Desorption of pentachlorophenol (PCP) from contaminated soils in mixed solvents of water and ethanol was investigated using desorption isotherm experiments. The following cosolvent volume fractions of ethanol in the mixed solvent were considered: 0, 0.3, 0.56, 0.79, 0.95, and 1.0. Three fractions of a synthetic soil (Edison soil) with approximately 1% organic matter were the main soils used in this study in addition to K-10 montmorillonite clay and Ottawa sand. The effect of soil organic matter and soil surface area on desorption in mixed solvents was evaluated. Analysis of desorption data revealed that PCP desorption increased with PCP solubility in mixed solvent up to 0.79, 0.95, and 0.56 fraction ethanol for Edison soil, K-10 montmorillonite, and Ottawa sand, respectively. Lower desorption of PCP from Edison soil in solvents with more than 0.79 fraction ethanol resulted from interactions between solvent and soil organic matter. For Edison soil, highest PCP desorption in all mixed solvents was obtained for the soil fraction with the smallest surface area. Desorption of PCP in mixed solvents containing more than 0.79 fraction ethanol was lower for soils with organic matter than for other soils.

**Introduction**

Pentachlorophenol (PCP) is a wood preserving compound often found in contaminated soils at wood preserving sites in the U.S. (1). Solvent washing of contaminated soils may be a viable soil cleanup technology (2, 3). In remediation of contaminated soils, the selection of solvent for either in-situ or ex-situ washing of soils with solvent depends on several factors that influence the effectiveness of the solvent in contaminant removal. The solubility of the organic pollutant in the solvent and the miscibility of the solvent with water are important factors. The fraction of the water-miscible organic liquid, the cosolvent, in an aqueous solution determines the solubility of the compound in that solution. Higher cosolvent fractions in the solution increase the solubility of the hydrophobic organic compounds (HOCs) in log-linear fashion (4–6).

The sorption of HOCs onto soil from an aqueous solution has been primarily attributed to sorption of HOCs to soil organic matter (7–10). Sorption, which is related to the concentration of the HOC in the liquid and the organic matter content of the soil, depends on the solubility of the HOC in the liquid. Equilibrium sorption studies have shown that the sorption of HOCs decreases with the solubility of the contaminant in the liquid in log-linear fashion (11–13). Lee et al. (14) showed that the equilibrium sorption of ionizable or dissociating HOCs also decreased with liquid solubility, similar to neutral HOCs.

Rao et al. (12) suggested that HOC sorption onto soils and solubility in solvents are determined by hydrophobic (solvent) interactions, where the hydrophobic surface of sorbent is in contact with a hydrophobic sorbate (solute). An increase in the fraction of organic cosolvent leads to an exponential decrease in sorption with a decreasing carbonaceous surface area for the sorbate, resulting in higher mobility of the HOC in the absence of hindrance by diffusion through the organic matter.

In sorption or physisorption of HOCs onto natural sorbents, negligible activation energy is required for physisorption of the HOC to an adsorptive surface or partitioning into an organic phase. In contrast, desorption of HOCs from the once-sorbed phase or surface generally requires activation to overcome sorptive interactions that may have developed between sorbate and sorbent after the initial sorption (15). Assessing different types of geosorbents and their inorganic and organic sorptive components during sorption—desorption of HOCs, Luthy et al. (16) suggested fast and slow desorption from amorphous (soft) and dense (hard) organic matter, respectively. Reversible sorption occurs when major sorbate-sorbent interactions have been overcome. In addition to physisorption, chemisorption of substituted phenolic compounds such as PCP may occur due to interactions between the substituted groups or the phenolate anion and the soil surface or soil organic matter. In the absence of specific sorbate-sorbent and sorbent-solvent interactions other than physisorption, desorption of HOCs from soils into aqueous solutions, therefore, is expected to increase with increasing liquid solubility of the HOC. A higher fraction of cosolvent in the mixed solvent is expected to enhance the desorption of HOCs.

The sorption of HOCs onto soils from aqueous and mixed solvents has been studied by numerous investigators, while the desorption of HOCs from soils into mixed solvents has not been studied as extensively. This research examined the desorption of PCP, a dissociating HOC and a U.S. EPA priority pollutant, from soils into mixtures of water and ethanol. Ethanol was selected as cosolvent in water—ethanol mixtures due to its high PCP solubility, its complete miscibility with water, and its low cost. Desorption of PCP in water—ethanol mixtures was investigated using soils with varied soil organic matter content and soil surface area (Table 1).

