ABSTRACT

Sorption of four chlorophenols (CPs) was studied in ten wetland soils with organic C contents between 1 and 44%, which were incubated under aerobic or anaerobic conditions to simulate wetland conditions. The objectives of the study were to (i) determine the influence of aerobic and anaerobic processes on sorption, and (ii) develop sorption models to predict the distribution coefficient based on chemical characteristics of soils and compounds. Aerobic soils consistently had lower pH than anaerobic treatments, which was a function of the amount of oxidizable constituents present in the sample. Depending on the pH, sorption may be limited by the formation of the nonseparable phase, which composed up to 8.6% of the total solid mass (depending on the soil redox status) and had similar distribution coefficients as the separable phase. This study demonstrated that microbial redox processes significantly influenced the soil properties and CP retention characteristics, and should be considered when designing a bioremediation plan for these compounds.

Chlorophenols are common contaminants in soils, sediments, surface waters, and groundwater, largely because of their widespread utilization in the last 50 yr as wood preservatives, and general biocides in industry and agriculture (ATSDR, 1998). Chlorophenols are also by-products of pulp mill effluent chlorination (Paasivirta et al., 1983; Kringska and Lindstrom, 1984), and chloro-aromatic transformations (Mikesell and Boyd, 1985). Pentachlorophenol (PCP) is toxic to all life forms, is commonly found at National Priorities List sites (about 20%), and is classified as a priority pollutant by the USEPA. Chlorophenols are subject to several abiotic and biotic processes, including photodegradation (Wong and Crosby, 1981), volatilization (Pignatello et al., 1983), plant and animal uptake (Weiss et al., 1982; Larsson et al., 1993), and microbial degradation (Laine and Jorgensen, 1997; D’Angelo and Reddy, 2000). A major factor controlling these processes is distribution of the pollutants between the solid phase and dissolved phase (sorption), which is governed by the physical and chemical properties of the solute, the sorbent, and the solvent.

Much research on organic pollutant sorption has demonstrated a strong link between the distribution ratio ($K_d$) and the lipophilicity of hydrophobic organic pollutants, as expressed by its $K_{ow}$, and the fractional amount of organic C of the sorbent ($f_{oc}$):

$$K_p = f_{oc} \times a(K_{ow})^b$$  \[[1]\]

where $a$ and $b$ are empirical constants that differ depending primarily on the nature of the pollutant. The relationship has been very useful for predicting sorption of many hydrophobic organic pollutants by a wide variety of sorbents; on occasion, however, it has been found to be deficient for ionizable organic compounds such as CPs.

In studies on the sorption of CPs in soils and sediments, Schellenburg et al. (1984) and Lagas (1988) found that the model for hydrophobic compounds had limited application because it did not account for the contribution of both the neutral species and the phenolate anion to overall sorption. Shimizu et al. (1992) derived a model that accounted for the contribution of both species to the distribution coefficient of PCP ($pK_a = 4.74$):

$$K_p = K_p^\phi \times \phi + K_p^\circ \times (1 - \phi)$$  \[[2]\]

where $K_p^\phi$ and $K_p^\circ$ are the distribution coefficients, and $\phi$ and $1 - \phi$ are the fractional amounts of the neutral species and phenolate species, respectively. They found that pentachlorophenolate sorption accounted for >90% of overall sorption when the pH was >6, even though the distribution coefficient for the anion ($K_p^\circ$) was up to 60 times lower than for the neutral species ($K_p^\phi$). They also observed that outside the pH range 6 to 8, there were considerable changes in the chemical nature of the sorbent and solvent that decreased the accuracy of the model. They warned that the model should be appropriately amended under these conditions.

In natural ecosystems, microbial breakdown of plant detritus, solubilization of humic substances, erosion, resuspension, and bioturbation events can contribute significant levels of dissolved and suspended organic and inorganic material.
mineral matter to the soil pore water and water column. Many studies have shown that suspended material can influence the retention of a wide range of organic contaminants (Chiou et al., 1986; Galil and Novak, 1995). Chiou et al. (1986) demonstrated that dissolved organic matter from soil and aquatic origins enhanced the solubility of relatively insoluble compounds (PCB and DDT). Galil and Novak (1995) also showed enhanced water solubility of more water-soluble compounds (PCP and 4 CP) by mineral and organic colloidal materials that were suspended in the dissolved phase.

