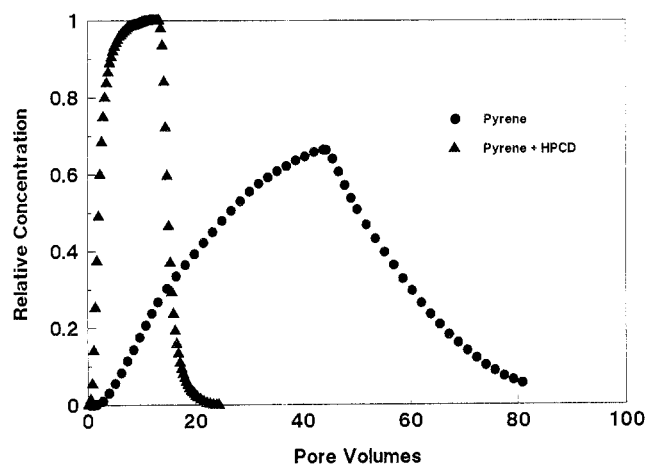
Transport of Low-Polarity Organic Compounds. Breakthrough curves obtained for the transport of selected

organic compounds in the absence and presence of HPCD are presented in Figures 2-5. Retardation factors for all experiments are reported in Table 3. As expected, the enhanced-transport effect is greatest for the most hydrophobic compounds. For example, the retardation factor for the transport of pyrene through the Borden material is reduced from a value of 161.8 to 2.4 in the presence of HPCD. The retardation factor for trichlorobiphenyl was not measured directly because of its very large sorption. A value of 828 was estimated by using a correlation between
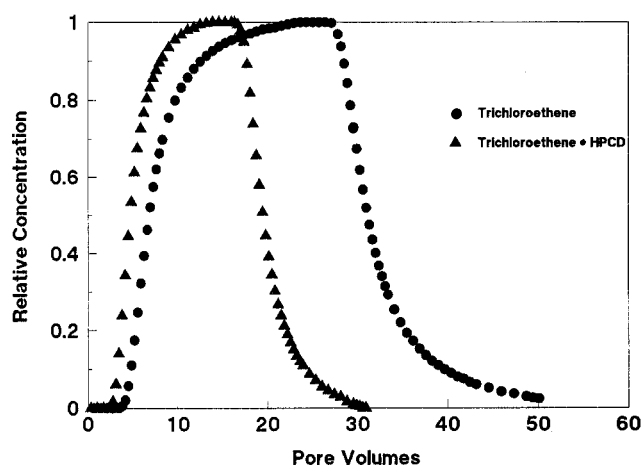
Figure 5. Breakthrough curves for transport of trichloroethene with and without HPCD through Mt. Lemmon soil.

Table 3. Measured and Predicted Retardation Factors

compound[a]	R^m, no HPCD[b]	R^m, with HPCD[b]	R^p, with HPCD[b]
trichloroethene	1.1	1.0	1.0
naphthalene	1.1	0.9	1.0
biphenyl	2.1	1.1	1.1
trichlorobenzene	2.2	1.1	1.1
2-chlorobiphenyl	5.0	1.1	1.1
anthracene	28.6	1.1	1.9
pyrene	161.8	2.4	2.6
2,4,4'-trichlorobiphenyl	828[c]	1.6	2.6
trichloroethene	8.0	5.2	5.6
naphthalene	92.0	15.7	15.6

[a] The Borden material was used for the first eight experiments; the Mt. Lemmon soil was used for the last two. [b] R^m denotes measured value, and R^p denotes predicted value; HPCD is hydroxypropyl-β-cyclodextrin. [c] This value is obtained from the equation K_d/f_{oc} = $0.19K_{ow} - 2120$, where f_{oc} is fraction of organic carbon; this equation was obtained by regressing the K_d/f_{oc} values obtained for the other seven compounds measured for the Borden material against pertinent K_{ow} values reported in Table 1.

K_d/f_{oc} and K_{ow} obtained for the Borden data (see Table 3). The measured retardation factor for transport of trichlorobiphenyl with HPCD is 1.6, which constitutes a very large reduction in retardation. The reduced effectiveness of HPCD for enhancing transport in the Mt. Lemmon soil is due to its much larger organic carbon content (12.6%). However, given this large value, the impact of HPCD on naphthalene transport in the Mt. Lemmon soil is remarkable.