---

**TABLE 1. Desorption of PCP from Soils Using Water—Ethanol Mixtures: Experimental Matrix**

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Ethanol Content (fraction)</th>
<th>Organic Matter Content</th>
<th>Soil Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edison</td>
<td>0.00</td>
<td>0.0%</td>
<td>Large surface</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>0.0%</td>
<td>Large surface</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>0.0%</td>
<td>Large surface</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>0.0%</td>
<td>Large surface</td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>0.0%</td>
<td>Large surface</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.0%</td>
<td>Large surface</td>
</tr>
</tbody>
</table>

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**References**


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TABLE 2. Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Specification</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCP</td>
<td>99%</td>
<td>Aldrich Chemicals, Milwaukee, WI</td>
</tr>
<tr>
<td>2,4,6-tribromo-phenol ethanol</td>
<td>190 proof, USP grade</td>
<td>Midwest Grain Products, Weston, MO</td>
</tr>
<tr>
<td>ethanol</td>
<td>200 proof, USP grade</td>
<td>Midwest Grain Products, Weston, MO</td>
</tr>
<tr>
<td>acetone</td>
<td>optima grade</td>
<td>Fisher Chemicals, Fairlawn, NJ</td>
</tr>
</tbody>
</table>

Experimental Section

**Chemicals.** The chemicals (solutes and solvents) used in this study are listed in Table 2. MilliQ grade deionized water (DI) with a resistivity greater than 18 MΩ was produced inside the laboratory by processing tap water through a MilliQ purification system (Millipore Corporation, Bedford, MA). The various water–ethanol mixtures were prepared from this DI water and the 95% ethanol solution.

**Soils.** Uncontaminated Edison soil, containing 31% sand, 6% no. 9 gravel, 28% silt, 20% top soil, and 15% clay, was obtained from the U.S. EPA Synthetic Soil Blending System. 6% no. 9 gravel, 28% silt, 20% top soil, and 15% clay, was obtained from the U.S. EPA Synthetic Soil Blending System. The soil fractions, except the >200 U.S. mesh fraction, were washed with water and dried in an oven at 105 °C prior to spiking with PCP. Other soils included K-10 montmorillonite clay and 20 U.S. mesh Ottawa sand. Some properties of the soils are listed in Table 3.

**BET Surface Area and Pore Size Analysis for Soils.** The BET (19) surface area, pore size, and pore size distribution for different soils were measured with an Accelerated Surface Area and Porosimetry system, ASAP 2010 (Micromeritics Instrument Corporation, Norcross, GA), using nitrogen adsorption/desorption isotherms.

**PCP Spiking.** Acetone was used as a wetting agent for spiking the soil with PCP. A solution of PCP in acetone was added to a dry soil fraction. This soil–PCP slurry (500 g of soil–100 mL of acetone) was placed inside a cylindrical tumbler with baffles and allowed to mix for 3 weeks at 16 rpm. The tumbler was a 304 stainless steel cylinder 12.7 cm long with a 10.1-cm ID. The tumbling procedure provided for slow deposition of the PCP onto the soil, while the acetone volatilized through 4-μm stainless steel frits placed inside portholes on the sides of the tumblor.

**PCP Analysis.** Liquid samples were filtered through Magna 0.45-μm nylon membranes (Micron Separations Inc., Westboro, MA) and acidified to pH 2 with concentrated hydrochloric acid. The samples were then extracted with toluene to transfer the PCP from the aqueous phase to the organic phase for gas chromatograph (GC) analysis. An internal standard calibration was performed using 2,4,6-tribromophenol. Internal standard was added to toluene before extraction. The toluene extracts were injected into the GC for PCP analysis. Extraction efficiency of PCP into toluene was greater than 98%. PCP analysis determined the total concentration of PCP species. Since PCP has a pK_a of 4.7, when liquid samples were acidified to pH 2, all the PCP species present in the sample were in the neutral (undissociated) form. Therefore, the reported PCP values include the total PCP extracted from the soil (pentachlorophenol and pentachlorophenate, C_6Cl_5OH and C_6Cl_5O^-).

PCP concentrations in liquid samples were analyzed using a J&W 30-m long, 0.53-mm i.d. DB-5 fused silica capillary column (J&W Scientific, Folsom, California) using a 5980 Series II HP (Hewlett-Packard, Palo Alto, CA) GC with an electron capture detector (ECD). Helium was the carrier gas, and a 95% argon–5% methane gas mixture was the makeup gas.

