

## 6. POTENTIAL FOR HUMAN EXPOSURE

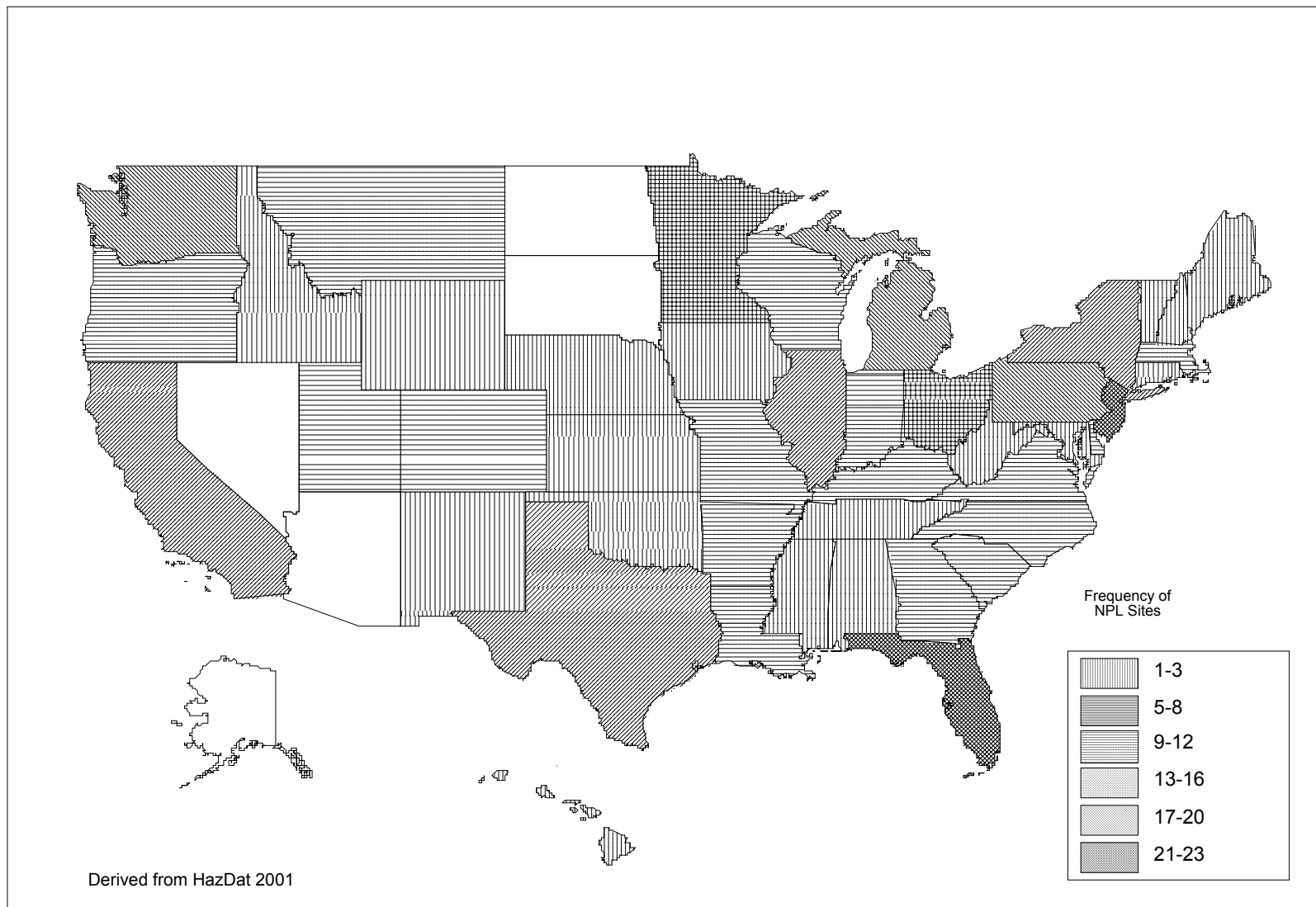
### 6.1 OVERVIEW

Pentachlorophenol has been one of the most heavily used pesticides in the United States. The compound is found in all environmental media (air, soil, and water) as a result of its past widespread use. In addition, a number of other chemicals, including hexachlorobenzene, pentachlorobenzene, and benzene hexachloride isomers, are known to be metabolized to pentachlorophenol. Current releases of pentachlorophenol to the environment are more limited as a result of decreasing volumes used, changing use patterns (e.g., phase-out of slimicide use in water cooling towers), and waste treatment practices (e.g., closing of on-site evaporation ponds at wood-treatment facilities). Pentachlorophenol is currently regulated as a restricted-use pesticide.

Pentachlorophenol is stable to hydrolysis and oxidation, but the compound is rapidly photolyzed by sunlight and can be metabolized by microorganisms, animals, and plants. Adsorption to soils and sediments is more likely to occur under acidic conditions than under neutral or basic conditions. The compound has been found to bioaccumulate to modest levels (e.g., bioconcentration factors of <1,000), but food chain biomagnification has not been observed. In recent decades, pentachlorophenol has been widely detected in human urine, blood, and adipose tissue among members of the general population. Human exposure to pentachlorophenol is believed to occur via inhalation of indoor and workplace air, ingestion of contaminated water and food, and direct dermal contact with pentachlorophenol-treated wood products. Since pentachlorophenol is no longer used in the treatment of wood products used in new residences and agricultural buildings, future indoor air exposure to this compound from these sources is likely to be minimal.

Pentachlorophenol has been identified in at least 313 of the 1,585 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2001). However, the number of sites evaluated for pentachlorophenol is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 312 are located within the United States and 1 is located in the Commonwealth of Puerto Rico (not shown).

Figure 6-1. Frequency of NPL Sites with Pentachlorophenol Contamination



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**6.2 RELEASES TO THE ENVIRONMENT**

Pentachlorophenol is ubiquitously distributed in the environment. It has been detected in surface waters and sediments, rainwater, drinking water, aquatic organisms, soils, and food, as well as in human milk, adipose tissue, and urine. The compound has been identified in at least 313 of the 1,585 hazardous waste sites on the NPL (HazDat 2001).

