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Effect of a NAPL on Migration of PCP in Soil Columns

J. WANG,[1] J.-M. WANG,[1]
S. K. BANERJI,[1] AND R. K. BAJPAI*[,2]

[1] Department of Civil Engineering; and [2] Department of Chemical Engineering, University of Missouri, Columbia, MO 65211

ABSTRACT

Pentachlorophenol (PCP) is a widely used wood-treating chemical that is applied to wood under pressure in the form of concentrated solution in solvents that are nonaqueous phase liquids (NAPL). As a result, any spill at a wood-treating site using PCP results in soil contamination with PCP in the presence of a NAPL. Hence, a study of migration of PCP was conducted in presence of kerosene as a NAPL in unsaturated soils. Addition of kerosene to soil caused a change in the effective size of soil particles; the porosity, pore velocity, and dispersion coefficients, all changed (as measured by bromide breakthrough) in soil columns contaminated with kerosene. Moisture content of soil was found to be a key parameter determining the residual NAPL content in the soils. PCP/kerosene breakthrough experiments showed that the organic phase penetrated deeper and faster into soils with higher moisture content, and the residual kerosene acted as a sorptive phase that retarded the migration of PCP.

Index Entries: Equilibrium partitioning; residual saturation; wood treatment; breakthrough curve; kerosene; pentachlorophenol.

INTRODUCTION

Pentachlorophenol (PCP) is a widely used wood-treating chemical that is applied to wood under pressure in the form of a concentrated solution in kerosene or other nonaqueous phase liquids (NAPL) (*1*). Spills at wood-treatment sites, therefore, contaminate soil by PCP as well as the NAPL. The spilled NAPL migrates downward through the vadose zone

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*Author to whom all correspondence and reprint requests should be addressed.

under the influence of gravity. Because of the capillary-pressure effects, the migrating fluid leaves behind blobs or ganglia trapped in the pores of the soil. The amount of NAPL left behind is referred to as residual saturation. Eventually, either the front exhausts itself or it reaches the water table. A number of publications describe the behavior of this downward movement of NAPL (*2,3*). The chemicals present in the NAPL are partitioned in the soil and vapor phases all along, according to their sorption characteristics and volatilities (*4*). As rain water seeps through the vadose zone, the residual NAPL acts as a source of contamination (*5*); the infiltrating water may displace the NAPL as well as dissolve the organic vapors or soluble components from the residual NAPL, depending on the interfacial tensions between various phases and the aqueous solubilities of NAPL components (*6*). Obviously, the migration of PCP in soil is attenuated by the presence of NAPL as a mobile and a residual phase. The objective of this study was to investigate the migration of PCP through unsaturated soil in presence of NAPL at different values of soil-moisture content.

MATERIALS AND METHODS

Soil

The soil used was an upper-horizon Menfro-series fine silty loam soil collected from a farm in Columbia, MO. The soil was sieved through a #10 screen (2 mm) prior to use. The physical and chemical properties of soil were characterized by the Soil Testing Laboratory, Department of Agronomy, University of Missouri, Columbia, and are presented in Table 1. Organic matter in the soil was insoluble in water. This type of soil is representative of many upper-horizon Missouri soils.

Chemicals

PCP (99.3% purity) and ^{14}C-PCP (7.9 mCi/mmol) were obtained as sodium salts from Sigma Chemical Co., St. Louis, MO; 0.5% (w/w) solutions of PCP in kerosene were employed in this study in order to avoid the problem of surface crystallization (blooming). Commercial formulations use higher concentrations of PCP and avoid crystallization by addition of cosolvents and antiblooming agents (*1,7*), but their addition was considered undesirable for this study, since cosolvents may also influence the transport of PCP. ^{14}C-PCP (100 μCi) was initially dissolved in 0.1 mL of toluene, followed by redissolution in 100 mL of 0.5% PCP/kerosene to form stock solution. The stock solution (activity 1 μCi/mL) was stored at 4°C until use. A typical dose of ^{14}C-PCP in column studies was 5 μCi. Reagent-grade kerosene and analytical-grade potassium bromide were obtained from Fisher Scientific Company, St. Louis, MO.