Realizing the potential importance of the nonseparable, or so-called “third phase,” on the apparent water solubility and sorption of hydrophobic organic compounds, Gschwend and Wu (1985) and Koelmans and Lijklema (1992) proposed three-phase sorption models that accounted for sorption behavior differences by the separable and nonseparable phases:

$$K_{D}^{true} = \alpha \times K_{D}^{N} + (1 - \alpha) \times K_{D}^{S}$$  \[3\]

where $K_{D}^{true}$, $K_{D}^{N}$, and $K_{D}^{S}$ are the respective distribution coefficients of the soil, nonseparable phase and separable phase, and $\alpha$ and $(1 - \alpha)$ are respective mass fractions of soil solids in the nonseparable phase and separable phase. In both studies, the apparent water solubility of hydrophobic organic compounds was enhanced, and the observed sorption was decreased in samples with high $\alpha$ and $K_{D}^{S}$ values. Gschwend and Wu (1985) concluded from these results that a three-phase approach should be used to evaluate sorption in the “real world” because of the likely implications on pollutant transport, bioaccumulation, and photo- and biodegradation.

Many environments that are contaminated with organic pollutants are characterized by spatial or temporal gradients in redox processes, which are a consequence of microbial consumption of different types of electron acceptors (e.g., $O_3$, $NO_3^-$, $Fe^{3+}$, $SO_4^{2-}$, and $CO_2$) during energy generation. Microbial redox processes can have a profound effect on many chemical properties of the soil-water environment (e.g., redox potential, solution composition), so it is expected that redox processes could influence the fate of organic pollutants. Several studies demonstrated that the type of microbial redox process influenced whether CPs are biodegraded or not (Mikesell and Boyd, 1985; D’Angelo and Reddy, 2000).

Unfortunately, there is limited or contradictory information about the effect of microbial redox processes on other organic fate processes.

Hunchak-Kariouk et al. (1997) observed that sorption of 2,2′,4,4′-tetrachlorobiphenyl by dissolved organic matter was increased several-fold after changing from anoxic to oxic conditions. Pederson et al. (1999) found the opposite results using the same compound but different sources of dissolved organic matter. The studies came to opposite conclusions regarding the mobility and bioavailability of tetrachlorobiphenyl under the different redox conditions.

The objectives of the study were to determine the influence of aerobic and anaerobic processes on CP sorption in a spectrum of wetland soils and to develop models to help predict sorption CPs based on the sorbent, dissolved phase, and solute chemical characteristics.

### MATERIALS AND METHODS

#### Soil Collection and Establishment of Aerobic and Anaerobic Conditions

Soils used in this study were collected from the surface depth (0–15 cm) of ten different wetlands in the USA (Table 1). Soils were sieved (0.5-cm mesh) to remove large plant roots and stones, and mixed with water collected from the sites.

Soil/water mixtures were pre-equilibrated under well-mixed conditions to establish either aerobic or anaerobic conditions and to avoid development of redox gradients in the samples. Soil/water mixtures (5-mL total containing between 0.13 and 1.1 g dry soil) and deionized, distilled water (15 mL) were pre-equilibrated in glass anaerobic culture tubes (27 mL) (Bellco Glass, Inc.; Vineland, NJ) sealed with Teflon-lined rubber stoppers/Al crimps (Wheaton, Millville, NJ). Samples were made either oxygenated by shaking with air (aerobic treatments) or deoxygenated by purging with $N_2$ (anaerobic treatments). Tubes were purged weekly with air or $O_2$–free $N_2$ and equilibrated horizontally on an orbital shaker (150 rpm and 28°C) for up to 4 mo. During this period, oxygen in the headspace of aerobic treatments was always $>$13 kPa and was not detected in anaerobic treatments, and methane in the headspace of anaerobic treatments accumulated to $>1.2$ kPa and was not detected in aerobic treatments.

#### Sorption Isotherms

After the pre-equilibration period, individual tubes were spiked with five levels (1, 10, 25, 50, 75 μL) of four CP conge-

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**Table 1. Origin, classification, and description of organic and mineral wetland soils used in the study.**

