

## ENVIRONMENTAL FATE

### Executive Summary

Pentachlorophenol (PCP) is stable (half life > 30 days) in sterile aqueous medium between pHs 5-9. PCP, however, photolytically degrades in sterile water (pHs 5-7) with a half life of 13-20 minutes. PCP is moderately mobile in sandy loam soil, with low organic carbon ( $K_d = 5.7$ ), and slightly mobile in sandy loam or silt loam soils with high organic carbon ( $K_d = 2.0$ ). Microbial metabolism appears as the major degradation route for PCP under aerobic and anaerobic soils and sediments with an observed half life of 63 days and 30-60 days respectively. It is moderately persistent in aqueous systems. PCP has a high Octanol/Water Coefficient ( $\log K_{ow} = 4.9-5.1$ ) and as such it bioaccumulates in bluegill fish. It, however, has been shown to depurate within 14 days. It is likely to bioaccumulate in aquatic organisms. No biomagnification of PCP in the food chain has been reported. A laboratory study on the leaching of PCP from pressure treated wood (0.50 lbs/ft<sup>3</sup>), it was shown that leaching increased with increasing pHs at a rate of 5.7, 36.2 and 65.5 ppm at pH 5, 7 and 9 respectively. The leaching rate decreased with high pH (0.1M HCl), the only 1.73 ppm PCP leached. A field study (EPRI) showed that concentration of leachate (PCP) decreased as the distance (maximum between 3 to 8 inches from the pole) from the pressure treated poles increased. Generally higher concentration of PCP was found on the surface soils, no general trend was observed with subsurface soils. Because of PCP has a tendency to be mobile in textured soils, a ground water contamination is possible in areas with textured surface soils.

### **Environmental Fate and Transport of Pentachlorophenol**

US EPA has conducted an environmental fate assessment based on the EPA database, submitted studies and published literature search.

#### Environmental Fate Assessment

a. Abiotic:\_\_\_\_\_

Hydrolytic study conducted under sterile conditions at pHs 5,7, and 9 showed that Pentachlorophenol is stable for 30 days and beyond. Similar results were observed for the buffer medium also. The ambient temperature was 25 ° C. Aqueous photolytic study showed that at the same pH s of 5, 7 and 9 and also in the buffer sterile aqueous medium, PCP is photolytically unstable with an observed half life between 13-20 minutes. Dichloromaleic anhydride was the major photolytic degradate at all pHs while tetrachlororescorcinol was a major degradate at pH 5 and becomes a minor degradate at pH 9. Tetrachlorohydroquinone and tetrachlorocatechol were minor degradates at pH 5, and 7.

b. Biotic Degradation

A guideline study showed that PCP metabolizes in aerobic soil (sandy loam) with a half life of less than 63 days (<sup>14</sup>C tagged PCP was less than 50% within 14 days). Published literature studies also showed that aerobic soil metabolism is rapid, with a half life of less than a month. Under aerobic aquatic conditions, PCP degraded with half life of 14 days while under anaerobic aquatic conditions, the observed half life of PCP degradation was 30-60 days.

PCP appears moderately persistent under aerobic and anaerobic soil/aquatic conditions.

Microbial degradation process appears as the major route under aerobic soil and aerobic aquatic/anaerobic aquatic conditions for PCP.

c. Mobility

PCP is slightly mobile in sandy loam (Georgia, Nebraska) with low % of organic carbon, while in the sandy loam soil with high % organic carbon (California), it became moderately mobile. PCP is not mobile with clay loam soil, even with high % organic carbon (Ohio).

Ground water contamination may likely occur when soil texture is sandy loam type.

d. Bioaccumulation

The high  $K_{ow}$  of 5.1 indicates that PCP should be bioaccumulative in aquatic organisms and data for bluegill fish shows that PCP is highly bioaccumulative in edible, non-edible and whole fish tissues. It degrades by day 14. PCP is likely to bioaccumulate in aquatic organisms.

e. Special Leaching or Aqueous Availability Study

PCP leaches out from the pressure treated wood (0.50 lbs/ft<sup>3</sup>) initially and is a function of pH. Leaching rate is higher at higher pH (low acidity) and lower at low pH (high acidity). Published literature studies show that leached PCP stays on the surface soil. Data on PCP concentration for subsurface soils is not clear. Maximum concentration of PCP is found around 3-8 inches from the PCP pressure treated utility pole.

Surface soil contamination is likely to occur around the PCP treated utility poles.

The environmental fate of PCP as addressed here is based mainly on the laboratory behavior of technical grade PCP (88.9% active ingredient) or purified PCP ( $\geq 98\%$  active ingredient) and in some cases, field studies based on published literature. It is noted that, technical grade PCP or PCP formulations contain impurities or microcontaminants including hexa-, hepta- and octachlorodibenzo-*p*-dioxins (polychlorinated dibenzo-*p*-dioxins; PCDDs) in varying amounts. The highly toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) has never been found in technical

grade PCP. Other impurities which have been found in technical grade PCP include chlorophenols, polychlorinated chlorodibenzofurans (PCDFs), phenoxyphenols, hexachlorobenzene, chlorodiphenyl ethers and hydroxychlorodiphenyl ethers.

The guideline studies did not address the environmental fate of the microcontaminants. Chlorinated dibenzodioxins have been reported to be extremely persistent in soil. While chlorinated dibenzodioxins are not reviewed here with PCP, it is noted that they have extremely low water solubility, have high adsorption to soils and high solubility in organic matter; in fish, the compounds have very high bioconcentration factors and are not rapidly depurated.