Table 1
Soil Characteristics

Sample	Clay <0.002 mm	Silty 0.002–0.05 mm	Sand 0.05-2 mm	pH_w	pH_s	% Organic matter
Air-dried soil	10.9	80.4	8.7	6.1	5.9	2.7
Soil after washing with water				7.1	6.6	3.0

Sample	Ca lb/acre	Mg lb/acre	K lb/acre	Na ppm	Electrical conductivity $m\Omega^{-1}/cm$
Air-dried soil	1841	161	456	254	1.5
Soil after washing with water	1912	138	398	208	0.5

Partitioning Studies

Equilibrium distribution of PCP in the three-phase (soil/kerosene/water) system was measured using ^{14}C-PCP at the soil solution pH of 6.5 and 22°C. A 10-mL kerosene-PCP solution was added to 10 g air-dried soil, and the mixture was equilibrated for 36 h. Twenty milliliters of distilled water were then added to the mixture, and equilibration was continued for another 36 h; the different phases were then separated and analyzed for PCP using a scintillation counter.

Column Preparation and Characterization

Soil columns were prepared in glass tubes of 6 cm internal diameter. Glass wool was placed at the bottom of the column, and then 200 g of air-dried soil was packed in increments of 50 g. Soil was compacted by tapping and tamping using a plastic rod. The top was covered with glass wool to ensure uniform distribution of influent flow across the column cross-section. The height of packed soil in the column was 7.5 cm. The columns were conditioned by saturating and continuously flushing (gravity flow) with water at a flow rate of 1 mL/min for 2 d. $HgCl_2$ (500 ppm) was added to the water in order to minimize bacterial activity in soil. Moisture content was adjusted to either 35 or 65% by passing dry air through the columns at controlled flow rates. The soil columns were characterized for residual saturation of kerosene, porosity, hydraulic permeability, and axial dispersivity.

Residual saturation in columns with different moisture contents were measured by first passing 200 mL kerosene through the column, draining the column under gravity for 24 h, and flushing the column with water until no more kerosene appeared in the effluent. All the effluent was collected, and the volume of kerosene in the effluent was measured after phase separation. Residual saturation was defined as the volume of kerosene per unit pore volume that remained trapped in the column after flushing with water. It may also be represented as retention capacity, g residual kerosene trapped in the column/g air-dried soil. The measurements of residual saturation were conducted in replicate for five different column conditions.

Porosity was measured by gravimetric method as well as by breakthrough of a nonreactive tracer (bromide). The bromide-breakthrough measurement (step up as well as step down) was conducted under gravity flow after the column was conditioned for 2 d as described earlier. The breakthrough curves were analyzed with a one-dimensional advection-dispersion model for flow of nonreactive tracer through saturated porous medium (*8*). The parameters of the model (porosity, permeability, and axial dispersivity) were estimated with the help of a nonlinear least-square curve-fitting program based on the maximum neighborhood method of Marquardt (*9*).

In order to study the effect of kerosene on column characteristics, a precharacterized column was drained under gravity for 2 d. This was followed by addition of 34 mL (~1/3 pore volume) kerosene on the top of column and allowing it to distribute itself under gravity for 24 h. A small vacuum was applied in order to facilitate introduction of kerosene in the saturated column. All of the kerosene was retained in the column. Bromide breakthrough was measured in this column; there were no traces of kerosene in the column effluent in this measurement. After the completion of the bromide breakthrough, the column was drained under gravity for 2 d. A second batch of 68 mL of kerosene was than added to the top of the column, it was allowed to distribute and drain under gravity for 24 h, and the column was subjected to bromide-breakthrough measurement. This time, approx 34 mL of kerosene were collected at the column effluent during draining and the bromide-breakthrough measurements. Thus, the column retained a total of approx 68 mL of kerosene. This corresponded to a residual saturation of 0.68 for kerosene in the column, a value close to the one obtained with saturated column.