The majority of pentachlorophenol annual releases during production and use are to the atmosphere (about 1.4 million pounds [620 metric tons]) from wood preservation plants and cooling towers, and to land (about 1.9 million pounds [890 metric tons]) from wood preservation and domestic use as a preservative. Pentachlorophenol is also released into the aquatic environment, especially in runoff waters and wood-treatment plant effluents. Based on the available information, discharges to water, both direct and through municipal waste water treatment facilities, were estimated to be about 26,000 pounds (12 metric tons) and 11,000 pounds (5 metric tons), respectively (EPA 1980f). It should be noted, however, that much of these data, and data discussed in the following sections, were collected before pentachlorophenol became a restricted-use pesticide. Current releases are more limited, as indicated by the releases reported to the Toxics Release Inventory (TRI). However, total current environmental releases may be higher than the TRI estimates because only certain types of facilities are required to report; the list of facilities is not exhaustive.

The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

**6.2.1 Air**

Pentachlorophenol is released directly into the atmosphere via volatilization from treated wood products. Evaporation of pentachlorophenol-treated industrial process waters from cooling towers was an additional source of historical atmospheric releases of the compound. Historical atmospheric releases included those from cooling towers, where pentachlorophenol and its sodium salt were used as slimicides in cooling tower waters. However, pentachlorophenol and its salt are no longer commonly used for this purpose (Vulcan Chemicals 1989) since the early 1980s, when its use was restricted (EPA 1984b).

Emissions during production are considered to be relatively insignificant in volume, and are geographically restricted to the Vulcan Materials facility in Wichita, Kansas (SRI 1998). Physical

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removal mechanisms, such as wet deposition, are important processes that decrease pentachlorophenol concentrations in the atmosphere.

Pentachlorophenol has historically been estimated to volatilize from the surface of pentachlorophenol-treated wood products at an estimated rate of 760,000 pounds (344 metric tons) annually, or roughly 2% of the total amount of preservative applied. These estimates are representative of usage of the compound in those applications in the 1970s (EPA 1980f).

As much as 500,000 pounds annually (228 metric tons) of pentachlorophenol, used in cooling tower waters as an anti-fouling agent, have been released to the atmosphere through volatilization with heated water and steam in the past (EPA 1980f). However, pentachlorophenol is no longer commonly used for this purpose (Vulcan Chemicals 1989).

According to the TRI, an estimated total of 1,306 pounds of pentachlorophenol, amounting to 1.3% of the total environmental release, was discharged to the atmosphere from manufacturing and processing facilities in the United States in 1999 (TRI99 2001) (Table 6-1). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Volatilization from treated wood poles and other outdoor-use wood also occurs; 30–80% of the pentachlorophenol applied to coniferous wood by dip or brush treatments may be lost by volatilization within 12 months (Bunce and Nakai 1989). Ingram et al. (1986) reported increased volatilization of pentachlorophenol from treated wood with increased temperature; similar results with temperature change were seen with each of numerous solvent systems utilized for application of the compound. Volatilization of pentachlorophenol was dependent on the carrier solvents and the wood coatings utilized; maximum volatilization occurred when methylene chloride or 100% mineral spirits were used as carrier solvents, while the minimum volatilization occurred with the use of the cosolvent WC-144.

Pentachlorophenol may be formed during the incineration of chlorine-containing waste material. Heeb et al. (1995) found that pentachlorophenol constituted 8% of polychlorinated phenols formed in the flue gas and 10% of the stack gas during the incineration of chlorine-containing waste material. It may also be released in stack emissions as a result of pyrolysis of polyvinyl chlorides (Blankenship et al. 1994).

**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Pentachlorophenol**

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
AL	7	459	813	No data	0	1,272	331	1,603
AR	2	250	5	No data	No data	255	115	370
CA	2	5	No data	No data	No data	5	No data	5
FL	1	No data	No data	No data	2,000	2,000	No data	2,000
GA	2	13	5	No data	No data	18	122	140
ID	1	5	No data	No data	43,000	43,005	No data	43,005
IL	1	2	No data	No data	0	2	74	76
KY	1	10	No data	No data	0	10	250	260
LA	2	8	34	No data	No data	42	23	65
MD	1	No data	No data	No data	No data	No data	No data	No data
MN	1	1	No data	No data	No data	1	No data	1
MO	1	255	0	No data	No data	255	1	256
MS	4	10	112	No data	0	122	15	137
NC	2	3	3	No data	No data	6	1,480	1,486
NE	1	255	No data	No data	No data	255	No data	255
NJ	1	2	0	No data	0	2	15	17
NV	1	2	No data	No data	No data	2	No data	2
OH	1	2	1	No data	No data	3	5	8
OR	4	16	251	No data	26,793	27,060	14,654	41,714
SC	2	6	0	No data	11,911	11,917	8	11,925

**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Pentachlorophenol  
(continued)**

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
SD	1	1	53	No data	No data	54	160	214
TX	2	0	0	5	No data	5	No data	5
UT	2	1	No data	No data	15,133	15,134	255	15,389
WA	4	No data	No data	No data	No data	No data	No data	No data
Total	47	1,306	1,277	5	98,837	101,425	17,508	118,933

Source: TRI99 2001

<sup>a</sup>Data in TRI are maximum amounts released by each facility.

<sup>b</sup>Post office state abbreviations are used.

<sup>c</sup>The sum of fugitive and stack releases are included in releases to air by a given facility.

<sup>d</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>e</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

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**6.2.2 Water**

Pentachlorophenol releases to surface water occur through direct discharge and direct entry from numerous nonpoint sources, including treated wood. In addition, pentachlorophenol is transported to surface waters from the atmosphere by wet deposition, and from soil by runoff and leaching.