## **APPENDIX**

### **PENTACHLOROPHENOL ENVIRONMENTAL FATE SCIENCE CHAPTER**

**The following studies from EPA database were reviewed for the development of this science chapter.**

#### **Abiotic Degradation:**

##### **Hydrolysis (161-1) 42481101 and the Registrant's Response to Comments (Dated 8/16/94)**

Pentachlorophenol was hydrolytically stable in sterile aqueous pH 5, 7 and 9 buffer solutions incubated at 25°C for up to 30 days.

##### **Photodegradation in Water (161-2) 42855401**

Pentachlorophenol photodegraded rapidly with half-lives of 13-20 minutes in sterile aqueous pH 5, 7 and 9 buffer solutions irradiated with natural sunlight at 42°N (in MA) on different days and at different times of the day in August/September, and was stable in dark controls under similar conditions; air temperatures during the studies ranged from approximately 8 to 36°C.

Dichloromaleic anhydride (more likely present as dichloromaleic acid) was reported to be the major degradate at all pHs, and reached respective maximums of 64.5-67.5% (80 minutes post-treatment), 100% (110 minutes), and 98.9% (90 minutes) of the applied radioactivity at pH 5, pH 7 and pH 9. Tetrachlororesorcinol was a major degradate at pH 5 (maximum of 34.8-36.1%) and pH 7 (maximum of 15.7%) and was a minor degradate at pH 9. Tetrachlorohydroquinone and tetrachlorocatechol were minor degradates at pH 5 and pH 7, but were not detected at pH 9.

#### **Biotic Degradation:**

##### **Aerobic Soil Metabolism (162-1) 42594302**

Pentachlorophenol degraded with an observed half-life of 7-14 days (calculated first-order half-life of 63 days) in sandy loam soil maintained at 75% of 0.33 bar moisture and incubated at 25°C for up to one year. An acclimation period for the microbial degradation was not observed. The degradation rate was observed to decrease with time; at 7 days, 54.7% of the applied radioactivity remained present as parent, while 23.5% was present as parent at 61 days (the interval closest to the calculated first-order half-life). No major degradates were observed. The minor degradates were various isomers of tetrachlorophenol (maximum of 2.3-2.4% of the applied) and trichlorophenol (maximum of 4.4%); individual isomers were not identified. By 12 months post-

treatment, 25.7% of the applied radioactivity had volatilized as CO<sub>2</sub> and 1.3% had volatilized as a trichlorophenol. Nonextractable [<sup>14</sup>C]residues increased throughout the study and were a maximum of 64.0% of the applied at 12 months, with the majority (76%) associated with the humic fraction of the soil organic matter.

#### **Anaerobic Aquatic Soil Metabolism (162-3) 42436801 and the Registrant's Response to Comments (Dated 7/27/94)**

Pentachlorophenol degraded with an observed half life of 1-2 months (calculated first-order half-life of 34 days) in flooded sandy loam soil incubated anaerobically (nitrogen atmosphere) at 25°C for up to one year. Initial PCP degradation was relatively slow (84% and 72% of the applied remained as parent at 14 days and 1 month, respectively), then accelerated after an apparent acclimation period; only 5% of the applied was present as parent compound at 2 months. Various isomers of tetrachlorophenol (maximum of 9.7%) and trichlorophenol (maximum of 82.7%) were formed as major degradates; individual isomers were not identified. Volatiles were negligible (1.4%), and nonextractable [<sup>14</sup>C]residues were 7.8% of the applied at 12 months. The soil/water distribution ratio for PCP was approximately 1:13 initially, then changed to 1:1 by 7 days, and was 4:1 at 1-12 months.

#### **Aerobic Aquatic Metabolism (162-4) 42288601**

Pentachlorophenol degraded in a flooded sandy loam soil with an observed half life of approximately 14 days (calculated first-order half-life of 4.9 days) in flooded sandy loam soil incubated aerobically (under continuous airflow) at 25°C for up to 30 days. Initial PCP degradation was less rapid (52% of the applied radioactivity remained as parent at 14 days) than that observed after an apparent acclimation period; only 7% of the applied was present as parent compound at 21 days. The major degradate 3,4-dichlorophenol was ≤0.30% of the applied prior to 30 days and was 36.6% at day 30. Various isomers of tetrachlorophenol (maximum of 10%) and trichlorophenol (maximum of 82.2%) were also formed as major degradates; individual isomers were not identified. Volatiles were negligible (0.9%), and nonextractable [<sup>14</sup>C]residues were 41% of the applied at 30 days. The soil/water distribution ratio for PCP was approximately 1:32 initially, then changed to approximately 1:1 by 14 days, and was 2.5:1 at 30 days.

#### **Mobility:**

#### **Leaching & Adsorption/Desorption (163-1) 42633709 and 43627000**

Based on batch equilibrium studies, pentachlorophenol, at approximately 1-14 ppm, was determined to be moderately mobile in one sandy loam soil and slightly mobile in two sandy loam soils, and was immobile in a clay loam soil. In silt loam soils designated as "high" organic matter soils, pentachlorophenol was moderately mobile in the lower pH soil and mobile in the higher pH soil. In silt loam soils designated as "low" organic matter soils, pentachlorophenol

was slightly mobile in the lower pH soil and mobile in the higher pH soil. The soil properties and the Freundlich adsorption coefficients ( $K_{ads}$ ) and associated exponents are listed in the following table. Desorption coefficients were not reported for the sandy loam or clay loam soils. Data were not provided for a coarse-textured soil such as loamy sand or sand.