PCP Breakthrough Experiments

Columns (containing 200 g air-dried soil) with known moisture contents (35 or 65%) were injected with specified volumes (5, 10, and 20 mL) of 0.5% (wt/wt) PCP/kerosene mixtures, allowed to equilibrate for 12 h, and then eluted with distilled water containing 500 ppm $HgCl_2$. Each batch of PCP/kerosene mixture contained 5 μCi of ^{14}C-PCP. The experiments were conducted at room temperature of 22°C, and the elution rate was 0.2 mL/min. The different fractions of effluent were analyzed for the activity of ^{14}C-PCP in a Packard Tricarb Model 1900 liquid scintillation counter using Packard's Ultima Gold Scintillation Cocktail. A 1-mL aliquot of effluent sample was added to 10-mL scintillation cocktail in a 20-mL counting vial for radioactivity analysis. Background activity was subtracted, and the counts per minute were converted to PCP concentrations.

RESULTS AND DISCUSSION

PCP Partitioning Between Soil/Water/Kerosene

In the three-phase partitioning system, PCP remained predominantly in the kerosene phase (Fig. 1). In the linear isotherm range, the partitioning of PCP among aqueous, soil, and kerosene phases was in the ratio of 1:3.5:20. For an aqueous-phase PCP concentration of 4 ppm, soil-phase concentration was 14 mg/kg, and the concentration in kerosene phase was 80 mg/kg. The soil appeared to have a finite capacity for adsorption of PCP.

Residual Saturation

The retention capacity of kerosene in soil columns was measured at three soil-moisture contents (35, 65, and 100%). The results are presented in Table 2. For unsaturated columns, the residual saturation of kerosene in soil increased with a decrease in the soil moisture content, but the maximum values were obtained with saturated soil (Table 2). Soil columns containing 35% moisture retained an average of 0.16 g kerosene/g dry soil, and those with 65% moisture retained 0.1 g kerosene/g dry soil. Saturated columns retained 0.27 g kerosene/g dry soil. The measured values of residual saturation in unsaturated soil are within the range of values reported by others *(10,11)* for fluids with similar density and viscosity. The trend in residual saturations is in agreement with the observations of Mercer and Cohen (*2*). According to Mercer and Cohen (*2*), the residual saturation of NAPL in soil is governed by its pore size distribution and wettability, the ratio of viscosity, density, and surface tension of NAPL and the eluting fluid, and pore velocity. NAPL acts as a wetting fluid in unsaturated soils, and the higher the degree of unsaturation, the more NAPL that gets into the soil pores. However, the NAPL behaves as a nonwetting fluid in saturated soils (*12*). This phenomenon results in higher values of residual saturation in saturated soils than in unsaturated soils (Table 2).

Effect of Kerosene on Column Characteristics

The results of bromide-breakthrough experiments involving a water-saturated column in which kerosene was introduced were analyzed using the advection-dispersion model. These are presented in Table 3. After addition of the first shot of kerosene to the column, pore velocity of water under gravity dropped to approximately half of its value before. The pore velocity of water reduced again when the second shot of kerosene was in-