<table>
<thead>
<tr>
<th>State</th>
<th>Soil name (symbol)</th>
<th>Taxonomic class</th>
<th>Organic C %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic soils</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Michigan</td>
<td>Houghton Lake peat–impacted by domestic waste (HLPI)</td>
<td>euc, mesic Typic Haplosaprists</td>
<td>38.5</td>
</tr>
<tr>
<td>Michigan</td>
<td>Houghton Lake peat–unimpacted by domestic waste (HLPU)</td>
<td>euc, mesic Typic Haplosaprists</td>
<td>43.1</td>
</tr>
<tr>
<td>Florida</td>
<td>Everglades–impacted by agricultural runoff (W2)</td>
<td>euc, hyperthermic Typic Haplohemists</td>
<td>43.6</td>
</tr>
<tr>
<td>Florida</td>
<td>Everglades–unimpacted by agricultural runoff (W8)</td>
<td>euc, hyperthermic Typic Haplohemists</td>
<td>44.1</td>
</tr>
<tr>
<td>Louisiana</td>
<td>Salt marsh (LSM)</td>
<td>euc, hyperthermic Typic Haplohemists</td>
<td>16.5</td>
</tr>
<tr>
<td>North Carolina</td>
<td>Belhaven muck (NCB)</td>
<td>loamy, mixed, dysic, thermic Terric Haplosaprists</td>
<td>21.8</td>
</tr>
<tr>
<td>Florida</td>
<td>Lake Apopka muck (LAAF)</td>
<td>euc, hyperthermic Typic Medifibrists</td>
<td>10.8</td>
</tr>
<tr>
<td>Mineral soils</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alabama</td>
<td>Talladega (TAL)</td>
<td>loamy-skeletal, mixed, Lithic-Rupta-Entic, Hapludult</td>
<td>8.5</td>
</tr>
<tr>
<td>North Dakota</td>
<td>Parnell (PPP)</td>
<td>fine, smectitic, frigid Vertic Argiaquolls</td>
<td>4.5</td>
</tr>
<tr>
<td>Louisiana</td>
<td>Crowley (CR)</td>
<td>fine, smectitic, hyperthermic Typic Albaquolls</td>
<td>0.9</td>
</tr>
</tbody>
</table>
ners (PCP, 2,3,4,5-tetrachlorophenol [TeCP], 3,4,5-trichlorophenol [TCP], and 3,5-dichlorophenol [DCP]) from a stock solution (1000 mg L$^{-1}$ of each CP in 0.05 M NaOH). Spike solutions were added to closed tubes using a hypodermic syringe, to avoid changing the redox status established during the pre-equilibration period. Initial dissolved CP concentrations ranged between 0.05 and 3.75 mg L$^{-1}$. All test levels were conducted as a single repetition except for the 75-µL level, which was conducted in triplicate to estimate the degree of analytical variation (coefficient of variation in CP recovery was <8%). Tubes were shaken horizontally on a reciprocal shaker for 24 h to achieve equilibrium conditions (Lee et al., 1990) and to avoid potential losses through biotransformations and other processes (D’Angelo and Reddy, 2000).

Individual dissolved, non-separable, and separable phases were obtained by a cascading centrifugal fractionation technique similar to that described by Perret et al. (1994). The separable phase was isolated from the other two phases by low force centrifugation of the suspension (100 × g for 15 min). The supernatant from this step was transferred to a Teflon centrifuge tube and centrifuged (10 000 × g for 30 min) to isolate the dissolved phase from the precipitated non-separable phase. Particle-size ranges of the separable, non-separable, and dissolved phases using this approach were >2.6 µm, between 0.2 and 2.6, and <0.2 µm respectively, as determined from Stoke’s Law and assuming particle densities were likely to be encountered in many different types between 1030 and 2500 kg m$^{-3}$ (Tchobanoglous and Schroeder, 1985).

Chlorophenols were extracted from each phase, prepared as acetyl derivatives, and analyzed by gas chromatography as described by Nicholsen et al. (1992). Briefly, CPs in the dissolved phase (2-4 mL) or the nonseparable phase were reacted with 0.5 M K$_2$CO$_3$ (10 mL), acetic anhydride (2 mL), and hexane (1 mL), and shaken every 20 min for 2. The aqueous and hexane layers were allowed to separate for 1 h. The hexane layer containing CP derivatives was transferred with a disposable glass pipette to an amber glass vial with Teflon-lined cap for later analysis. Chlorophenols in the separable phase were first extracted overnight with acetonitrile (1:20, soil/solution ratio), followed by centrifugation (400 × g for 5 min). Acetonitrile extracts (1 or 2 mL) were derivitized as described above. Extraction efficiency was >95% using this approach.

The hexane phase was analyzed using a Shimadzu Model 14A gas chromatograph (Shimadzu, Columbia, MD) with $^{60}$Ni electron capture detector and autosampler, and equipped with SPB-50 column (30 m by 0.25 mm with 0.25-µm phase thickness; Supelco, Bellefonte, PA). Injector and detector temperatures were 175 and 300°C respectively, and the following oven temperature program was used to separate different CPs: 80°C held for 5 min, ramp at 5°C min$^{-1}$ to 200°C and held for 5 min.

Distribution coefficients for each CP were obtained by averaging the ratio of concentrations in two phases determined at the five amendment levels. The increase in apparent water solubility of CPs by the nonseparable phase was calculated by taking the ratio of the mass of chemical in the nonseparable phase divided by that in the dissolved phase and multiplying by 100 to convert to a percentage. Statistical differences between treatments were determined by Student’s t test at the p = 0.05 level using Excel 97 (Microsoft Corp. Redmond, WA).