In the acceptable adsorption/desorption guideline studies, PCP was moderately mobile in one sandy loam soil ( $K_{ads}$  value of 5.7) and slightly mobile in two sandy loam soils ( $K_{ads}$  values of 10-11); data indicated that the mobility decreased as both pH (5.9-7.9) and organic matter content (0.4-2.6%) increased. These results indicated that the mobility of PCP in the sandy loam soils studied was primarily affected by the organic matter content, as an increase in pH would have otherwise been expected to lead to increased mobility of the compound. In a clay loam soil with a relatively high organic matter content (3.7%) and a relatively low pH (5.3), PCP was immobile, with a  $K_{ads}$  value of 75. In two silt loam soils designated as “high organic matter” soils, PCP was less mobile at the lower pH (5.8) than at the higher pH (7.5), with respective  $K_{ads}$  values of 8.3 and 2.0. Similarly, in two silt loam soils designated as “low organic matter” soils, PCP was much less mobile at the lower pH (4.2) than at the higher pH (6.6), with respective  $K_{ads}$  values of 18 and 1.3. However, the mobility determinations made in the guideline studies were based on Freundlich adsorption coefficients which had associated 1/N values of <0.9, indicating that the Freundlich equation may not accurately describe the adsorption of the compound equally well across all concentrations. Likewise, the organic carbon normalized partition coefficient,  $K_{oc}$ , cannot be validly used to predict adsorption for PCP since it is an ionizable compound and its adsorption does not increase linearly with increasing PCP concentration (Christodoulatos et al. 1994). In an acceptable guideline study on the mobility of the major PCP degradates 2,3,4-trichlorophenol (TCP) and 2,3,4,5-tetrachlorophenol (TeCP), both degradates were determined to be slightly mobile in sandy loam soil (pH 6.3); no other degradate mobility data were submitted. As with parent PCP, the associated 1/N values were <0.9, indicating that the Freundlich isotherm was not completely appropriate. Mobility data for PCP were not provided for a coarse-textured soil such as loamy sand or sand.

Soil Series or Origin	Texture	% OM	pH	$K_{ads}$	1/N (ads)
Georgia	Sandy loam	0.4	5.9	5.72	0.81
Nebraska <sup>1</sup>	Sandy loam	1.2	6.9	9.96	0.86
California	Sandy loam	2.6	7.9	10.8	0.87
Ohio	Clay loam	3.7	5.3	74.6	0.88
	Silt loam	high	5.8	8.3	
	Silt loam	high	7.5	2.0	
	Silt loam	low	4.2	18	
	Silt loam	low	6.6	1.3	

<sup>1</sup>Indicates the same “blue sandy loam” soil utilized in all other guideline laboratory studies.

K<sub>d</sub> values were also obtained in a second acceptable study on the major pentachlorophenol degradates 2,3,4-trichlorophenol and 2,3,4,5-tetrachlorophenol in a sandy loam soil (pH 6.3, 1.6% organic). Based on batch equilibrium studies, the pentachlorophenol degradates 2,3,4-trichlorophenol and 2,3,4,5-tetrachlorophenol were both determined to be slightly mobile in one sandy loam soil. No data were submitted for the PCP degradates dichloromaleic acid, tetrachlororesorcinol, or other isomers of tri- and tetrachlorophenol.

	2,3,4-trichlorophenol	2,3,4,5-tetrachlorophenol
<b>K<sub>ads</sub></b>	10.2	14.6
<b>K<sub>oc</sub></b>	1080	1550
<b>1/N</b>	0.78	0.78

#### **Bioaccumulation in Fish (165-4) 42633710, 42855402**

Pentachlorophenol residues bioaccumulated in bluegill sunfish exposed to pentachlorophenol, at a nominal concentration of 2.5 ug/L in a flow-through system (pH 6.7-7.2) for 28 days, with bioconcentration factors (BCF) of 190x for the edible tissue, 790x for the nonedible tissue and 490x for the whole fish. Maximum mean concentrations of [<sup>14</sup>C]residues were 640 ppb, 2800 ppb and 1500 ppb in edible, nonedible and whole fish tissues, respectively. Total [<sup>14</sup>C]residues at exposure day 28 were 170 ppb in edible tissues, 930 ppb in nonedible tissues and 500 ppb in whole fish tissues. At day 28, all of the residues in the edible tissues were identified as pentachlorophenol; in the nonedible tissues, 87-94% of the accumulated [<sup>14</sup>C]residues were identified as pentachlorophenol and 6-13% as glucoronide conjugates of pentachlorophenol. Depuration was rapid, with over 97% of the accumulated residues eliminated from all tissues by day 14. The exposure to the parent may not have been constant. [<sup>14</sup>C]Residues in the water were not adequately characterized; approximately 24% of the [<sup>14</sup>C]residues in the water at days 26 and 28 (the only water samples characterized) were not present as the parent compound.

#### **Aqueous Availability from Treated Wood (166-xxxx) 43205001**

Maximum and average leaching rates for southern pine wood (11-inch length and 1-inch in diameter) treated with pentachlorophenol at 0.50 lbs/ft<sup>3</sup> are reported in the following table. Reported data indicated that the average leaching rate and the maximum leaching rate of pentachlorophenol increased with increased pH.