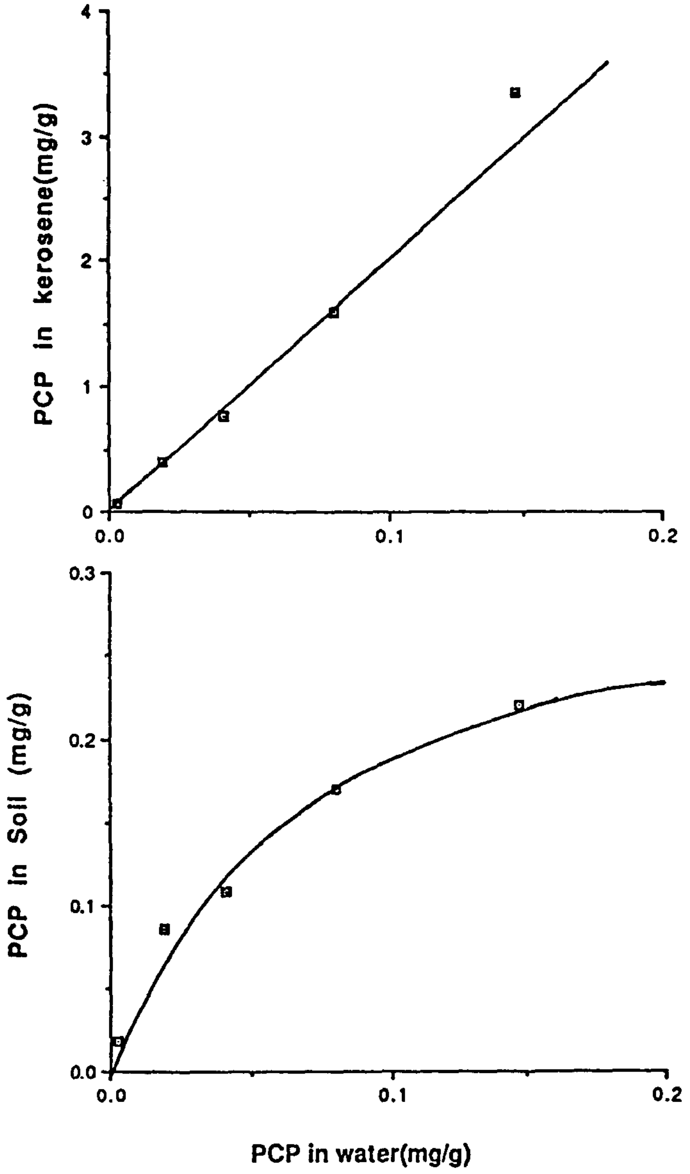

Fig. 1. Equilibrium partitioning of PCP in soil/kerosene/water system.

troduced in the column. In order to test if these variations were the effect of kerosene addition or temporal, the pore velocity was measured again during a repeated bromide-breakthrough experiment after letting the column drain under gravity for 24 h. As shown in Table 3, the column characteristics remained substantially unchanged between the two successive bromide-breakthrough experiments. Hence, it may be concluded that the changes in column characteristics presented in Table 3 are a result of addition of kerosene.

Table 2
Residual Saturation of Kerosene in Soil

Column #	Amount of soil	Moisture conent	Residual satuation[a] mL/mL void volume	Retention capacity[a] g kerosene/ g air-dried soil
1	200	35	0.40	0.157
2	300	35		0.162
3	200	65	0.17	0.096
4	300	65		0.098
5	200	100	0.66	0.269

[a] Average of two measurements from replicate columns.

Table 3
Effect of Kerosene on Column Charcteristics

Column conditions	Porosity	Pore velocity, cm/h	Dispersion coefficient, cm^2/h	Dispersivity, cm	Effective particle diameter, μm
New column (no kerosene)	0.48	10.8	14.28	1.32	14.4
After addition of 1/3 pore volume kerosene	0.42	5.58	3.42	0.61	12.8
After addition of another 2/3 pore volume kerosene	0.42	2.73	2.95	1.08	8.2
Same as above (repeated KBr breakthrough)	0.42	2.53	3.64	1.44	7.6

Since the dielectric constant of hydrocarbons is higher than that of water, the displacement of moisture by hydrocarbons in soil particles causes a reduction of repulsive forces between layers of soil-lattice; this results in a shrinking of the particles (*13*). The effective particle diameters in the soil column, calculated by fitting the observed data for pressure drop, pore velocity, and porosity in Ergun's equation for flow through packed columns (*14*), are also presented in Table 3, and these support the above observation concerning shrinking of soil particles (*13*). When hydrocarbons are introduced in soil beds, the shrinkage of particles often causes development of fissures and cracks that ultimately increase the hydraulic conductivity of the bed (*13*). The observations of pore velocity in this work, however, contradicted such a trend. It is not clear if these observations are a result of the scale of the column employed or of the