Approximately 90% of wood-treatment plants evaporate their waste water and, consequently, have no direct discharge to surface waters. The remainder of the plants discharge to municipal waste water treatment facilities. Total annual pentachlorophenol releases to municipal waste water treatment facilities were estimated to be 12,000 pounds (5.3 metric tons) (EPA 1980g).

About 2 metric tons of pentachlorophenol used as a biocide in cooling tower waters were estimated to have been discharged to surface waters in 1978 (EPA 1979a). In addition, industries such as leather tanning and textile factories may have released up to 4,400 pounds (2 metric tons) and 12,000 pounds (5.5 metric tons) of pentachlorophenol, respectively, in their waste water discharges to surface waters on an annual basis in the 1970s (EPA 1980f). Pentachlorophenol is no longer used in these applications (Weinberg 1997).

Chlorination of phenolic compounds during water treatment has been reported to produce detectable levels of pentachlorophenol (Detrick 1977; Smith et al. 1976). In addition, common pesticides such as lindane, hexachlorobenzene, pentachlorobenzene, and pentachloronitrobenzene are known to be metabolized to pentachlorophenol by plants, animals, and/or microorganisms, but the contribution of the metabolism of these pesticides to environmental levels of pentachlorophenol is unknown (Dougherty 1978).

According to the TRI, an estimated total of 1,277 pounds of pentachlorophenol, amounting to 1.25% of the total environmental release, was discharged to water from manufacturing and processing facilities in the United States in 1999 (TRI99 2001) (Table 6-1). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

**6.2.3 Soil**

Pentachlorophenol is released to soils as a result of its past use as a herbicide, leaching from treated wood products, atmospheric deposition in precipitation (such as rain and snow), spills at industrial facilities using pentachlorophenol, and at hazardous waste sites.

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Most of the pentachlorophenol removed from effluent streams by waste water treatment processes is adsorbed to sludge solids. Sludges from wood preservation industries historically have been estimated to contain up to 31,500 pounds (14.3 metric tons) of pentachlorophenol annually. Pentachlorophenol in solid wastes from wood-treatment facility evaporation ponds was estimated to total an additional 133,000 pounds (60.2 metric tons) annually in the 1970s (EPA 1980f). However, most wood-treatment facilities have closed, or are in the process of closing, on-site evaporation ponds (Vulcan Chemicals 1989).

According to the TRI, an estimated total of 98,837 pounds of pentachlorophenol, amounting to 97.5% of the total environmental release, was discharged to soil from manufacturing and processing facilities in the United States in 1999 (TRI99 2001) (Table 6-1). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

### 6.3 ENVIRONMENTAL FATE

Pentachlorophenol released into the atmosphere from treated wood can be transported back to surface waters and soils via wet and dry deposition. Atmospheric pentachlorophenol is transformed via photolysis; the compound may slowly undergo free radical oxidation with an estimated half-life of approximately 2 months.

In surface waters, pentachlorophenol undergoes biotransformation and photolysis, and is adsorbed to sediments. Hydrolysis, oxidation, and volatilization do not significantly affect surface water concentrations.

In soils and sediments, pentachlorophenol is metabolized by acclimated microbes, under both aerobic and anaerobic conditions, or is adsorbed. Pentachlorophenol may also be methylated to form pentachloroanisole, a more lipid soluble compound. Adsorption of pentachlorophenol in soils is pH dependent. The compound has a  $pK_a$  value of 4.7 and consequently exists in the ionic forms at environmentally relevant pH values. For example, at pH 4.7, pentachlorophenol is 50% ionized, whereas at pH 6.7, the compound is about 99% ionized (Crosby 1981). Adsorption decreases in neutral and basic soils and is strongest in acidic soils. Therefore, the compound is most mobile in neutral-to-basic mineral soils and least mobile in acidic organic soils. Volatilization and photolysis do not appear to be important transport and transformation processes for pentachlorophenol in soils.



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**6.3.1 Transport and Partitioning**

A Henry's law constant of  $2.75 \times 10^{-6}$  atm m<sup>3</sup>/mol has been reported for pentachlorophenol; the value for the salt or ionic form of this compound is expected to be much less. Therefore, volatilization of the solvated anionic form from an aqueous system is not considered to be a significant transport mechanism under ambient conditions. Pignatello et al. (1983) reported that volatilization loss of pentachlorophenol as vapor and aerosol from treated river water in outdoor manufactured channels was #0.006% of the initial test concentration. Volatilization of pentachlorophenol from soil is also not expected to be a major transport pathway. Kilzer et al. (1979) determined the volatilization rates of pentachlorophenol from water and three soil types under laboratory conditions. The volatilization rates (expressed as percentage of applied pentachlorophenol per mL evaporated water) from water, sand, loam, and humus were 2.57, 0.13, 0.31, and 0.10%, respectively, in the first hour after application of 50 µg/L pentachlorophenol. During the second hour, the volatilization rates were 2.11, 0.12, 0.15, and 0.12%, respectively.

Pentachlorophenol is volatilized from treated wood surfaces. Walls in a closed room treated with pentachlorophenol released the chemical into the air, with concentrations reaching 1 ng/m<sup>3</sup> on the first day after treatment and 160 ng/m<sup>3</sup> on the fourth day (Gebefugi et al. 1976).

The adsorption or mobility of pentachlorophenol in soils is controlled primarily by soil pH. The amount of pentachlorophenol adsorbed at a given pH increases with increasing organic content of the soil (Chang and Choi 1974). Pentachlorophenol is adsorbed to soil or sediment under acidic conditions, but the compound is mobile under neutral or alkaline conditions (Kuwatsuka and Igarashi 1975). 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).

Schellenberg et al. (1984) investigated the adsorption of chlorinated phenols to natural sediments and aquifer materials. These authors demonstrated that adsorption of pentachlorophenol was highly dependent on the organic content of the adsorbent. An average  $K_{oc}$  of 32,900 was measured for pentachlorophenol in lake sediment, river sediment, and aquifer materials.