<b>Final Concentration mg/L</b>	<b>Max. Leaching Rate x 10<sup>-2</sup> mg/kg leachate/in<sup>2</sup>/day</b>	<b>Average Leaching Rate x 10<sup>-3</sup> mg/kg leachate/in<sup>2</sup>/day</b>
pH 5            5.73	1.04	0.51

pH 7	36.2	2.28	3.27
pH 9	65.5	3.32	6.33
0.1N HCl	1.73	0.6	0.17
Seawater	22.7	3.11	2.21
Purified water	6.57	0.66	0.61

**The following studies were reviewed from published literature for the development of this science chapter**

Pentachlorophenol is used mainly as a wood preservative and is usually applied to wood as a liquid formulation (5% solution) composed of PCP plus hydrocarbon diluents such as P-9 oil, No. 2 fuel oil, kerosene or mineral spirits. Formulated products may include from 5% to greater than 80% active ingredient and typically include water repellents such as paraffin. Treated wood products include but are not limited to utility poles, cross arms, railroad ties and fenceposts. Introduction of PCP into the environment may occur from spills and runoff, and through releases from treated wood by leaching and/or volatilization; these may occur at wood treatment, storage and disposal sites as well as at the locations of wood usage. Pentachlorophenol may also enter the environment by wastewater discharge or holding pond overflow, both of which may occur at wood treating facilities.

In general, the environmental fate and mobility of pentachlorophenol in soil and water will depend on the pH of the systems. The chemical behavior and the physical properties of pentachlorophenol will depend on whether it exists primarily as the phenol (under more acidic conditions) or the phenolate anion (under basic conditions).

***Abiotic Degradation***

Pentachlorophenol is a relatively volatile compound, while its sodium salt is nonvolatile. In the atmosphere, volatilized PCP may undergo photolytic degradation or may react with photochemically produced hydroxyl radicals. Atmospheric PCP which is associated with particulate matter or moisture will be lost from the atmosphere through wet deposition.

Pentachlorophenol is hydrolytically stable in water at pH 4-9, precluding hydrolysis as a major degradation process in the environment. Chemical degradation of PCP in water will occur mainly through photodegradation resulting from absorption of sunlight in the ultraviolet region, with a maximum absorbance at  $\lambda = 320$  nm (for NaPCP in solution). In surface water, PCP will be rapidly photodegraded when exposed to direct sunlight, with more rapid degradation occurring with increased pH (when the compound is dissociated). Upon irradiation, PCP will



undergo photoreductive dechlorination to produce tetrachlorophenols (2,3,4,6- and 2,3,5,6-) and trichlorophenols. The tetrachlorophenols further react (with the addition of a hydroxyl group) to form tetrachlorobenzenediols (tetrachlororesorcinol at pH 5, 7 and 9; and tetrachlorohydroquinone and tetrachlorocatechol at pH 5 and 7), which are quickly oxidized and may undergo further dechlorination and/or ring cleavage to eventually form chloranil, hydroxyquinones and the major degradate 2,3-dichloromaleic acid (DCM). Although the photolysis of DCM ( $\lambda_{\text{max}} = 265 \text{ nm}$ ) is somewhat less rapid than that of PCP and the intermediate degradates, the acid will eventually degrade to  $\text{CO}_2$ , HCl, and small organic fragments (Wong and Crosby, 1981). In the environment, the rate of photodegradation of PCP in surface waters will attenuate with the increasing depth of the water. The irradiation by natural sunlight of the sodium salt of PCP (sodium pentachlorophenate or NaPCP) or of PCP at high concentrations (1000 ppm) in water has been observed to produce octachlorodibenzo-*p*-dioxin (OCDD); the highly toxic compound 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was not detected (Crosby et al. 1978).

Published data on soil photolysis obtained from the literature and information from the acceptable mobility and metabolism studies indicate that photodegradation is not a significant route of PCP degradation in the soil, particularly in situations where microbial degradation and binding to soil are the dominant processes. However, while the rate of photodegradation on soil will not approach the rapid rates of photolysis observed in aqueous solution, photolytic losses on the soil surface may be of increased importance under certain environmental conditions. Donaldson and Miller (1997) observed that the rates of photolysis on soil samples in the laboratory increased when near-saturated conditions were utilized, which increased the evaporative flux and translocated the compound to the surface 0.5 mm of the soil where photochemical degradation could occur. Under near-saturated flow conditions in loamy sand soil, up to 55% more degradation was observed in the irradiated samples than in the dark controls in 14 days.

Based on data from both the guideline studies and the literature, abiotic degradation is an important process only in surface water exposed to direct sunlight or in soil solution at the surface 0.5 mm of water saturated soils. Hydrolysis and soil photolysis, under normal soil conditions, are not significant degradation processes in the environment.

### ***Mobility***

The mobility of PCP in the environment is dependent, among other things, on the pH of the system. Pentachlorophenol is a weakly acidic compound ( $\text{pK}_a = 4.74$ ) in aqueous solution that will exist in increased proportions in the ionized form with increased pH. At pH 6.5 and higher, the majority of the PCP present in a system will occur as the phenolate anion. Because ionized PCP has substantially greater solubility in water than does unionized PCP, the aqueous solubility of PCP increases with increased pH, indicating that the mobility of the compound and, thus, the potential for groundwater contamination, is greater when the pH of the water/soil solution is more alkaline. In addition, PCP will be less soluble in organic matter in soils of higher pH.