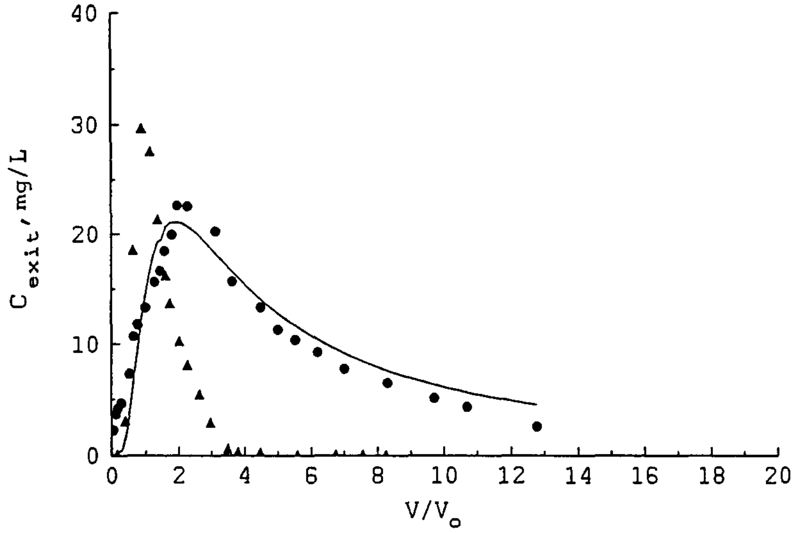

Fig. 2. PCP-breakthrough curve in soil column with 35% moisture. ●, —: Experimental data and simulation results with loading of 5 mL PCP/kerosene in 200 g air-dried soil. ▲: Experimental data when aqueous solution of PCP was loaded on the column.

type of the soil used. Similar reductions in hydraulic conductivities of soil beds on introduction of hydrocarbons in soil beds have been reported in literature (*13*) also, but these are an exception rather than a norm. It is likely that in the case of the exceptions, significant residual amounts of hydrocarbon phase remain immobile in the macropores of the soil matrix and thus prevent the penetration of infiltrating water to all of the newly created pore space. As a result, a net decrease in porosity may also be observed. In our experiments, we noted that up to 2/3 original pore volume was occupied by the residual kerosene in the column. Visual observations of the soil bed did not show any physical signs of changes in any of the columns on introduction of kerosene.

Migration of PCP in Presence of Kerosene

These experiments were conducted with soil columns with moisture levels of either 35% or 65% in which 5, 10, or 20 mL of 0.5% solutions of PCP in kerosene (0.5 μCi ^{14}C-PCP) were added. In all the cases except one, no kerosene-PCP solution appeared at the column exit during kerosene loading and subsequent draining for 12 h. Approximately 4 mL of kerosene were collected in the drained fluid when 20 mL of kerosene were added to column with 65% moisture. Flushing with water was initiated 12 h after the addition of kerosene. Some typical observations of the concentration of PCP in the effluent are shown in Figs 2–4.

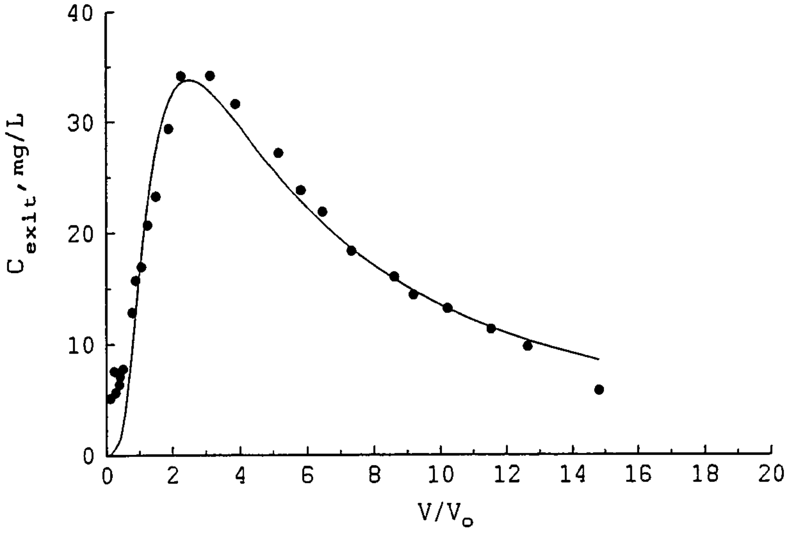

Fig. 3. PCP-breakthrough curve in soil column with 35% moisture and kerosene loading of 10 mL PCP/kerosene in 200 g air-dried soil. ●: Experimental data; —: simulation results.