However, normalized partition coefficients (i.e.,  $K_{oc}$ ) do not accurately predict adsorption for ionizable compounds such as pentachlorophenol since its adsorption does not increase linearly with increasing concentration (Christodoulatos et al. 1994). The use of the equation to normalize partition coefficients is not valid in such cases. Davis et al. (1994) investigated the retardation of pentachlorophenol in

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groundwater at a former wood treating facility. Data were not well represented by the Freundlich or Langmuir isotherms. The authors observed that retardation of the compound in the aquifer was greater at lower concentrations ( $<40 \mu\text{g/L}$ ) than at higher ones ( $>1000$  or  $10,000 \mu\text{g/L}$ ), indicating that pentachlorophenol will move at rates closer to that of the groundwater when present at higher concentrations ( $>10,000 \mu\text{g/L}$ ). The authors stated that the results indicated that at the lower concentrations found at plume peripheries, pentachlorophenol would be attenuated and then biodegraded, while at higher concentrations such as at the source, the compound would be mobile.

Pentachlorophenol is applied to wood as a liquid formulation composed of pentachlorophenol dissolved in hydrocarbon diluents such as oils, kerosene, or mineral spirits. The presence of cosolvents such as alcohols or petroleum hydrocarbons decreases the adsorption of pentachlorophenol in soils by increasing its solubility in the soil solution (Christodoulatos et al. 1994). This may also be important at spill, storage, and hazardous waste sites where a large amount of cosolvent would be expected. Based on the results of a study of the mobility of pentachlorophenol, pentachlorodibenzodioxins, and pentachlorodibenzofurans in soils contaminated with wood-preserving oil, Jackson and Bisson (1990) indicated that decreased adsorption of the compounds in soil would result from the presence of a subsurface, contaminated oil phase. They predicted that upon contact with groundwater, the compounds would be partitioned into the aqueous phase. In a study of desorption of chlorophenols in contaminated soils, pentachlorophenol was desorbed more readily in the presence of methanol and exhibited a positive correlation with increasing methanol concentration (You and Liu 1996).

Decreased adsorption may also occur without the presence of a cosolvent/contaminant such as methanol or a petroleum hydrocarbon. The release of soil organics and colloids in the presence of dissolved pentachlorophenol was investigated. When pentachlorophenol was added to soil at aqueous concentrations of  $1,000$ – $10,000 \mu\text{g/L}$ , surface organics (tentatively identified as fulvic acids) were solubilized and acted as a cosolvent, decreasing the adsorption of pentachlorophenol (Galil and Novak 1995). Enhanced mobility of pentachlorophenol was also predicted from the observed increased stability of soil colloids that adsorbed 3–13% of the compound, but were released from soil particle surfaces into the soil solution.

Pentachlorophenol can be leached from treated wood into surrounding soil. For example, Arsenault (1976) reported that pentachlorophenol migrated from the surface of utility poles to the adjacent soil, which had an average pentachlorophenol concentration of  $654 \text{ mg/L}$ . However, mobility in soil was

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limited, as indicated by the average soil concentration of 3.4 mg/L pentachlorophenol at a distance of 12 inches from the poles.

In a review paper, McAllister et al. (1996) reported that available data on the plant uptake and transformation of pentachlorophenol are inconsistent among studies and are inconclusive with regard to the abilities of specific plants to take up the compound. It was observed that the biodegradation of pentachlorophenol by microorganisms and its adsorption to soil limit the availability of the compound for plant uptake. Among the pentachlorophenol metabolites found in plants are tetrachlorophenols and anisoles (McAllister et al. 1996); additionally, oxidation products (tetrachlorobenzenes), conjugated forms of chlorinated phenols, and insoluble metabolites (lignin-incorporated residues) have been observed (Engelhardt et al. 1986).

Veith et al. (1985) demonstrated that chemicals with a log  $K_{ow}$  value greater than 4.0 are likely to bioaccumulate in organisms and food chains. The log  $K_{ow}$  presented in Chapter 4 is 5.01 for the un-ionized form, which suggests that pentachlorophenol will bioaccumulate. However, the extent of bioaccumulation will depend on the pH of the medium and physiological pH, since at higher pH levels, pentachlorophenol converts to the more water-soluble pentachlorophenate anion. Bluegill sunfish exposed to 100  $\mu\text{g/L}$  pentachlorophenol accumulated the compound in various tissues (edible, nonedible, or whole fish) to levels of 10–350 times the ambient water concentration in a 16-day static/renewal bioassay. Pentachlorophenol was rapidly eliminated upon transfer of the test organisms to clean water (Pruitt et al. 1977). Pentachlorophenol was reported to have a bioconcentration factor (BCF) of 81–461 in the soft tissue of a freshwater mussel; however, the compound was rapidly cleared by the test organisms (52% loss within 12 hours) (Makela et al. 1991). Other bioaccumulation tests with aquatic organisms include BCF values of 30–40 in carp muscle tissue and 300–400 in all other tissues (Gluth et al. 1985) and BCF values of 218 (whole fish) to 1,633 (fish lipid basis) for juvenile American flagfish (Smith et al. 1990). In the latter test, which was a flow-through bioassay, the half-life of pentachlorophenol in the tissues was reported to be about 16 hours. Bioaccumulation of pentachlorophenol in algae, aquatic invertebrates, and fish (with BCFs of up to 10,000) has been demonstrated. Representative BCFs are as follows: goldfish, 1,000; polychaete, 3,830; bluegill sunfish, 13; blue mussel, 324; and eastern oyster, 78 (EPA 1986c).

Biomagnification of pentachlorophenol in terrestrial or aquatic food chains has not been observed. In a 110-day study with rainbow trout, where pentachlorophenol was administered in the diet at a maximum concentration of 3,000  $\mu\text{g/kg}$ , maximum concentrations of the compound in fish tissues were 40  $\mu\text{g/kg}$

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after 50 days and 20 µg/kg at the end of the test period. In a 28-day depuration test, tissue half-life of the compound was about 7 days. According to the investigators, these results suggest that pentachlorophenol bioconcentration in fish occurs primarily through direct uptake from water rather than through ingestion of food. The similar pentachlorophenol tissue concentration levels of prey and predator salmonid fish from Lake Ontario were cited as additional evidence of the limited food chain bioaccumulation of the compound (Niimi and Cho 1983).