Physical and Chemical Analyses

Several soil constituents were measured in the reaction vessels based on whether they were expected to govern CP sorption or indicated the type of redox processes in the samples. The oven-dry mass (60°C) and total organic C content (Dohrman DC 190, Cincinnati, OH; or Carla Erba Model 1500, ThermoQuest, Austin, TX) were determined on the dissolved, dissolved + nonseparable, and separable fractions, with amounts in the nonseparable fraction determined by difference. The H$^+$ ion concentration of the dissolved phase was determined using a pH electrode and meter (Fisher Accumet pH Meter 915; Pittsburgh, PA; Orion Sureflow Ross Semimicroelectrode; Beverly, MA). Ionic strength was determined from electrical conductivity (YSI Conductance Meter 35 and YSI Conductivity Electrode 3417; Yellow Springs, OH) (Griffin and Jurinak (1973). Dissolved NH$_3$ was determined by the salicylate-nitroprusside technique using an Autoanalyzer (Terrytown, NY); SO$_4^{2-}$ and NO$_3^-$ by ion chromatography ( Dionex 4500i Ion Chromatograph; Sunnyvale, CA), and Fe$^{2+}$ by ferrozine-hepes colorimetric method (Lovley and Phillips, 1987). Oxygen and methane in the headspace were determined by gas chromatography with thermal conductivity for oxygen and flame ionization for methane (D’Angelo and Reddy, 1999).

RESULTS AND DISCUSSION

Aerobic and Anaerobic Treatment Effects on Soil Properties

The soils used in this study had a wide range in organic C and other physical and chemical characteristics that were likely to be encountered in many different types of wetland ecosystems in the eastern USA (Tables 1 and 2). Soil pH values ranged between 3.9 and 7.5, and were decreased by between 0.1 and 2.7 units in the aerobic treatments compared with anaerobic treatments. This was expected because of the well-known effects of redox reactions on pH. A comparison of the solution composition between aerobic and anaerobic treatments in Table 2 clearly showed that several redox reactions took place in the samples, including nitrification, and oxidation of Fe$^{2+}$ and H$_2$S. Assuming a stoichiometric amount of H$^+$ was generated from the oxidation of these electron donors with O$_2$ as electron acceptor, about 79% of the variability in the pH change could be explained by these three redox reactions (Fig. 1). Thus, samples with high amounts of readily oxidizable material, such as in Louisiana salt marsh (LSM), Houghton Lake Peat–impacted (HLPI), Talladega (TAL) soils (see Table 1 for soil descriptions), would generally be expected to have the greatest change in pH under different redox conditions. In contrast, Pederson et al. (1999) observed the opposite effect of aeration on pH in estuarine samples, which they explained was caused by ferric hydroxide precipitation and H$_2$S stripping. While these reactions may have occurred in the present study as well, evidently they were not sufficient enough to counteract more important H$^+$ generating redox processes in the wetland samples.

Soil organic C contents ranged between 0.9 and 44%. Soils with higher organic C content had proportionately higher dissolved organic C (DOC), however the amount of DOC was also influenced by the pre-equilibration conditions in most of the samples. The anaerobic treatments typically had greater amounts of DOC than aerobic treatments for all samples except for HLPI in which there was no difference. Several factors likely contributed to increased DOC in anaerobic treatments. First, it was likely that less organic matter was decomposed
under anaerobic conditions, allowing more DOC to accumulate. Second, it was likely that greater amounts of organic matter were solubilized at the higher pH level of the anaerobic treatments. Additionally, the formation of ferric hydroxides is known to coprecipitate DOC in aerated soil samples (Pedersen et al., 1999; Hunchak-Kariouk et al., 1997). However even in the TAL sample undergoing the most ferric hydroxide formation, DOC was still higher under anaerobic conditions indicating that the first two factors were probably more important in this investigation.

Ionic strength ranged between 1 and 37 mmol L$^{-1}$, and as expected, it was much greater for the salt marsh soil (LSM) compared with freshwater samples (Table 2). Ionic strength was increased in the aerobic treatments for all soils except for Crowley (CR), Houghton Lake Peak–unimpacted (HLPU), and Parnell (PPP) soils, in no significant difference between redox treatments. In four samples, there was a statistically significant difference between aerobic and anaerobic treatments at the 95% confidence interval.

Table 2. Influence of pre-equilibration conditions on selected soil properties. Samples were incubated under aerobic (aer) and anaerobic (an) conditions. Each value represents the mean of three replications.