**PCP Solubility.** An equal volume of 100 mL of different water–ethanol mixtures was placed inside 160 mL glass hypovals. Excess PCP was added to each bottle at a PCP/ethanol mixing ratio of 0.63 g/g (50 g of PCP/78.9 g of neat ethanol or 50 g of PCP/100 mL of ethanol). This PCP/ethanol ratio of 0.63 was approximately 21% in excess of 0.52, the PCP/ethanol ratio reported by Bevenue and Beckman (20) for the solubility of PCP in neat ethanol at 30 °C (52 g of PCP/100 g of ethanol). After shaking the bottles on a rotating shaker at 18 rpm for 7 days at 24 °C, an excess of solid PCP remained in each bottle. The concentration of PCP in liquid was determined with the GC.

**Desorption Isoterm.** Similar to sorption, reverse sorption or desorption of HOCs from soils into solution may be described by a linear partition equation

$$q_p = K_p C_e$$  

where $q_p$ (mg/kg) is the concentration of sorbate (solute) remaining on the soil at equilibrium, $K_p$ (mg/L) is the equilibrium concentration of solute in the liquid, and $K_p$ (L/kg) is the sorption constant (sorption or partition coefficient). A nonlinear equation for describing sorption is the Freundlich (21) equation

$$q_p = K_f C_e^{1/n}$$  

where the Freundlich constants $K_f$ and 1/n are empirical constants that may be related to the capacity or affinity of the sorbent for the sorbate and the intensity of sorption, respectively.

In this study, soil spiked with PCP was mixed with clean solvent to determine the removal of the sorbate from the soil by the liquid (release of sorbate by the sorbent into the solvent). In desorption isotherm experiments, the following range for the soil:solvent mass to volume contact ratio (g: solvent) was used: 1:1 to 1:200. Different masses of PCP-spiked soil were placed inside 160 mL glass bottles; solvent was added to each bottle using various soil:solvent contact ratios. The bottles were then capped and placed inside a rotating shaker at 18 rpm. Desorption isotherm experiments were conducted at 24 °C. After 3 weeks of shaking, the PCP concentration in the liquid phase ($C_l$) was measured with the GC. The values for $q_p$, the concentration of PCP remaining on the soil after desorption (PCP sorbed onto the soil), were calculated from the measured PCP concentrations in the liquid phase by mass balance: $q_p = q_s - C_l(V/W)$, where $q_s$ is the initial PCP concentration in soil (mg/kg), $V$ is the volume of solution (L), and $W$ is the soil mass (kg).

**Results**

**PCP Solubility.** A log-linear solubility model proposed by Rubin and Yalkowsky (5) for an exponential increase in solubility of HOCs in mixtures of water and water-miscible cosolvent is

$$\log S_m = \log S_w + \sigma f_c$$  

$$\log(S/S_w) = \sigma$$  

where $f_c$ is the cosolvent volume fraction in the mixed solvent, $\sigma$ is the cosolvency power of the solvent for the solute, and $S_m$, $S_w$, and $S_s$ are solubilities in mixed solvent, pure cosolvent, and water, respectively. The solubility of PCP in several water–ethanol mixtures is shown in Figure 1. A cosolvency power ($\sigma$) of 4.75 was calculated from the measured solubili-

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ties of PCP in water and neat ethanol (eq 4). Linear regression of the experimental solubility data determined a value of 4.70 \(R^2 = 0.98\), a 1% deviation from the \(\sigma\) given by the log-linear solubility model (eq 3).

Deviation from the log-linear model has been observed for HOC solubility in mixed solvent systems. Using water–ethanol mixed solvents and several organic solutes with different structures, Rubino and Yalkowsky (6) observed a positive deviation from the log-linear solubility prediction for the 0.6 volume fraction of ethanol in mixed solvent, attributing this deviation to cosolvent–water interactions. Similar deviations from log-linear solubility in water–ethanol mixed solvents were observed for several polycyclic aromatic compounds (4, 22, 23).

**Linear Analysis of Desorption Isotherm Data for Edison Soil.** Sorption constants were obtained from linear regression of PCP desorption data. The linear regression of data results in an \(y\)-intercept for the line which is presented by

\[
q_e = K_m C_e + 1
\]

(5)

where \(q_e\) (mg/kg) and \(C_e\) (mg/L) are the same as in eq 1, \(K_m\) (L/kg) is the linear sorption constant for the mixed solvent (similar to \(K_f\)), and \(I\) (mg/kg) represents the amount of PCP that did not desorb from the soil.