Pentachlorophenol bioconcentration by earthworms has also been studied by several investigators. In 14-day exposure tests, BCFs of 3.4–13 were reported for uptake of pentachlorophenol adsorbed to soil particulates (Haque and Ebing 1988; van Gestel and Ma 1988). However, when bioconcentration was calculated on the basis of concentration of test compound in soil solution, BCF values of 426–996 were obtained (van Gestel and Ma 1988).

### 6.3.2 Transformation and Degradation

#### 6.3.2.1 Air

Atmospheric pentachlorophenol is probably photolyzed in the absence of water, although mechanisms for this reaction are not well known (Crosby and Hamadad 1971; Gab et al. 1975). Photolysis of sorbed or film-state pentachlorophenol in the presence of oxygen has also been observed (Gab et al. 1975). The reaction products were similar to those found in aqueous photolysis. Bunce and Nakai (1989) estimated the rate of photolysis in the atmosphere based on measured quantum yields (254 nm) in the laboratory, molar absorptivity values, and solar intensity values for midday in summer at 40 EN; the estimated loss of pentachlorophenol to vapor-phase photolysis was 6.2% per hour. This rate represents the maximum rate at 40 EN; the average rate of photolysis for pentachlorophenol will be lower.

No empirical data were found describing the reactivity of pentachlorophenol to free radical oxidation in the atmosphere. Bunce and Nakai (1989) calculated the potential atmospheric degradation of pentachlorophenol due to hydroxyl radical attack. The estimated loss rate was 1.5% per hour (half-life of 66 hours) as calculated from an estimated rate constant of  $4.7 \times 10^{-13}$  cm<sup>3</sup>/molecule-sec, assuming a peak noon summer hydroxyl radical concentration of  $6.2 \times 10^6$  radicals/cm<sup>3</sup>. Based on the estimated relative rates of photolysis and degradation by hydroxyl radicals, it was concluded that the former process would likely be the dominant of the two. It is noted that the estimate by Bunce and Nakai did not take into account the adsorption of the compound to particulates in the atmosphere. Using the method of Meylan

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and Howard (1993), a half-life of 58 days for the vapor-phase reaction of pentachlorophenol with hydroxyl radicals can be obtained from an estimated rate constant of  $5.5 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec and an average hydroxyl radical concentration of  $5.5 \times 10^5$  molecule/cm<sup>3</sup>. Adsorption of pentachlorophenol to particulate matter, however, will attenuate the rate of this process in the atmosphere.

**6.3.2.2 Water**

Photolysis and biodegradation are believed to be the dominant transformation processes for pentachlorophenol in aquatic systems. Hydrolysis and oxidation are not important mechanisms for removal of the compound from surface waters.

The molecular structure of pentachlorophenol is indicative of its stability to hydrolysis or oxidation (EPA 1979e). Wong and Crosby (1981) reported that pentachlorophenol did not hydrolyze in aqueous solutions (serving as dark controls in an aqueous photolysis study) at pH 3.3 or 7.3 when held at 26 EC for up to 100 hours.

Wong and Crosby (1981) reported that pentachlorophenol in aqueous solutions at 100 mg/L was photolyzed under laboratory ultraviolet (UV)-light irradiation with estimated half-lives of about 100 hours at pH 3.3 and 3.5 hours at pH 7.3. Photolysis of pentachlorophenol in aqueous solution following exposure to sunlight was also rapid; in laboratory experiments, concentrations of pentachlorophenol in water were reduced from 9.3 to 0.4 mg/L in 24 hours, and approached zero at the end of 48 hours (Arsenault 1976). Wong and Crosby (1981) also reported rapid photolysis in sunlight (July); pentachlorophenol in pH 7.3 aqueous solution at 100 mg/L photolyzed with a half-life of 48 hours (total elapsed time) and a total disappearance time of 10 days. Degradates formed during photolysis included tetrachlorophenols, three tetrachlorodiols and their respective quinones, chloranilic acid, and eventually 2,3-dichloromaleic acid, which also undergoes photolysis, but at a slightly slower rate than pentachlorophenol. The final products from the complete photolytic degradation of pentachlorophenol were carbon dioxide and chloride ions. In outdoor tests conducted with river water in manufactured channels, Pignatello et al. (1983) demonstrated that photolysis of pentachlorophenol (applied as the sodium salt) was rapid at the water surface (half-life of 0.70 hour at a depth of 0.5 cm). However, photolysis was greatly attenuated with increasing depth of the water column (half-life of 9.63 hours at a depth of 13.8 cm). Photolytic degradation accounted for a 5–28% decrease in the initial test concentration of the compound after 3 weeks.

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Pentachlorophenol is biotransformed in aqueous systems by acclimated microorganisms. In a 40-day study of sterile and nonsterile stream water samples that were not amended with acclimated microbial cultures, Baker et al. (1980) reported negligible biodegradation of pentachlorophenol at 0 and 20 EC. Pignatello et al. (1983) reported that microbial transformation became the primary removal mechanism of pentachlorophenol (applied as the sodium salt) added to river water in tests conducted in outdoor manufactured channels. After about a 3-week acclimation period, microbial transformation accounted for a 26–46% decline in the initial test concentration of pentachlorophenol. The majority of the microbes responsible for the mineralization of pentachlorophenol were associated with rock and macrophyte surfaces or surface sediments rather than existing in the water phase. In a follow-up study utilizing the same type of outdoor tests, Pignatello et al. (1985) found that biotransformation accounted for a 55–74% decrease in concentration of applied pentachlorophenol after a 3–5-week adaptation period.