<table>
<thead>
<tr>
<th>Soil†</th>
<th>pH aer</th>
<th>pH an</th>
<th>NH$_4^+$ aer</th>
<th>NH$_4^+$ an</th>
<th>NO$_3^-$ aer</th>
<th>NO$_3^-$ an</th>
<th>Aqueous phase</th>
<th>Fe$^{3+}$ aer</th>
<th>Fe$^{3+}$ an</th>
<th>Organic C aer</th>
<th>Organic C an</th>
<th>Ionic strength‡</th>
<th>Mass fraction of soil (c) aer</th>
<th>Organic C fraction§</th>
<th>Mass fraction of soil (c) an</th>
<th>Organic C fraction§</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPI</td>
<td>5.6$^*$</td>
<td>6.6</td>
<td>1.7$^*$</td>
<td>111</td>
<td>44$^*$</td>
<td>0</td>
<td>142$^*$</td>
<td>0.2</td>
<td>0.8$^*$</td>
<td>10</td>
<td>86</td>
<td>92</td>
<td>3.9$^*$</td>
<td>4.3</td>
<td>0.016$^*$</td>
<td>0.036</td>
</tr>
<tr>
<td>HLPU</td>
<td>5.4$^*$</td>
<td>5.8</td>
<td>8.6$^*$</td>
<td>19</td>
<td>2.4$^*$</td>
<td>0</td>
<td>1.9$^*$</td>
<td>0</td>
<td>2.2$^*$</td>
<td>5.0</td>
<td>69$^*$</td>
<td>109</td>
<td>1.4</td>
<td>1.2</td>
<td>0.025$^*$</td>
<td>0.033</td>
</tr>
<tr>
<td>W2</td>
<td>6.5$^*$</td>
<td>7.2</td>
<td>0.9$^*$</td>
<td>46</td>
<td>35$^*$</td>
<td>0</td>
<td>28$^*$</td>
<td>0</td>
<td>0.3</td>
<td>0.4</td>
<td>216$^*$</td>
<td>253</td>
<td>6.8$^*$</td>
<td>5.7</td>
<td>0.012$^*$</td>
<td>0.020</td>
</tr>
<tr>
<td>W8</td>
<td>6.5$^*$</td>
<td>7.0</td>
<td>0.5$^*$</td>
<td>37</td>
<td>32$^*$</td>
<td>0</td>
<td>61$^*$</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>129$^*$</td>
<td>137</td>
<td>7.4$^*$</td>
<td>6.5</td>
<td>0$^*$</td>
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<td>6.6</td>
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<td>0</td>
<td>156$^*$</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>26$^*$</td>
<td>85</td>
<td>37$^*$</td>
<td>31</td>
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<tr>
<td>NCB</td>
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<td>5.8</td>
<td>0.1$^*$</td>
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<td>11$^*$</td>
<td>0</td>
<td>0.8$^*$</td>
<td>0.1</td>
<td>0.7$^*$</td>
<td>2.1</td>
<td>24$^*$</td>
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<td>0.9</td>
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<td>0.044</td>
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<tr>
<td>LAAF</td>
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<td>7.5</td>
<td>0.1$^*$</td>
<td>8.8</td>
<td>8.7$^*$</td>
<td>0</td>
<td>1.6$^*$</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>34$^*$</td>
<td>45</td>
<td>6.4$^*$</td>
<td>5.6</td>
<td>0.005$^*$</td>
<td>0.005</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil†</th>
<th>pH aer</th>
<th>pH an</th>
<th>NH$_4^+$ aer</th>
<th>NH$_4^+$ an</th>
<th>NO$_3^-$ aer</th>
<th>NO$_3^-$ an</th>
<th>Aqueous phase</th>
<th>Fe$^{3+}$ aer</th>
<th>Fe$^{3+}$ an</th>
<th>Organic C aer</th>
<th>Organic C an</th>
<th>Ionic strength‡</th>
<th>Mass fraction of soil (c) aer</th>
<th>Organic C fraction§</th>
<th>Mass fraction of soil (c) an</th>
<th>Organic C fraction§</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAL</td>
<td>4.1$^*$</td>
<td>5.6</td>
<td>0.7$^*$</td>
<td>16.2</td>
<td>14$^*$</td>
<td>0</td>
<td>2.8$^*$</td>
<td>0</td>
<td>0$^*$</td>
<td>19</td>
<td>18$^*$</td>
<td>49</td>
<td>1.9$^*$</td>
<td>1.2</td>
<td>0.011$^*$</td>
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</tr>
<tr>
<td>PPP</td>
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<td>6.0</td>
<td>0.2$^*$</td>
<td>9.4</td>
<td>9.3$^*$</td>
<td>0</td>
<td>0.9$^*$</td>
<td>0</td>
<td>0.6</td>
<td>0.4</td>
<td>4.7$^*$</td>
<td>23</td>
<td>1.4</td>
<td>1.5</td>
<td>0.046$^*$</td>
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</tr>
<tr>
<td>CR</td>
<td>7.4$^*$</td>
<td>7.5</td>
<td>0.1$^*$</td>
<td>4.2</td>
<td>4.4$^*$</td>
<td>0</td>
<td>0.6$^*$</td>
<td>0</td>
<td>0.1</td>
<td>3.8</td>
<td>8.4</td>
<td>16$^*$</td>
<td>2.4$^*$</td>
<td>2.4</td>
<td>0.043$^*$</td>
<td>0.096</td>
</tr>
</tbody>
</table>