The data from the desorption isotherms for the 100 \(\times\) 140 U.S. mesh soil with an initial PCP loading of 99 mg/kg are presented in Figure 2. The data from Figure 2 indicate that solvents containing 0.56 and 0.79 fraction ethanol achieved the highest PCP removals from the 100 \(\times\) 140 U.S. mesh soil. Low PCP recoveries were obtained with water and neat ethanol. The solvents containing 0.3 and 0.95 fraction ethanol produced PCP recoveries between those yielded by water and neat ethanol and those given by the solvents containing 0.56 and 0.79 fraction ethanol. The PCP recovery levels achieved with the 0.56 and 0.79 ethanol fractions in solvent were comparable to each other. Similar trends were observed for the 20 \(\times\) 40 and \(\times\) 200 U.S. mesh soil fractions. At high volumes of mixed solvent (high soil:solvent contact ratio), low concentrations of PCP were measured in the liquid, resulting in less precision in the measured sorbed mass of PCP remaining on the soil (calculated from mass balance), reflected by the scatter of desorption data in Figure 2 for low PCP concentrations.

The \(K_m\) values determined from the slopes of the lines in Figure 2 are plotted in Figure 3a against the fraction of ethanol in mixed solvent in log-linear (semilog) fashion. The data presented in Figure 3a show exponential behavior for the desorption of PCP from soil with increasing fraction of ethanol in solvent from 0 to 0.56 fraction ethanol. PCP desorption decreased for soils in contact with solvents containing more than 0.79 fraction ethanol. Smaller values of \(K_m\) (lower sorption) were indicative of greater PCP desorption from the soil. The results for 100 \(\times\) 140 U.S. mesh soil indicate low \(K_m\) values for the 0.56 and 0.79 ethanol fractions, intermediate \(K_m\) values for the 0.3 and 0.95 ethanol fractions, and high \(K_m\) values for water and neat ethanol. The linear sorption constants from Figure 3a show that the desorption of PCP from the three fractions of Edison soil followed in similar fashion with respect to the fraction of ethanol in mixed solvent, where desorption from three fractions of Edison soil occurred in descending order for soil particle size (U.S. mesh): 20 \(\times\) 40, 100 \(\times\) 140, \(\approx\) 200.

The values for \(I\) in Table 5 show that between 5.4 and 23.3 mg/kg PCP did not desorb from the 100 \(\times\) 140 U.S. mesh soil fraction. Higher values of \(I\) were obtained for all three fractions of Edison soil using neat ethanol (23–34 mg/kg) and for 20 \(\times\) 40 and \(\times\) 200 U.S. mesh soil fractions using water (23–30 mg/kg).

**Nonlinear Analysis of Desorption Data for Edison Soil.** The PCP desorption data were analyzed using the Freundlich equation. The solid lines in Figure 4 represent the fit of the desorption data to the Freundlich equation for the 100 \(\times\) 140 U.S. mesh Edison soil. Figure 5a shows the Freundlich constant \(1/n\) determined from the slopes of the solid lines in Figure 4. The \(1/n\) values from Figure 5a indicate that the lowest sorption intensity of PCP for the 20 \(\times\) 40 U.S. mesh soil was obtained with the 0.56 fraction ethanol, while the 0.79 fraction ethanol gave the lowest sorption intensity of PCP for the 100 \(\times\) 140 and \(\approx\) 200 U.S. mesh fractions. The data from Figure 5a indicate that for most mixed solvents, the desorption of PCP was greatest from the 20 \(\times\) 40 U.S. mesh soil, the fraction with the largest particle size. The values for Freundlich constant \(K_f\) determined from the data in Figure 5a are listed in Table 6; higher \(K_f\) values were obtained for water and neat ethanol, and the lowest value was obtained for the mixed solvent containing 0.79 fraction ethanol.  

**Analysis of Desorption Data for Other Soils.** The PCP desorption isotherms for the 20 \(\times\) 30 U.S. mesh Ottawa sand and 20 \(\times\) 30 U.S. mesh Montmorillonite clay show an increase in desorption of PCP from soil with increasing fraction of ethanol in mixed solvent. The linear sorption constants are presented in Figure 3b. The data for the 20 \(\times\) 30 U.S. mesh Edison soil are included for comparison. The desorption data presented in Figure 3b demonstrate a rapid increase in desorption of PCP from K-10 Montmorillonite for solvents containing from 0.3 to 0.56 fraction ethanol, then a more sluggish increase in
PCP desorption from 0.56 to 0.95 fraction ethanol, and finally a decrease in desorption with neat ethanol. The data from Figure 3b indicate an increase in desorption of PCP from Ottawa sand for an increase from 0 to 0.56 fraction ethanol in mixed solvent. For K-10 montmorillonite, desorption of PCP decreased with neat ethanol, while for Ottawa sand, PCP desorption did not change significantly from 0.56 to 1.0 fraction ethanol in mixed solvent. Sorption constants for water were the greatest. The PCP sorption constant for the various soils ranged from 0.02 to 0.2 L/kg for 0.56 fraction ethanol in mixed solvent.