Biotransformation in the water column above sediments occurred at a greater rate under aerobic than under anaerobic conditions. Ingerslev et al. (1998) reported that in a study utilizing a battery of shake flask tests, pentachlorophenol at 1 and 100 mg/L biodegraded in 10–30 days under aerobic conditions in surface water from an unpolluted stream after an acclimation period of approximately 55 days. The addition of either sterilized or unsterilized sediment to the samples resulted in reduced acclimation periods, but did not affect the postacclimation degradation rates in water.

In a study using radiolabeled pentachlorophenol, Arsenault (1976) demonstrated that the compound was transformed to carbon dioxide, water, and hydrochloric acid in an activated sludge treatment plant. On a pilot-plant scale, the same investigator also showed that a waste stream from a wood-preserving facility containing 23 mg/L of pentachlorophenol could be treated successfully to produce a final effluent concentration of 0.4 mg/L of pentachlorophenol.

In a microcosm study of unfiltered aquifer samples (geologic material and groundwater) contaminated with polycyclic aromatic hydrocarbons and pentachlorophenol, a loss was observed. Although reductions in the parent compound concentration occurred, only 1% of the applied radiolabeled pentachlorophenol had mineralized by 56 days (Mohammed et al. 1998). Neither nutrient addition nor sample sterilization had a significant effect on mineralization. The observed decreases in the pentachlorophenol concentrations were attributed to adsorption to particulate material and not to biodegradation.

In four simulated lentic environments, Boyle et al. (1980) tested the effects of dissolved oxygen, light, pH, and the presence of a hydrosol (i.e., pond soil/sediment) on the transformation of pentachlorophenol (applied as the sodium salt). The persistence of pentachlorophenol was associated with three

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environmental variables: absence of light and hydrosoil; pH near or below pKa; and low oxygen concentration. Major reaction products were pentachloroanisole, 2,3,4,5-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, and 2,3,5,6-tetrachlorophenol; only pentachloroanisole was found in the water phase, and then only in the aerobic systems maintained in light.

**6.3.2.3 Sediment and Soil**

Photolysis of pentachlorophenol on soil surfaces is not a major transformation process. Hebert and Miller (1990) reported that UV light was >90% attenuated in the surface 0.2 mm of soil. However, while they will not approach rates of photolysis observed in aqueous solution, photolytic losses on the soil surface may be increased under certain conditions. The effect of upward evaporative flux on the rates of photolytic loss of pentachlorophenol, applied at 1,500 µg/L, was examined in soils maintained at various moisture levels. It was observed that the rates of photolysis on soil 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 occurs (Donaldson and Miller 1997). 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.

The rate of pentachlorophenol degradation from adsorption and metabolism in soil is not dependent on soil texture, clay content, free iron oxides, or the degree of base saturation; however, it is partially dependent on the ion exchange capacity of the soil (Engelhardt et al. 1986). The rate of pentachlorophenol transformation in laboratory tests is more rapid in soils with high organic content than in those with low organic content, and greater when moisture content is high and soil temperature approaches the optimum for microbial activity (Young and Carroll 1951).

Biodegradation is considered the major transformation mechanism for pentachlorophenol in soil. Half-lives are usually on the order of 2–4 weeks. Pentachlorophenol is metabolized rapidly by most acclimated microorganisms (Kaufman 1978). In a study by Edgehill and Finn (1983) inocula of a strain of pentachlorophenol-acclimated *Arthrobacter* bacteria was added to soils in laboratory and enclosed outdoor tests. The soils were amended with 120–150 mg pentachlorophenol/L and 34 kg pentachlorophenol/hectare, respectively. In the laboratory test conducted in the dark at 30 EC, the half-life of pentachlorophenol in inoculated samples was about 1 day, whereas the half-life in uninoculated samples was 12–14 days. Pentachlorophenol loss from uninoculated control plots in outdoor tests was 25% after 12 days at ambient temperatures (8–16 EC), while losses from inoculated plots were 50–85%.

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*Pseudomonas* biotransformed [<sup>14</sup>C]-pentachlorophenol rapidly and released radiolabeled carbon dioxide as well as the intermediate metabolites tetrachlorophenol and tetrachlorohydroquinone. In another study, strains of *Pseudomonas putida* and *Acinetobacter calcoaceticus sp.* were found to be able to use pentachlorophenol as a sole carbon and energy source (Martins et al. 1997)

An investigation was conducted by Frisbie and Nies (1997) to determine whether aged pentachlorophenol residues from contaminated soil at a former wood-treatment site would be biodegraded in the laboratory under aerobic and anaerobic conditions by indigenous microbes from that site. Under aerobic conditions, both existing and newly added pentachlorophenol was biodegraded following a short acclimation period. The degradates 2-monochlorophenol and 4-monochlorophenol were rapidly degraded, but 3-monochlorophenol did not undergo significant degradation. Under anaerobic conditions, pentachlorophenol was degraded to 3-monochlorophenol, which accumulated and was then further degraded; however, approximately 30% of the initial pentachlorophenol was not degraded.

Pentachlorophenol has been observed to degrade more rapidly in anaerobic environments than in aerobic ones. Pentachlorophenol degraded in a paddy soil at 28 EC with a half-life of about 3 weeks; reducing conditions increased the rate of reaction slightly (Ide et al. 1972). These observations were confirmed by Kuwatsuka and Igarashi (1975) in 10 different soil types. Pentachlorophenol biotransformation rates were higher under anaerobic (flooded) conditions than under aerobic (upland) conditions. The half-life for pentachlorophenol under flooded conditions ranged from 10 to 70 days, while under upland conditions, the range was 20–120 days, and the rate of reaction increased with the organic matter content. Pentachlorophenol transformation was assumed to proceed by both chemical and microbial means, based on the effects of sterilization, soil temperature, and nature of the reaction products, which included pentachloroanisole; 2,3,4,5-, 2,3,4,6-, and 2,3,5,6-tetrachlorophenol; and 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6-, and 3,4,5-trichlorophenol. The major products were 2,3,4,5-tetrachlorophenol, and 2,3,6- and 2,4,6-trichlorophenol. Tetrachloro-*p*-benzoquinone and 2,6-dichlorohydroquinone have also been implicated as metabolic intermediates for pentachlorophenol (Reiner et al. 1978).