† HLPI, Houghton Lake peat–impacted by domestic waste; HLPU, Houghton Lake peat–unimpacted by domestic waste; W2, Everglades–impacted by agricultural runoff; W8, Everglades–unimpacted by agricultural runoff; LSM, salt marsh; NCB, Belhaven muck; LAAF, Lake Apopka muck; TAL, Talladega; PPP, Parnell; CR, Crowley.
‡ Determined from the temperature-corrected electrical conductivity and relationship of Griffin and Jurinak (1973) (Ionic strength (mmol L$^{-1}$) = 0.013 × electrical conductivity (μmhos cm$^{-1}$)).
§ Carbon content of the nonseparable fraction was not significantly different between aerobic (aer) and anaerobic (an) samples.

Fig. 1. Effect of redox processes on pH changes in ten wetland soils. The pH generated from redox processes (mmol H$^+$ kg$^{-1}$) was greater in aerobic treatments, allowing more DOC to accumulate. Second, it was likely that greater amounts of organic matter were solubilized at the higher pH level of the anaerobic treatments. Additionally, the formation of ferric hydroxides is known to coprecipitate DOC in aerated soil samples. Ionic strength at aerobic conditions compared with anaerobic conditions, and differences tended to be greater for PCP and TeCP compared with TCP and DCP. Probably the main reason for this was the effect of redox on pH, which in turn governed the proportion of molecules in the neutral

Aerobic and Anaerobic Treatment Effects on Distribution Coefficients

The sorption isotherms for the various CP congeners generally conformed to a linear model in the concentration range of the study. Example isotherms determined under aerobic and anaerobic conditions in the LSM soil are provided in Fig. 2. Examination of Fig. 2 and Table 3 showed that distribution coefficients were considerably increased in samples pre-equilibrated under aerobic conditions compared with anaerobic conditions, and differences tended to be greater for PCP and TeCP compared with TCP and DCP. Probably the main reason for this was the effect of redox on pH, which in turn governed the proportion of molecules in the neutral
and anion forms. Since the different CP forms have significantly different distribution coefficients, pH plays a major role in governing sorption (Schellenburg et al., 1984; Lagas, 1988). Redox and pH effects were most evident for PCP (pKₐ = 4.74) and TeCP (pKₐ = 6.64) probably because pH changes bracketed the contaminant pKₐ values, thus causing one or the other species to dominate in the aerobic or anaerobic treatments. Thus, for compounds whose pKₐ is the environmental pH range of 4 to 7.5, it will usually be necessary to consider sorption by both neutral and ionic forms when estimating the overall retention, using Eq. [2] or similar relationship.

**Organic Carbon Effects on Distribution Coefficients**

Several investigations have concluded that pH and organic C content of the sorbent are the main parameters that govern sorption of CP compounds. A plot of $K_{oc} (K_{oc} = K_p / K_a$ obtained from Tables 1 and 3, respectively) and pH (Table 2) tended to confirm these results (Fig. 3). Irrespective of whether the samples were in an aerobic or anaerobic state, they all tended to follow the same relationship for a given CP compound. Thus it appears from Fig. 3 that it is possible to accurately predict (within a factor of 2) the distribution coefficient of a particular CP congener from the pH and organic C content of the sorbent in the pH range of 4 to 7.5.

It was desired to determine whether $K_{oc}$ values were dependent on the lipophilicity of the compounds, and whether a relationship like Eq. [1] could be derived for the CP congeners in this investigation. Such a relationship may prove useful for estimating distribution coefficients for many other CP congeners under a wide range of pH and other conditions.