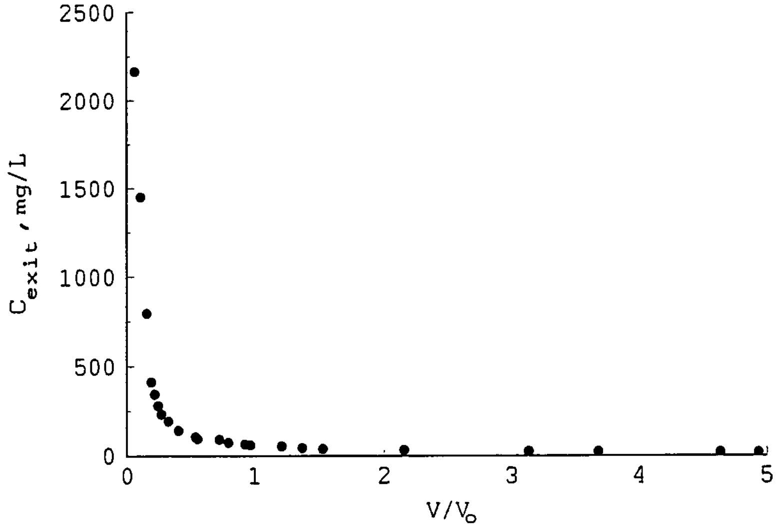

Fig. 4. PCP-breakthrough curve in soil column with 65% moisture and kerosene loading of 20 mL PCP/kerosene in 200 g air-dried soil. ●: Experimental data; —: simulation results.

In all the cases, PCP breakthrough occurred quickly on resumption of water flow, suggesting deep penetration of PCP-kerosene into the column. The breakthrough curves were generally unimodal in nature; several were a characteristic response of pulse input of tracer in the influent. Figure 2 shows the experimental data for breakthrough of PCP in two columns when PCP was applied to the soil as an aqueous solution and as

Table 4
PCP, Recovery in Column Effluent

Column		Kerosene added to column	PCP recovered in effluent
Moisture %	Void volume mL	mL	%
35	101	5	50.7[a]
	93[a]	10	42.3[a]
	91	20	44.9
65	87	5	64.3
	97[a]	10	65.2[a]
	117	20	74.3

[a] Average of two replicate measurements.

a solution in kerosene. On elution with water, the breakthrough curve of PCP exhibits a strong tendency for tailing in presence of kerosene. PCP breaks through the column sooner in the presence of kerosene (e.g., Figs. 3 and 4). The breakthrough occurred earlier in case of higher loadings of kerosene and at higher soil moisture content. In the case where 20 mL of kerosene were loaded on the columns, the highest concentrations of PCP were observed at the very beginning of elution (Fig. 4). Preliminary attempts to simulate the breakthrough curves using one-dimensional advection-dispersion equations with linear adsorption isotherm between mobile and immobile phases (*15*), were not successful, except in case of 5-and 10-mL additions of PCP/kerosene solution to soil column containing 35% moisture content. The solid lines in Figs. 2 and 3 show the best-fit obtained. A model accounting for the distribution of kerosene in the soil, partitioning of PCP between soil/water, and kerosene/water interfaces is being developed to analyze the experimental data.

The data for total PCP recovered in the column effluent are presented in Table 4; the highest recoveries were still under 75%, even though the washout experiments were conducted for extended periods, further supporting serious tailing problems. In these experiments, microbial degradation of PCP could be ruled out since the columns were treated with mercuric chloride. Volatilization losses of PCP can also be excluded since Acher et al. (*4*) have reported that moisture content >4% completely inhibits vapor penetration in kerosene-soil systems. Higher recoveries were found in soil columns containing 65% moisture content at the beginning of contamination. At this moisture content, the residual saturation values were also the lowest (Table 2). Hence, it appears that high residual NAPL saturation is responsible for high residual retention of miscible solute as well. As suggested by Fig. 1, the residual kerosene can hold approx 7 to 10 times as much PCP as soil coming in contact with water. Under conditions of saturation, the residual kerosene resides mainly in the pores (*2*) through which aqueous flow does not take place and the miscible solvent continues to seep out of the soils slowly.

CONCLUSIONS

The results presented herein show that the introduction of PCP in soil along with kerosene increases its penetration in the soil column; the residual NAPL also significantly increases the retention of PCP in the soil columns. On one hand, it retards the mobility of PCP through soil during water seepage; on the other hand, it continues to act as major source of contamination of the soluble components. It suggests that attempts should be made either to remove residual NAPL from soil pores by use of surface-active agents or to conduct *in situ* degradation of the NAPL.

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