Maximum adsorption has been reported at soil pH values of 4.6–5.1, with no adsorption above pH 6.8 (Choi and Aomine 1974). As a result of the increased solubility in water and the decreased adsorption to the soil, the mobility of the phenolate anion in the environment at pHs of greater than 6 can be substantial in the absence of degradation. The results of studies in the literature also indicate that desorption of PCP is also greater at higher pHs (Banerji and Wei 1993; You and Liu 1996); this implies that previously adsorbed PCP transported on particles to environments of higher pH may be desorbed at the new site.

Although the mobility of PCP in soils is strongly affected by the soil pH, the soil organic matter content also affects the adsorption of the compound. At a given pH, the adsorption of PCP increases with increasing soil organic matter content of the soil (Chang and Choi 1974). However, it has been demonstrated that PCP may solubilize surface organics (tentatively characterized as fulvic acids) on soil particles which then act as cosolvents and thereby decrease the relative adsorption of the compound by increasing its solubility; this effect increases as the concentration of PCP increases (Galil and Novak, 1995). Additionally, the presence of PCP in soils may also stabilize soil colloids which adsorb PCP and enhance its mobility by means of colloidal transport (Galil and Novak 1995). The presence of compounds such as alcohols or petroleum hydrocarbons (which are used as cosolvents in PCP formulations) in the environment will also serve to decrease the adsorption of PCP in soils by increasing its solubility (Christodoulatos et al. 1994; You and Liu 1996). Literature data indicate that PCP will tend to partition to the oil phase in a three-phase system consisting of oil, soil and water; similar results were observed for the dibenzodioxin and dibenzodifuran contaminants of PCP (Jackson and Bisson 1990). The results of the study indicated that PCP and its major contaminants will be more mobile in a saturated soil when it is contaminated with an oil phase, such as may occur at or near a wood treatment site where soil contamination with wood-preserving oil is most likely.

It has been demonstrated in the literature that the overall degradation rate of PCP, which is affected by both adsorption and metabolism, is not dependent on soil texture or clay content (Englehardt et al. 1986). However, it has been observed that the mobility of PCP in soil is partially dependent on the cation exchange capacity (CEC) of the soil (Christodoulatos et al. 1994); generally, sand soils have lower CECs than finer textured soils, and therefore may better represent a worst-case scenario for mobility. Additionally, sand soils generally tend to have lower organic matter contents and, thus, lower total microbial activity relative to medium or fine textured soils.

Literature data have demonstrated that the concentration of PCP may affect the mobility of the compound in groundwater (Davis et al. 1994). In a study of the groundwater under a former wood treating facility, retardation of PCP in the aquifer was greater at lower concentrations (<0.04 ppm) vs. higher concentrations (1-10 ppm or >10 ppm). The results of the study indicated that the compound would therefore be more mobile in areas of higher concentrations, such as at a source, while PCP would be less mobile in areas of lower concentrations, such as at a plume periphery.

Based on data from both the guideline studies and the literature, adsorption is a major fate process for PCP in soils and sediments at lower pHs, and is also of some importance in aquifers. Generally, PCP has moderate mobility in medium textured soils (loams), but may be immobile in soils with certain characteristics such as high organic matter content or relatively low soil pH. Because the mobility of PCP increases with increased pH, the potential for groundwater contamination is greater when the pH of the water/soil solution is more alkaline; adsorption is not a significant process at pHs of greater than 6. However, data also indicated that organic matter content has a significant effect on adsorption and may be of more importance than pH in determining adsorption in some soils. The concentration of PCP in the soil or in groundwater also has an effect on its mobility; adsorption of the compound to aquifer material or soil may be decreased as PCP concentrations increase. The presence of alcohols or petroleum hydrocarbons (cosolvents/carriers in PCP formulations) in the soil may also increase the mobility of the compound.

### ***Biodegradation***

Microbial metabolism is a major degradation process for PCP in both aerobic and anaerobic (flooded) soils and sediments. Results of studies reported in the literature indicate that biodegradation in soil is moderately rapid (half-lives are generally <1 month) once acclimation occurs. Literature data indicate that the major degradation products of PCP are 2,3,4,5-tetrachlorophenol; and 2,3,6- and 2,4,6-trichlorophenol (Kuwatsuka and Igarashi, 1975). Other degradates include pentachloroanisole; 2,3,4,6- and 2,3,5,6-tetrachlorophenol; and 2,3,5- and 2,3,4-trichlorophenol (or 2,4,5-trichlorophenol). A study utilizing acclimated (di-, tri- and tetrachlorinated phenols) anaerobic microbes in sewage sludge demonstrated that PCP was degraded to lower chlorinated phenols, including dichlorophenols (Mikesell and Boyd 1986). Engelhardt et al. (1986) noted in a review paper that the degradates 3,4- and 3,5-dichlorophenol were also observed in biodegradation studies of PCP, and noted that pentachloroanisole was a major degradate in aerobic soils, but was only present in minor amounts in anaerobic soils. Methylation to pentachloroanisole is considered to be a limited reaction under anaerobic conditions, while interconversion between PCP and pentachloroanisole may occur to a great extent under aerobic conditions (Murthy et al. 1979). In anaerobic systems, pentachlorophenol is biodegraded mainly through reductive dechlorination, and the degradates 3,5-dichlorophenol and 3-chlorophenol may accumulate; complete dechlorination to phenol and its subsequent mineralization to methane and carbon dioxide have been observed in studies utilizing anaerobic cultures (Mikesell and Boyd 1986; Frisbie and Nies 1997). Literature data in other studies have demonstrated that a chlorine present in the *meta* positions (as in 3,5-dichlorophenol and 3-chlorophenol) is more resistant to degradation than when it is present in the *ortho* or *para* positions (Baker et al. 1980; Bryant et al. 1991). Metabolic intermediates in the biodegradation of PCP include tetrachloro-*p*-benzoquinone and 2,6-dichlorohydroquinone (Reiner et al. 1978). Weiss et al. (1982) reported that, based on the identified degradates, metabolism of PCP in soil resulted from four reaction mechanisms: reductive dechlorination, methylation, conjugation, and incorporation into insoluble macromolecules. In a review paper on the biodegradation of PCP, McAllister et al. (1996) reported that the various intermediates found in numerous studies