To investigate this possibility, a least squares fit was made between the log $K_{oc}$ (and log $K_p$) data and published log $K_{ow}$ of the compounds (Fig. 4). The log $K_{oc}$

**Table 3. Effect of aerobic (aer) and anaerobic (an) conditions on the distribution coefficients ($K_p$) of four chlorophenols† in 10 wetland soils.**

<table>
<thead>
<tr>
<th>Soil‡</th>
<th>PCP</th>
<th>TeCP</th>
<th>TCP</th>
<th>DCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLPi</td>
<td>889*</td>
<td>107</td>
<td>1727*</td>
<td>362</td>
</tr>
<tr>
<td>HLPu</td>
<td>591*</td>
<td>344</td>
<td>1777*</td>
<td>1365</td>
</tr>
<tr>
<td>W2</td>
<td>236*</td>
<td>111</td>
<td>648*</td>
<td>205</td>
</tr>
<tr>
<td>W8</td>
<td>222*</td>
<td>136</td>
<td>601*</td>
<td>306</td>
</tr>
<tr>
<td>LSM</td>
<td>1675*</td>
<td>81</td>
<td>823*</td>
<td>276</td>
</tr>
<tr>
<td>NCB</td>
<td>447*</td>
<td>352</td>
<td>823*</td>
<td>918</td>
</tr>
<tr>
<td>LAAF</td>
<td>66</td>
<td>49</td>
<td>146*</td>
<td>84</td>
</tr>
<tr>
<td>TAL</td>
<td>452*</td>
<td>49</td>
<td>3336*</td>
<td>202</td>
</tr>
<tr>
<td>PPP</td>
<td>111*</td>
<td>33</td>
<td>235*</td>
<td>160</td>
</tr>
<tr>
<td>CR</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>&amp; 3</td>
<td>4</td>
<td>8</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>&amp; 3</td>
<td>4</td>
<td>8</td>
<td>5</td>
<td>11</td>
</tr>
</tbody>
</table>

---

* There was a statistically significant difference between aerobic and anaerobic treatments at the 95% confidence interval.  
† PCP, pentachlorophenol; TeCP, 2,3,4,5-tetrachlorophenol; TCP, 3,4,5-trichlorophenol; DCP, 3,5-dichlorophenol.  
‡ HLPi, Houghton Lake peat-impacted by domestic waste; HLPu, Houghton Lake peat-unimpacted by domestic waste; W2, Everglades-impacted by agricultural runoff; W8, Everglades-impacted by agricultural runoff; LSM, salt marsh; NCB, Belhaven muck; LAAF, Lake Apopka muck; TAL, Talladega; PPP, Parnell; CR, Crowley.
values for PCP<sub>o</sub> (3.80), TeCP<sub>o</sub> (3.44), TCP<sub>o</sub> (2.98), and DCP<sub>o</sub> (2.69) were determined by substituting a pH value of one unit below the chemical pK<sub>a</sub> value into the appropriate K<sub>oc</sub>–pH relationship in Fig. 3, at which point the neutral CP makes up 90% of the total CP pool (i.e., φ = 0.90). The log K<sub>oc</sub> values for PCP<sup>−</sup> (2.69) and TeCP<sup>−</sup> (2.51) were determined by substituting a pH value of two units above the pK<sub>a</sub>, at which point the anionic form makes up 99% of total CP pool. The K<sub>oc</sub> values for TCP<sup>−</sup> and DCP<sup>−</sup> could not be determined because their pK<sub>a</sub> values fell above the experimental pH range. The K<sub>ow</sub> values were 5.24 for PCP<sub>o</sub>, 4.87 for TeCP<sub>o</sub>, 4.11 for TCP<sub>o</sub> (Schellenburg et al., 1984), 3.66 for DCP<sub>o</sub> (IPCS/CEC, 1993), and 3.16 for PCP− (Klaus et al., 1982).

There was a highly significant relationship (r<sup>2</sup> = 0.96) between K<sub>oc</sub> and K<sub>ow</sub> of the CP congeners, which suggested that hydrophobic bonding was the dominant sorption mechanism for the soils in this study (Fig. 4). Even data for PCP<sup>−</sup> followed the same trend as congeners in the neutral form. While specific interactions between pentachlorophenolate and surface functional groups of soil may occur at elevated pH (DiVincenzo and Sparks, 2001), evidently they were masked by hydrophobic bonding in the present study. It is likely that alternative sorption mechanisms may dominate in certain situations, such as organic-poor samples (<1% organic C), elevated pH (>pK<sub>a</sub>), and ionic strength (>0.1 M) (Westall et al., 1985). This combination of conditions is uncommon in most wetland environments.