The values of the Freundlich constant 1/n determined from the desorption data for other soils are presented in Figure 5b. The data for the >200 U.S. mesh soil are shown for comparison. These data indicate that for Ottawa sand, the highest desorption intensity was given by the mixed solvent containing 0.56 fraction ethanol, while for K-10 montmorillonite, the desorption intensity decreased with increasing fraction of ethanol in mixed solvent.

The values of the Freundlich constant 1/n determined from the desorption data for Ottawa sand are presented in Figure 5b. The data indicate that for Ottawa sand, the highest desorption intensity was given by the mixed solvent containing 0.56 fraction ethanol, while for K-10 montmorillonite, the desorption intensity decreased with increasing fraction of ethanol in mixed solvent.

**Solution pH.** The pH of mixed solvent was measured before and after the experiments at several soil:solvent ratios for solvents used in the desorption isotherm experiments. The data presented in Figure 6 (parts a and b) show the pH of the mixed solvents in contact with clean and PCP-spiked Edison soil, respectively. The pH data for the clean soil indicate that the soil pH (Table 3) affected the solvent pH after soil-solvent contact for 0, 0.3, 0.56, and 0.79 ethanol fractions in mixed solvent. With a higher fraction of ethanol in mixed solvent, the solvent pH was less dependent on the soil pH (lower solution pH values). A similar trend was observed for the pH data for spiked soils presented in Figure 6b; the slightly higher pH values were possibly affected by contact between soil and acetone during the spiking of soil with PCP. The solution pH values for K-10 montmorillonite listed in Table 4 show that the pH of solution was less than 4.7 for all mixed solvents.

**Discussion**

**Linear and Freundlich Sorption Constants.** The linear sorption constants for Edison soil shown in Figure 3a indicate an increase in desorption from all three fractions of Edison soil with increasing fraction of ethanol for f_c from 0 to 0.79 followed by a decrease in desorption from all three fractions of Edison soil for f_c ≥ 0.95. The Freundlich constants 1/n for Edison soil shown in Figure 5a indicate an increase in desorption for f_c from 0 to 0.3 fraction ethanol before a decrease in desorption with neat ethanol.
linear sorption constants show a similar trend for desorption from the three soil fractions in descending order of soil particle size: 20 × 40, 100 × 140, >200 U.S. mesh, whereas the nonlinear sorption constants do not indicate a similar trend for soil particle size although showing that highest desorption occurred for the 20 × 40 U.S. mesh fraction. The linear and nonlinear sorption parameters for Edison soil, listed in Tables 5 and 6, respectively, show higher regression coefficients in regression of linear isotherm desorption data.

For K-10 montmorillonite, the linear sorption constants from Figure 3b show an increase in desorption with increasing fraction of ethanol from 0 to 0.95 fraction ethanol in mixed solvent, whereas the Freundlich sorption constants from Figure 5b do not show an increase in desorption with increasing fraction of ethanol. Similar results were obtained for Ottawa sand. The linear and Freundlich sorption constants for Edison soil shown in Figures 3b and 5b, respectively, are greater than the linear and Freundlich sorption constants for K-10 montmorillonite and Ottawa sand. In Figure 3b, for \( f_c \geq 0.59 \), sorption constants are higher for Edison soil than for K-10 montmorillonite and Ottawa, indicating lower desorption of PCP from Edison soil than from the other soils. Lower desorption of PCP from Edison soil may be attributed to the organic matter present in the soil, since K-10 montmorillonite and Ottawa sand had negligible organic matter. The nonlinear constants in Figure 5b indicate that, for soils with very low organic matter content, the Freundlich constant \( 1/n \) does not show a trend in the desorption of PCP with respect to the fraction of ethanol in mixed solvent. For K-10 montmorillonite and Ottawa sand, soils with very low organic matter content, the data in Table 3 show a difference in the desorption of PCP from K-10 montmorillonite and Ottawa sand, showing that desorption was not affected by the difference in soil surface area for soils with very low organic matter.

**Solution pH.** In octanol–water distribution of PCP, Westall et al. (24) and Jafvert et al. (25) observed appreciable hydrophobicity of dissociated PCP. Schellenburgh et al. (26) evidenced that the sorption of pentachlorophenolate onto natural sorbents was predominantly a partitioning process between the aqueous and organic phases. Jafvert (27) showed that the sorption of pentachlorophenolate to natural sorbents was predominantly due to hydrophobic interactions between solute and sorbent, modified by electrostatic interactions due to the changes in soil-solution pH. Miller and Faust (28) observed that PCP sorption onto an organo-clay from a solution containing 0.15 fraction of ethanol in mixed solvent. For K-10 montmorillonite and Ottawa sand, showing that desorption was not affected by the difference in soil surface area for soils with very low organic matter.