indicated that microbial degradation of the compound occurs by different mechanisms which are associated with specific microbial consortia. Several species of bacteria and some fungi have demonstrated the ability to biotransform or biodegrade (i.e., mineralize) PCP in the soil (McAllister et al. 1996).

In the literature, some study authors have reported that in soil/water systems contaminated with PCP, slightly more rapid degradation was observed with more reducing conditions (i.e., with decreasing redox potentials; Ide et al. 1972), while others have reported slower degradation associated with lower redox potentials (DeLaune et al. 1983). In the latter study, however, greater adsorption of PCP was observed with the oxidized sediment *vs.* the reduced sediment, which would effectively decrease the bioavailability of the compound under more oxidized conditions. Murthy et al. (1979) also reported increased bound residues with aerobic soils *vs.* anaerobic soils. McAllister et al. (1996) stated that aerobic microbes can generally biodegrade PCP at higher concentrations than anaerobic microbes are able.

Pentachlorophenol has been observed to degrade in both sewage sludge and freshwater sediments (Mikesell and Boyd, 1986; Hendriksen et al. 1991; Bryant et al. 1991). As observed in the guideline studies, the degradation products reported in the literature consist of various isomers of tetrachlorophenol and trichlorophenol, as well as 3,5-dichlorophenol and 3-chlorophenol. It was reported in the literature that the amendment of freshwater sediment with activated sludge which was pre-exposed to PCP led to more rapid degradation and shorter or no acclimation periods (Ingerslev, 1998).

Because PCP is mobile in environments at higher pHs, the occurrence and extent of PCP biodegradation in subsurface soils is important from the perspective of assessing the potential for groundwater contamination. Additionally, the subsurface biodegradation of PCP degradates is important, as mobile degradates leaching downward from surface soils may also have an impact on groundwater. While microbial metabolism may be a major degradation process in surface soils, subsurface soils generally have decreased organic matter and microbial activity. Literature data from one study indicated that biodegradation of PCP and some of its degradates may be a significant process in subsurface soils from both saturated and unsaturated zones when present at relatively low concentrations (55 ppm; Smith and Novak 1987). The degradation of PCP was more rapid in soils from the unsaturated zone, possibly due to the presence of more microbes or of different types of microbes in those soils *vs.* the saturated zone soil. The degradation of the PCP degrade 2,4,6-trichlorophenol was observed to occur more rapidly than that of 2,4-dichlorophenol, but at a rate similar to that of PCP. However, the literature data were obtained from systems of relatively low pH (4.5-4.7); PCP would exist in an ionized form and would therefore be more soluble in systems of higher pH. At higher pHs and/or when PCP is present at higher concentrations (>55 ppm), the biodegradation of the compound may not be as significant in subsurface soils due to its biocidal activity.

In surface water, biodegradation of PCP is a dominant process (in addition to photolysis) by which the compound is transformed. As with soil or sediment systems, acclimation of the

microbial community in the water is generally required prior to significant biodegradation of PCP. Results reported in one study indicated, however, that the biodegradation of PCP in surface water of an outdoor man-made channel was mainly associated with microbes present on rock, macrophyte and sediment surfaces rather than those existing in the water phase (Pignatello et al. 1983). The same author reported that biotransformation in the water column above sediments occurred more rapidly under aerobic conditions *vs.* anaerobic conditions. In a laboratory study (shake flask tests), PCP biodegraded in stream water samples at similar rates prior to and following the addition of sterilized or unsterilized sediment; however, the addition of either sediment led to reduced acclimation periods (Ingerslev et al. 1998). In a study of simulated lentic environments, PCP was observed to degrade more rapidly and more completely in systems which contained pond soil/sediment and which had higher dissolved oxygen concentrations (Boyle et al. 1980). In that study, persistence of the compound was associated with dark conditions, low dissolved oxygen content, and the lack of sediment in the test systems. In a study which examined the biodegradation of PCP separately in aerobic sediment and in stream water at 0 and 20 °C, the concentration of the compound was reduced to some extent (12-29%; partly attributed to adsorption) in sediment samples, with greater loss occurring at 20 °C, but did not biodegrade in stream water samples (either non-sterile or sterile) at either temperature (Baker et al. 1980). The lack of biodegradation in the stream water *vs.* the sediment samples was attributed to greater microbial activity in the sediment samples, and may have been related to the greater surface to mass ratio of the microbes in the water which would allow for more rapid PCP adsorption and possibly lead to biocidal effects in the microbial populations in the water. In a study conducted in experimental ponds (pH 8.4), PCP degraded rapidly (half-lives of 2-4.7 days), but at a near-constant rate, indicating that the degradation may have been due to photolysis rather than to biodegradation (Crossland and Wolff 1985).