A strong K<sub>oc</sub>–K<sub>ow</sub> relationship indicated that distribution coefficients for other CP compounds could be determined from its K<sub>ow</sub> and from the organic C content and pH of the sorbent:

\[
\log K_{oc}^{\text{eq}} = 0.64x + 0.31 \quad r^2 = 0.96 \quad [4]
\]

\[
K_{oc} = \phi \times K_{oc}^{\text{eq}} + (1 - \phi) \times K_{oc}^{\text{eq}} \quad [5]
\]

At present, one of the main limitations in applying Eq. [4] is finding experimental K<sub>ow</sub> values for the various anionic CP congeners in the literature. These values are necessary to predict the distribution coefficient for CP congeners whose pK<sub>a</sub> values are in the range of soil pH.
at which point the anionic form contributes significantly to sorption (i.e., the $1 - \phi$ term in Eq. [5] is large). Chlorophenol congeners in this category include mostly other tetra- and trichlorophenols. For the less chlorinated congeners, the anion contribution can usually be neglected, such as observed for DCP in Fig. 3.

Another potential pitfall in predicting distribution coefficients of CP congeners from $K_{oc}$ is the great deal of variability in $K_{oc}$-water relationships for CP congeners determined in various investigations (Fig. 4). For example, the $K_{oc}$ values obtained by Lagas (1988) and Schellenburg et al. (1984) were considerably higher than those measured in the present study or by Bellin et al. (1990). Variations are likely attributed to differences in the chemical composition of sorbents, which were obtained from diverse sources, including aquatic, terrestrial, and wetland environments. Clearly an improvement needs to be made in the ability to characterize the chemical nature of the sorbents to account for the differences in sorption behavior.

Aerobic and Anaerobic Treatment Effects on Apparent Water Solubility Enhancement

The distribution coefficients in the previous discussion were determined by combining the amount of contaminants in the separable and nonseparable phases. However, in “real world” environments, a significant fraction of the contaminants may be associated with the nonseparable phase, especially in organic matter-enriched wetland soils that easily become suspended in the water column and soil pore water by gas ebullition, bioturbation, water currents, etc. Therefore, it was deemed necessary to determine the potential of the nonseparable phase to increase the apparent water solubility of CP congeners in the wetland soils. Water solubility enhancement by the nonseparable phase ranged between 0 and 247% (Table 4), indicating that the potential was large for mobilization of contaminants in association with the nonseparable phase.

Water solubility enhancement by the nonseparable phase was not influenced by redox treatment in half of the samples; however there was an equal split in the remaining samples between those with higher solubility in the aerobic or anaerobic treatments. Two opposing effects of redox conditions probably explain these results. First, distribution coefficients were typically greater in the aerobic treatments, which explain why higher water solubility enhancements were observed in some aerobic soils. Distribution coefficients of the nonseparable phase were similar to those of the separable phase under both redox conditions (data not shown). The second effect of redox treatment was on the formation of the nonseparable phase, which was either higher in the anaerobic treatments or not significantly different between treatments (Table 2). These results explain why some anaerobic treatments demonstrated greater water solubility enhancements by the nonseparable phase. While the experimental conditions may not match reality with respect to soil/water ratio or mixing, there seems to be a large potential for the formation of nonseparable phase in the wetland samples, governed by complex set of factors that could affect the apparent water solubility and mobility of contaminants in the wetland environment.

### CONCLUSIONS

Sorption experiments demonstrated that the redox status of soils influenced the distribution coefficients and apparent water solubilities of several CP congeners in wetland soils. The main role of redox on distribution coefficients was its influence on $pH$, in which the oxidation of reduced constituents (e.g., organic matter, $H_2S$, $NH_4^+$, $Fe^{2+}$) decreased $pH$ and led to an increased conversion of $CP$ to the neutral form. Distribution coefficients of neutral $CP^+$ and $TeCP^+$ were about 25 times greater than ionic forms. In the $pH$ range of most samples, however, both species contributed significantly to overall sorption. Isotherms for all CP congeners conformed to a linear model and distribution coefficients were strongly related to $K_{oc}$, which suggested that hydrophobic binding was the dominant sorption mechanism in the wetland samples. A model was derived to aid in estimating the distribution coefficient from the $K_{oc}$ and $pK_a$ of the CP, and the $pH$ and soil organic C content of the sorbent. The formation of a nonseparable phase in the soil suspensions considerably increased the apparent water solubility of CP congeners in most samples. However, there was no rule regarding the influence of redox processes on water solubility enhancements because of opposing effects on the formation and partitioning processes. It can be concluded from this study that redox conditions appreciably influenced the sorption and the potential mobility of CPs that should be taken into consideration when predicting the fate of these compounds in wetland environments.
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