The degradates 3,4- and 3,5-dichlorophenol were also observed in biodegradation studies of pentachlorophenol (Engelhardt et al. 1986). These authors noted that pentachloroanisole was a major degradate in aerobic soils, but was present in minor amounts in anaerobic soils. In anaerobic systems, pentachlorophenol is biodegraded only through reductive dechlorination, and the degradates 3,5-dichlorophenol and 3-monochlorophenol may accumulate; complete dechlorination to phenol and its subsequent mineralization to methane and carbon dioxide have been observed (Frisbie and Nies 1997). In



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a review paper on microbial degradation of pentachlorophenol, 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.

Pentachlorophenol is degraded under anaerobic conditions in sewage sludge and sediments. After 6 months of operation, about 60% of the initial concentration of pentachlorophenol added to laboratory-scale, fixed-film reactors containing a digested municipal sewage sludge microbial inoculum was removed. Removal from reactors supplemented with glucose attained 98% of the initial charge over the same time frame. Trichlorophenol and tetrachlorophenol were observed as degradation products (Hendriksen et al. 1991). In other laboratory tests, reductive dechlorination of pentachlorophenol was found to be more rapid in freshwater sediments containing microbial communities adapted to dechlorinate 2,4-dichlorophenol and 3,4-dichlorophenol than in nonadapted sediment microbial communities. Degradation products identified included 2,3,5,6-tetrachlorophenol, 2,3,5-trichlorophenol, 3,5-dichlorophenol, 3-chlorophenol, and phenol (Bryant et al. 1991). Ingerslev et al. (1998) also reported more rapid degradation and shorter or no acclimation periods in freshwater sediments amended with activated sludge which was preexposed to pentachlorophenol at various levels. At concentrations ranging from 10 to 20,000 µg/L, the acclimation periods were reduced from 8.6–21.1 days to 0.1–3.2 days when sediments were amended with preexposed activated sludge compared with activated sludge which was not preexposed to pentachlorophenol; only at a toxic concentration of 74,000 µg/L was the acclimation period increased (15.5–59.4 days). At concentrations of 10, 100–2,500, and 20,000 µg/L, preexposure reduced the respective postacclimation half-lives from 32, 3.7–5.6, and 108 days to #2.2 days; at 74,000 µg/L, the postacclimation half-life decreased from 80 days to >51.6 days.

#### 6.3.2.4 Other Media

Laboratory studies were conducted to determine the effect of artificial light and sunlight on concentrations of pentachlorophenol and chlorinated dibenzo-*p*-dioxins in wood treated with pentachlorophenol (Lamparski et al. 1980). Although chlorinated dibenzo-*p*-dioxins are known to be present in pentachlorophenol products as impurities, formation of octachlorodibenzo-*p*-dioxin (OCDD) as well as heptachlorodibenzo-*p*-dioxin (HpCDD) and hexachlorodibenzo-*p*-dioxin (HxCDD) was observed even when purified pentachlorophenol was irradiated. Based on the relative levels of the isomers observed, HxCDD and HpCDD were presumed to be degradation products of OCDD, not condensation products of tetrachlorophenol and pentachlorophenol. The formation of OCDD was greatly reduced when hydrocarbon oil was utilized as the carrier solvent in place of methylene chloride.

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**6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT**

Pentachlorophenol historically has been widely detected in environmental media as a result of its widespread past use by industry, the agricultural sector, and the general public, as a cooling-tower algicide and fungicide, herbicide, molluscicide, paint preservative, plywood and fiberboard waterproofing agent, and drilling mud and photographic solution biocide. Pentachlorophenol is now regulated as a restricted-use pesticide. Therefore, it can only be purchased and used by certified applicators, and only for the applications covered by the applicator's certification. Pentachlorophenol is no longer available to the general public. Although the compound has been detected in indoor air, surface waters, groundwater, drinking water, soils, rainwater, and a variety of foods in older monitoring studies, current contamination of these media by the compound is probably more limited given the restricted current usage of pentachlorophenol and its limited environmental persistence.

**6.4.1 Air**

Limited information is available on the levels of pentachlorophenol in ambient air. EPA (1980f) estimated atmospheric concentrations of pentachlorophenol using air models. A cumulative concentration estimate based on all emission sources was 0.15–136 ng/m<sup>3</sup>. The lower end of this range coincides with the upper end of the range of computed air concentration estimates based on pentachlorophenol concentrations in rainwater in Hawaii (0.002–0.063 ng/m<sup>3</sup>) where pentachlorophenol has been used extensively as an herbicide and wood preservative. A Canadian study (Cessna et al. 1997) reported the amount of pentachlorophenol in air in Saskatchewan (Regina and Waskesiu) and Northwest Territories (Yellowknife). The concentrations of pentachlorophenol in the vicinity of Yellowknife ranged from 0.43 to 3.68 ng/m<sup>3</sup>, with a mean concentration of 1.53 ng/m<sup>3</sup>. At both the Regina and Waskesiu sites, the concentrations ranged from 0.06 to 0.58 ng/m<sup>3</sup> with a mean value of 0.30 ng/m<sup>3</sup>.

**6.4.2 Water**

Of 497 surface water observations in EPA's STORET database as of March 1979, 82% were at the detection limit; 84% of the remaining observations fell between 0.1 and 10 µg/L, with a total range of 0.01–100 µg/L (EPA 1979b). These data imply that ambient levels of pentachlorophenol in surface water are usually below 1 µg/L, with much higher levels in more industrialized areas.

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Pentachlorophenol levels monitored in surface water include the following: 0.1–0.7 µg/L in the Willamette River (Buhler et al. 1973); 9 µg/L in a river below a paper mill (Rudling 1970); 0.1–1 µg/L in the Great Lakes (EPA 1980f); <1 µg/L in a river at a sewage discharge site in Sacramento, California (Wong and Crosby 1978); 38–10,500 µg/L in a stream running through an industrial district in Pennsylvania (Fontaine et al. 1975); and 0.01–0.48 µg/L in streams in Hawaii (Young et al. 1976).