In the groundwater, as in surface water, biodegradation of PCP is generally considered to be the major process by which the compound is transformed. Literature data indicate that biodegradation of PCP in groundwater is affected by its concentration, in part since concentration may affect the compound's mobility (Davis et al. 1994). Based on study results, at high PCP aqueous concentrations (>20 ppm), biodegradation may not occur since the compound can act as a biocide. The authors concluded that in areas of lower PCP concentration (0.5-20 ppm), biodegradation may occur to a greater extent than in areas of high concentrations since PCP will be less mobile (and, thus, more bioavailable) at the lower concentrations; in areas of very low concentrations (<0.5 ppm), it is expected that biodegradation will be limited since the compound will likely adsorb to aquifer material (Davis et al. 1994). As was also observed with surface water in several studies in the literature, the loss of PCP in groundwater may be related to adsorption of the compound to the solids in the systems, rather than resulting from actual biodegradation. In unfiltered aquifer samples contaminated with pentachlorophenol, there was negligible mineralization of PCP by 56 days; observed decreases in PCP concentration were attributed to adsorption (Mohammed et al. 1998). Neither nutrient addition nor sample sterilization had a significant effect on mineralization of PCP. In a study of contaminated groundwater from the American Creosote Works Superfund site, PCP (at 52 ppm) was not biodegraded in groundwater samples treated with indigenous soil microorganisms from the site

and incubated for 14 days (Mueller et al. 1991). These results concur with those of Davis et al. (1994) and Mohammed et al. (1998) in that the PCP, which was present at a relatively high concentration, did not biodegrade by microbes present in the water phase, likely due to the toxicity of PCP to the microbes.

Based on data from both the guideline studies and the literature, microbial metabolism is a major degradation process for PCP in both aerobic and anaerobic (flooded) soils and sediments. However, in water (surface or groundwater), PCP may not be significantly degraded without the presence of a soil/sediment phase (except by photolysis at the upper layers of surface water). The biodegradation of PCP in soils, sediments and soil/sediment/water systems usually requires an acclimation period or lag phase, after which the degradation is moderately rapid (half-lives of <1 month). The degradation or removal of PCP in such systems is also partially due to adsorption of the compound to soil particles and organic matter; the adsorption of the compound at lower pHs may decrease the bioavailability of PCP and, thus, the mineralization of the compound. The removal of PCP in environmental systems is also dependent on its concentration; relatively high concentrations of PCP may inhibit its biodegradation.

### ***Bioaccumulation in Fish***

Based on the  $\log K_{ow}$  of 5.01 (unionized, 25 °C), PCP can be expected to bioaccumulate in aquatic organisms. However, because the aqueous solubility of PCP changes as pH changes, the extent of bioaccumulation of the compound is dependent on the pH of the environment. Studies in the literature have demonstrated that bioaccumulation of PCP in fish is greater in acidified lakes vs. non-acidified lakes in the same geographical region (Larsson et al. 1993).

The results of the guideline study agree with those found in the literature in that the BCFs were generally less than 1000 and the depuration of residues was rapid (Howard et al. 1993). Based on the literature, biomagnification of pentachlorophenol in terrestrial or aquatic food chains has not been observed. The results of one study indicate that PCP bioconcentration in fish occurs primarily by direct uptake of the compound from the water, rather than through ingestion of food; similar PCP concentrations were observed in the tissue of prey and predator fish (Niimi and Cho 1983).

### ***Aqueous Availability from Treated Wood***

Wood treated with PCP may release the compound through volatilization or leaching. Additionally, PCP may be photodegraded on the wood surface, making degradates available for leaching. All three processes are affected by the solvent systems/carriers used in the application of the compound. The leaching of PCP out of utility poles may also partially depend on the method of application (pressure or thermal treatment). Pentachlorophenol may be leached from the poles as the compound moves with either aqueous solution (as from rain) or with the solvent down the pole, either at the surface or within the pole. Based on experimental data, it was determined in one study (The Weinberg Group 1997) that the main mechanism for the leaching of PCP and its microcontaminants is the downward migration of the oil carrier along the vertical

axis of the pole, designated as “Gravitational Induced Downward Migration of Oil” (GIDMO). Leaching of PCP in aqueous solution from rainwater is not considered to be as important as GIDMO, as the replenishment rate at pole surfaces is a limiting factor with respect to the availability of the compound for leaching. Thus, contamination of subsurface soil found in the vicinity of utility poles may result from the downward movement of PCP within the pole, with subsequent leaching from the bottom part of the pole to the soil surface or to the subsoil near the underground portion of the pole, as well as from the downward movement of PCP from the surface soils to the subsoil. When leaching of PCP from treated poles occurs, the simultaneous leaching of the carrier solvents may affect the mobility of the compound in the soil, as noted previously in the mobility discussion.

Literature data indicate that PCP applied in oil is rapidly transported from the upper portion of the poles to the underground portion for the first few years of use (Cooper 1991). Laboratory studies have also demonstrated a relatively high initial rate of depletion from the wood surface, which became relatively constant with time. Rainwater from treated cedar (oil carrier) maintained a relatively constant PCP concentration of 0.3-0.7 ug/ml over a one-year period (Cserjesi, 1976). Literature data of leaching from wood by rainfall study, conducted using a bundle of 15 utility poles of douglas fir (16- to 27-in diameters) which were held in storage areas, indicated that the release of PCP was relatively constant throughout the four-month study period, with PCP concentrations of 1.57-2.85 mg/L of rainfall (Whiticar, 1994). In a leaching study utilizing class 5 red pine poles which were pressure-treated with PCP, sealed to simulate in-service poles, and subjected to simulated acid rainfall (pH 4.2) for 10 days at 20 °C, the mean PCP loss per leaching event was 23.3 mg/pole section with a total mean loss of 232 mg (range of 159.7 to 330 mg); the maximum concentration of PCP was 4.4 mg/L (Buchanan 1991).