In water—methanol mixtures, Lee et al. (29) indicated that the \( K_a \) of PCP increased with increasing fraction of methanol in mixed solvent from 4.7 in water to 8.6 in neat methanol, an alkaline shift in the organic acid dissociation constant in a solvent with low dielectric constant. Although conditional \( pK_a \) values for PCP in water—ethanol mixtures were not determined in this study, the conditional \( pK_a \) values of PCP are expected to increase with higher fraction of ethanol in mixed solvent, similar to water—methanol mixtures. Higher \( pK_a \) values result in lower dissociation of PCP at higher cosolvent fractions. The pH data from Figure 6 indicate that desorption of PCP in water occurred primarily as dissociated PCP, pentachlorophenolate. Due to the expected increase in \( pK_a \) for PCP in mixed solvents with increasing fraction of ethanol, the solution pH values from Figure 6 indicate that PCP desorbed from Edison soil as both pentachlorothanophenolate and neutral PCP in mixed solvents with \( f_c \geq 0.3 \), with more neutral PCP at higher \( f_c \). The pH of mixed solvents in contact with K-10 montmorillonite and Ottawa sand was

---

**TABLE 4. Solution pH in Extraction of PCP from K-10 Montmorillonite**

<table>
<thead>
<tr>
<th>volume fraction of ethanol in solvent, ( f_c )</th>
<th>soil:solvent ratio (g:mL)</th>
<th>( \text{pH} ) solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1:10</td>
<td>4.24</td>
</tr>
<tr>
<td>0.3</td>
<td>1:100</td>
<td>5.74</td>
</tr>
<tr>
<td>0.56</td>
<td>1:10</td>
<td>5.84</td>
</tr>
<tr>
<td>0.79</td>
<td>1:100</td>
<td>6.21</td>
</tr>
<tr>
<td>0.95</td>
<td>1:100</td>
<td>6.43</td>
</tr>
<tr>
<td>0.95</td>
<td>clean solvent</td>
<td>7.04</td>
</tr>
</tbody>
</table>

**TABLE 5. Linear Analysis for Desorption of PCP from 100 × 140 U.S. Mesh Edison Soil**

<table>
<thead>
<tr>
<th>volume fraction of ethanol in mixed solvent, ( f_c )</th>
<th>linear sorption constant, ( K_a ) (L/kg)</th>
<th>nonreversible sorption, ( f ) (mg/kg)</th>
<th>regression coeff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.3</td>
<td>2.19</td>
<td>95.7</td>
</tr>
<tr>
<td>0.3</td>
<td>0.56</td>
<td>1.12</td>
<td>53.9</td>
</tr>
<tr>
<td>0.79</td>
<td>0.95</td>
<td>1.12</td>
<td>62.1</td>
</tr>
<tr>
<td>0.95</td>
<td>1</td>
<td>1.12</td>
<td>61.2</td>
</tr>
<tr>
<td>1</td>
<td>1.43</td>
<td>1.12</td>
<td>79.9</td>
</tr>
</tbody>
</table>

decrease at 0.56 fraction ethanol. A comparison of the linear and nonlinear sorption constants from Figures 3a and 5a shows that, for linear isotherms, highest desorption occurred at 0.79 fraction ethanol for all three soil fractions, while for nonlinear isotherms, highest desorption occurred at 0.56 fraction ethanol for 20 × 40 U.S. mesh soil and at 0.79 fraction ethanol for 100 × 140 and >200 U.S. mesh fractions.
less than 4.3 and 8.9, respectively, indicating that the desorption of PCP from K-10 montmorillonite occurred primarily in the form of neutral PCP, whereas PCP desorbed from Ottawa sand primarily in the form of dissociated PCP. 

Sorption Constant $K_m$. Rao et al. (12) and Fu and Luthy (13) derived expressions for predicting the effect of a miscible cosolvent on sorption of HOCs by soil from solvent–water mixtures by relating the sorption constant and the organic carbon dependency of sorption to the log-linear solubility relationship to obtain an equation of the form

$$\log K_m = \log K_w - \alpha \sigma f_c$$  \hspace{1cm} (6)

where $K_m$ and $K_w$ are sorption (partition) constants in mixed solvent and water, respectively, and $\alpha$ is an empirical constant which accounts for solvent-sorbent interactions. When $\alpha = 1$, the sorption of HOCs decreases log-linearly with the solubility of the solute in mixed solvent, independent of any sorbent-solvent interactions.