The magnitude of the enhanced-transport effect is expected to depend, in part, on the mass of HPCD in solution (i.e., eq 4). To test this, an experiment was designed to evaluate the influence of HPCD concentration on contaminant removal. Elution curves for the removal of biphenyl from the Borden soil were obtained by flushing a precontaminated column with different solutions. The results of this experiment are presented in Figure 6, wherein curves produced with solutions containing HPCD are compared to the elution curve obtained with water (no HPCD). A significant enhancement effect is observed only when the concentration of HPCD is greater than 0.01 g/L.

The magnitude of the enhanced flushing effect obtained with HPCD concentrations greater than 0.01 g/L is quite significant, especially for the lower solubility compounds. For example, due to large retention and rate-limited desorption, approximately 1800 pore volumes of water would be required to remove 99% of the total mass of
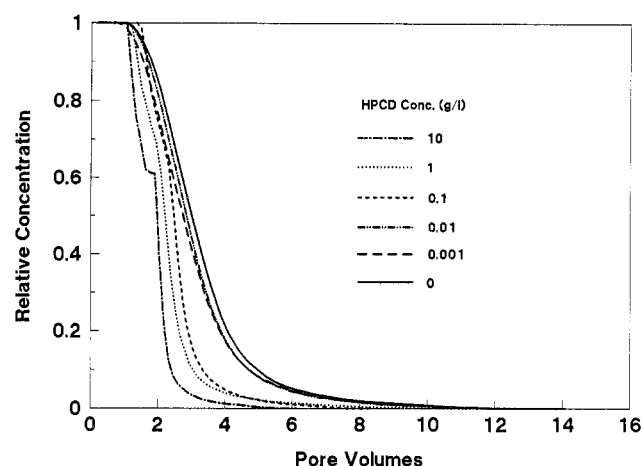

Figure 6. Influence of HPCD concentration on elution of biphenyl from Borden soil. Lines are used in place of measured data points to enhance visual contrast between results.

pyrene retained by the Borden material under conditions of maximum retention. Conversely, the same amount of pyrene could be removed with just 1 pore volume of solution containing 10 g/L of HPCD.

It is well-established that K_d values for the sorption of low-polarity organic compounds can be correlated to K_{ow}, the octanol–water partition coefficient (cf., ref 17). A correlation between K_c and K_{ow} has also been reported (3). Thus, for a given porous medium, the concentration of HPCD required to achieve a given level of transport enhancement should be essentially the same for all solutes if the magnitudes of the correlations are roughly similar (see eq 4). This contention is supported by the results reported in Table 3, wherein R values measured for HPCD-facilitated transport are very similar for a series of compounds whose log K_{ow} values vary by 3 orders of magnitude.

The influence of HPCD on transport of the organic compounds can be predicted by using eq 4. The bulk density (ρ), porosity (n), and HPCD concentration (X) are known parameters, and K_d can be obtained from the transport experiments performed without HPCD. Values for K_c can be obtained from solubilization experiments; in this case the data reported by Wang and Brusseau (3) were used. Predicted retardation factors were calculated in this manner and are reported in Table 3. The predicted values are within 10% of the measured values, with the exception of anthracene and trichlorobiphenyl. These results suggest that the impact of HPCD on solute transport can be accurately quantified with the simple modified retardation factor.

The magnitude of the enhanced-transport effect observed for HPCD is greater than that typically reported for other organic materials. The transport of phenanthrene through soil was enhanced by a factor of less than 2 by dissolved organic matter (DOM) (8) and by dextran (16). Similar results were reported for hexachlorobenzene/dextran (6) and hexachlorobiphenyl/DOM (18). A greater enhancement effect has been reported for Triton, a nonionic surfactant (7). The retardation factor for phenanthrene transport in a sandy soil was reduced from a value of 234 to 8 in the presence of a 2 g/L solution of Triton. The magnitude of this reduction is similar to that observed for HPCD. However, Triton was significantly sorbed by soil, whereas HPCD was not. The results of this study, namely, the great enhanced-transport effect

coupled with observations of no retardation or pore exclusion of the cyclodextrin, suggest that cyclodextrins have great potential for use in subsurface remediation efforts.

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