In a study conducted by the Electric Power Research Institute (EPRI 1995a), soils adjacent to in-service utility poles (mainly southern pine) in NY, were analyzed for PCP and other compounds as a means of examining the release of PCP from treated wood in the environment. The soils were mainly classified (USCS system) as “lean clay” and “clayey sand” (43% each) and the PCP carrier on 28 of the 31 poles was petroleum. Although soil characteristics and levels of PCP contamination (site maximums of 0.35-1900 ppm, with the majority at <100 ppm) varied throughout the sites, a general trend was observed with respect to the changes in concentration of PCP with increasing distance from the poles. Pentachlorophenol was observed to decrease as the distance from the pole increased; a decrease as great as two orders of magnitude, with an average of one order of magnitude, was observed between 3 and 8 inches from the poles. While higher concentrations of PCP were generally observed in surface soils, a general trend with respect to depth was not observed across all soils, nor was there a general trend with respect to the location of the maximum concentration of PCP. Because PCP could reach the subsurface soil through other means than directly leaching from the soil surface down through the soil, it was concluded that the concentration of PCP in the surface soils would not accurately predict subsurface concentrations. Other means by which PCP could reach subsurface soil include leaching from the below-ground surface of the poles, particularly when a fluctuating water table is present near the bottom of the poles. The soil concentrations of lower-chlorinated phenols were generally

lower than the levels of PCP detected. Neither concentrations of PCP in the poles, PCP application rates, nor the age of the poles correlated well with the concentration of PCP detected in the soils near the poles.

In a second EPRI study (EPRI 1995b), soils adjacent to in-service utility poles in 16 states throughout the U.S. were analyzed for PCP. Results of the study were similar to those of the EPRI study conducted in NY state: 1) the concentration of PCP decreased as the distance from the pole increased; 2) higher concentrations of PCP were generally observed in surface soils, but a general trend with respect to depth was not observed across all soils; and 3) the concentration of PCP in the soils near the poles did not correlate well with pole parameters.

Because of the demonstrated tendency for PCP to adsorb to soils and the moderately rapid degradation of the compound in the environment, it is not likely that groundwater contamination will result from usage of utility poles, except in situations where the bottom of the pole is directly in contact with the water table (or with a fluctuating water table) or where the leaching occurs from multiple poles in a wood storage or treatment area.

### ***Dissipation and Persistence***

In published literature study, the fate of radiolabeled PCP applied as a seed-coat treatment (to alfalfa and ryegrass) was examined in a terrestrial microcosm chamber; results were compared with those of other compounds including pentachloronitrobenzene (PCNB), hexachlorobenzene (HCB), captan and dieldrin, which was used as a reference compound (Gile and Gillett 1979). Compared with the other chemicals studied, PCP had the highest mobility, while HCB and dieldrin were immobile. By the end of the study (41 days) radioactivity was present in both the soil (65%) and plant (9%) residues as PCP metabolites or bound residues; parent PCP was not detected, while HCB and dieldrin were present mainly as the parent compound. In general, PCP was bioaccumulated by macroinvertebrates to a greater extent (0.3% of the applied) than were the other compounds; however, PCP accumulations in animals were relatively low (up to 6.2 ppm).

In another study performed in a terrestrial microcosm chamber, the fate of radiolabeled PCP applied to wood posts which were placed in soil planted with ryegrass for 84 days was examined (Gile et al. 1982). The majority (96%) of the applied PCP remained in the wood posts, while 3.6% of the applied was detected in the soil near the posts; all soil residues were detected within 10 cm of the wood posts and did not leach below 10 cm. Residues detected in the soil were identified as the parent compound, pentachloroaniline, or tetrachlorohydroquinone.

In a study investigating the fate of radiolabeled PCP applied to flooded rice soil in a plant growth chamber and followed over the course of two vegetation periods, 55% of the applied radioactivity was volatilized (and assumed to be present mainly as CO<sub>2</sub>) and 15.4% was accumulated in plants during the study period (Weiss et al. 1982). Although 36.5% and 30.1% of the applied radioactivity remained in the soil after the two vegetation periods, respectively, neither the parent compound nor conjugated PCP were present at greater than 1%; approximately



29% and 26% of the applied was present as bound residues at those times, with the majority associated with the humic acid and humin fractions of the soil organic matter. The extractable residues were identified as 2,3,4,5-tetrachlorophenol; the six isomers of trichlorophenol, with the majority as 3,4,5-trichlorophenol; four trichloroanisole isomers; two tetrachloroanisole isomers; and pentachloroanisole.

Based on the data obtained from the literature, PCP is not likely to be persistent in the environment when it is used as a wood preservative or seed coating. The tendency of the compound to adsorb to the soil (particularly at lower pHs) and to biodegrade supports this conclusion. However, although it has been reported that PCP degradates are more readily degraded than parent PCP, Englehardt et al. (1986) have noted that pentachloroanisole may be more persistent than PCP.

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