The slopes ($\alpha\sigma$) of the log-linear plots presented in Figure 3 were calculated from $f_c = 0.0$ (water) to $f_c = 0.56$ (50% ethanol by mass) for all soils. The $\alpha$ values listed in Table 7, which were determined from eq 4 using a $\nu$ value of 4.747, range from 0.56 to 0.68 for Edison soil and from 0.56 to 0.85 for all soils. The deviation of $\alpha$ from 1 indicates that, although desorption of PCP from soil into mixtures of water–ethanol was primarily solubility limited, sorbent-solvent interactions also affected the desorption process. The value of $\alpha$ obtained for K-10 montmorillonite, 0.85, was closest to 1.0. Since the organic matter content of K-10 montmorillonite was very low, most of the PCP was adsorbed on the surface of the clay. Since the pH for K-10 montmorillonite was 3.26, the majority of the sorbed PCP on the surface of soil was undissociated PCP. In the absence of significant sorbent-solvent interactions affecting the desorption process, the desorption of neutral PCP increased with fraction of ethanol in mixed solvent.

In sorption isotherm experiments using a Webster silty clay loam with 3% organic carbon content, Lee et al. (29) found that the sorption of PCP onto soil from water–methanol mixed solvents was linear. Similar to the results from this study presented in Figure 3a, they observed a log-linear decrease in $K_m$ with increasing fraction of methanol, reaching a minimum at 0.9 volume fraction methanol before increasing in neat methanol. The $\alpha\sigma$ values for Edison soil listed in Table 6 are in the range of $\alpha\sigma$ values reported by Lee et al. (14, 29) of 3.88 and 2.56 for sorption of neutral and anionic species of PCP, respectively.

In sorption of several HOCs onto a soil with 1.94% organic carbon content using water–methanol and water–acetone mixtures, Fu and Luthy (13) obtained $\alpha$ values between 0.44

![FIGURE 4. Desorption of PCP from 100 × 140 U.S. mesh Edison soil: Freundlich isotherms.](image-url)

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and 0.57, attributing this deviation to the hydrophobicity of the solute and sorbent-solvent interaction. They observed that the more hydrophobic solute effected a smaller deviation from the relationship between log-linear sorption and log-linear solubility (\( R^1 \)).

**Nonreversible Sorption.** The amount of sorbate remaining on the sorbent after the desorption or extraction process has been called the irreversible or nonreversible sorption (\( I \) in eq 4). Desorption is influenced by the interactions occurring between solute and sorbent during the previous sorption process. In spiking of all soils with PCP, the duration of the sorption process was 3 weeks. For Edison soils, the spiking process involved primarily the sorption of PCP from the acetone phase into soil organic matter. During contact between acetone and soil organic matter for several weeks, PCP had the opportunity to penetrate the soil organic matter matrix. In this study, for all mixed solvents, a fraction of PCP was nonextractable from PCP spiked soils. The nonextractable fraction of sorbed PCP, not available to solvent, was retained in the soil organic matter by sorptive forces other than physical or hydrophobic forces.

Issacson and Frink (30) reported nonreversible sorption of phenol, 2-chlorophenol, and 2,4-dichlorophenol on soils, observing hysteresis in the desorption of solute between the sorption and desorption experiments using aqueous solutions. Their desorption data were obtained under nonequilibrium conditions using the lowest flow rates. They attributed the nonreversible sorption to the previous sorption process (prior to desorption) based on specific sorbate-sorbent interactions. In batch desorption experiments using a soil with high organic matter content (20–30%), Warith et al. (31) obtained a 20–90% irreversible sorption of PCP on soil in contact with water. Among other chlorophenols sorbed on several soils with synthetic and natural organic matter, Lagas (32) found a fraction of the sorbed PCP to be nonextractable with hexane at pH 9.3. Banerji and Wei (33) observed 27 to 52% nonreversible sorption during recovery of PCP from several soils loaded with 500 mg/kg PCP using...
successive extractions with water and 2-propanol. In contrast, in sorption–desorption isotherm experiments using aqueous solutions, Bellin et al. (34) observed that sorption of PCP in several alkaline soils with organic carbon contents from 0.12 to 0.95% was completely reversible.

**Sorbent-Solvent and Solute-Sorbent Interactions.** For soils with very low organic matter, a sharp decrease in desorption did not occur for richer ethanol solutions (f_e < 0.95). For K-10 montmorillonite, desorption decreased slightly in neat ethanol, while for Ottawa sand, no significant decrease in desorption occurred for f_e > 0.56. For Edison soil, the data presented in Figure 3a show an exponential increase in PCP desorption with increasing solubility of PCP in mixed solvents with higher fractions of ethanol up to 0.79 ethanol fraction and an exponential decrease in desorption of PCP in solvents with 0.95 and 1.0 fraction ethanol.

The PCP desorption in ethanol solutions with f_e ≥ 0.95 was not solubility limited (solute–solvent interaction) but was influenced by sorbent-solvent interactions. The ethanol-rich solvents (f_e ≥ 0.95) affected a lower desorption of PCP from soil despite greater solubilities of PCP in the solvents. The pH data from Figure 6 show that, for f_e = 0.95, the pH values for the solution before and after contact with Edison soil were similar. Although no pH reading was taken in neat ethanol, the pH data for f_e = 0.95 indicate that soil pH would not affect a significant sorbent-solvent interaction for solutions with f_e ≥ 0.95.

For K-10 montmorillonite, the decrease in PCP desorption with neat ethanol may be attributed to sorbent-solvent interactions. Although the soil surface area and soil pore volume of K-10 montmorillonite are approximately 1 order of magnitude greater than those of > 200 U.S. mesh Edison soil (Table 3), the desorption data do not indicate the relative decrease in desorption from K-10 montmorillonite in mixed solvent with f_e ≥ 0.95. The desorption data from Figure 3b suggest that sorbent-solvent interactions occurring for Edison soil were due to soil organic matter rather than the soil surface area.

The soil property data for Edison soil in Table 3 show that the specific surface area and pore volume for the smallest soil fraction (> 200 U.S. mesh) were approximately twice as great as the values for the largest soil fraction (20 × 40 U.S. mesh). The specific surface area and pore volume data indicate that there were more sorption–desorption sites available in the > 200 U.S. mesh fraction than in the 20 × 40 U.S. mesh fraction. For an equal initial concentration of sorbed PCP in different fractions of Edison soil, the desorption constants from Figure 3a indicate lower desorption with increasing number of sorption–desorption sites.

Lower desorption of PCP from Edison soil in solvents with f_e ≥ 0.95 was primarily due to the effect of hydrophobic solvents on soil organic matter, a sorbent-solvent interaction. Freeman and Cheung (35) suggested that desorption of HOCs from soils and sediments in solvent was affected by the swelling of the three-dimensional matrix of the nonpolar polymeric organic matter into a gel when organic matter absorbs the solvent. They extracted less HOC from the gel-like organic matter with methanol than with hexane or dichloromethane, attributing higher desorption to the greater swelling of the gel. They suggested maximum swelling (and HOC desorption) depended on the respective polarities of the solvent and the gel.

Solute preference for the solvent, the soil organic matter, or the soil mineral surface depends on competing attractive forces. Major attractive sorption forces other than hydrophobic interaction include hydrogen bonding, van der Waals, London forces, and ion exchange. Boyd (36) suggested hydrogen-bonding between the hydroxyl group of monochlorophenol and the soil surface groups, extending this capability to higher chlorophenols. Choi and Aomine (37) reported adsorption of PCP in the dissociated form onto several alkaline clays and adsorption of neutral PCP to humus. Nose (38) suggested that the electrophilic chlorines on the aromatic ring of PCP induced a partial positive charge on the hydroxyl group of PCP, leading to adsorption of PCP in the neutral form onto soil surfaces with negative charge. The incorporation of chlorophenols into soil organic matter through oxidative coupling of the phenolic hydroxyl group immobilizes chlorophenols in soil. Bollag and Liu (39) showed the copolymerization of PCP into polymeric quinoid and phenolic oligomers using a model humic component. Using radiolabeled 14C-PCP in soil, Weisset et al. (40) recovered 28.6% of the initial radioactivity in soil in the form of unextractable soil residues containing humic and fulvic acids. Besides incorporation into soil organic matter, the sorbed HOCs can become physically trapped inside the organic carbon matrix by clustering, formation of hydrogen and covalent bonds inside the organic matter matrix (41).

**Conclusions**

Mixtures of water and ethanol ranging from 0.59 to 0.95 ethanol fraction in mixed solvent were effective in desorbing PCP from synthetic and natural soils. For all soils, linear analysis of desorption data showed a log-linear increase in desorption with increasing fraction of ethanol in mixed solvent. The desorption of PCP increased exponentially up to 0.79, 0.95, and 0.56 ethanol fractions in mixed solvents for Edison soil, K-10 montmorillonite, and Ottawa sand, respectively. In concentrated ethanol solutions, desorption of PCP from Edison soil was affected by sorbent-solvent interactions due to the effect of hydrophobic solvent on soil organic matter. For Edison soil, desorption increased with increasing soil particle size.

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