Pentachlorophenol has also been detected in drinking waters at the following levels: 0.04–0.28 µg/L in Corvallis, Oregon (Buhler et al. 1973); a mean concentration of 0.07 µg/L in 108 samples surveyed by the National Organics Monitoring Survey (NOMS); and <1–800 µg/L (an average of 227 µg/L) in seven drinking water wells in Oroville, California (Wong and Crosby 1978).

Pentachlorophenol was detected in raw effluent from a series of wood-treatment plants at levels ranging from 25,000 to 150,000 µg/L (Dust and Thompson 1972) and in influent (1–5 µg/L) and effluent (1–4 µg/L) at streams at a sewage plant in Corvallis, Oregon (Buhler et al. 1973). The compound has also been detected (concentrations unspecified) in surface water and groundwater samples taken at a wood-treatment facility in Arkansas (McChesney 1988), in the surface water (68 µg/L) at a wood-treatment facility in Louisiana (ATSDR 1995), in groundwater (up to 19,000 µg/L) at a wood-preserving site in South Carolina (ATSDR 1993a), in groundwater (0.6 µg/L) at an inactive landfill in Florida (ATSDR 1993b), and in groundwater (up to 4,300 µg/L) at Camilla Wood Preserving Company, Camilla, Georgia (Anonymous 1999).

#### 6.4.3 Sediment and Soil

Although several investigators (Fontaine et al. 1975; Pierce and Victor 1978) refer to possible soil contamination as a source of pentachlorophenol levels in water samples, very little data are available on actual measurements of pentachlorophenol in soil. Arsenault (1976) reported pentachlorophenol concentrations of 3.4–654 ppm in soil within 12 inches of treated utility poles. Pentachlorophenol was detected in the soil samples taken from a depth of 0–3 inches at (320–2,300 µg/kg) and in subsurface soil (820–200,000 µg/kg) at a wood-treatment facility, a NPL site, in Louisiana (ATSDR 1995). It was also found in soil at an inactive landfill in Florida, also a NPL site, at a maximum concentration of 21,000 µg/kg (ATSDR 1993b). Pentachlorophenol was found in on-site (up to 13,000 µg/kg) and off-site (up to 1,300 µg/kg) soil samples from the Camilla Wood Preserving Company in Camilla, Georgia (Anonymous 1999).

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**6.4.4 Other Environmental Media**

Levels of pentachlorophenol in food are examined as a part of FDA's ongoing food monitoring studies. In 1973–1974, 10 out of 360 composite food samples contained pentachlorophenol at 10–30 ppb: 1 in dairy products, 1 in cereals, 1 in vegetables, and 7 in sugar (Manske and Corneliussen 1976). In the next year, 13 out of 240 composites contained pentachlorophenol (10–40 ppb), again mostly in sugars (Johnson and Manske 1977). Pentachlorophenol was detected in all of a series of random samples of Florida food at levels of 1–1,000 ppb, principally in grain products (Dougherty and Piotrowska 1976). Pentachlorophenol was also detected at low levels in peanut butter (1.8–62  $\mu\text{g}/\text{kg}$ ) and chicken (6–12  $\mu\text{g}/\text{kg}$ ) (Farrington and Munday 1976).

Pentachlorophenol concentrations in fish tissue for the years 1976–1979, reported in EPA's STORET database, ranged from below the limit of detection to 50 mg/kg. Mean concentrations by region were as follows: Lake Michigan, 0.002 mg/kg; lower Mississippi, 0.478 mg/kg; Pacific Northwest, 16.38 mg/kg; Alaska, 5.0 mg/kg; Western Gulf, not detected; and south central lower Mississippi, not detected (EPA 1979b).

Levels of pentachlorophenol ranging from 10 to 270  $\mu\text{g}/\text{L}$  were reported in 9 out of 65 samples of children's paints in the Netherlands (Van Langeveld 1975).

Another study (Thompson et al. 1997) estimated the amount of pentachlorophenol in the atmosphere by measuring the amount of pentachlorophenol in pine needles. The lipid coating of pine needles has been shown to absorb contaminants from the atmosphere and, therefore, measurement of pollutants in pine needles provides an indirect way of estimating the atmospheric pollutants. The pentachlorophenol concentrations in the vicinity of a utility pole storage site were found to range from 29 to 570 ng/g of the needles. In comparison, pentachlorophenol concentration in the pine needles from sites further away from the pole storage locations was found to be  $<0.5$  ng/g.

It should be noted that most of the data discussed above are 13–17 years old (more recent data are not available). Use of pentachlorophenol has decreased in the intervening years because of restrictions placed on its use. Therefore, levels of pentachlorophenol found in other environmental media have presumably decreased since the time these data were published.

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**6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

Humans may be exposed to pentachlorophenol in occupational settings through inhalation of contaminated workplace air and dermal contact with the compound or with wood products treated with the compound. General population exposure may occur through contact with contaminated environmental media, particularly in the vicinity of hazardous waste sites. Important routes of exposure appear to be inhalation of contaminated air, ingestion of contaminated groundwater used as a source of drinking water, ingestion of contaminated food and soils, and dermal contact with contaminated soils or products treated with the compound.

Before being regulated as a restricted-use pesticide, pentachlorophenol was used extensively in treating wood. Today, this use is restricted to the treatment of utility poles, railroad ties, and wharf pilings where it is widely used. Dermal exposure to pentachlorophenol by members of the general population may occur upon contact with these wood products. Since pentachlorophenol is readily absorbed through skin (Qiao et al. 1997; Wester et al. 1993), this represents a relevant route of low level exposure. Pentachlorophenol is known to volatilize from treated wood products (Bunce and Naki 1989) at a rate that is temperature-dependent (Ingram et al. 1986), and low level inhalation exposure may also occur with increased levels expected during the summer months. In older residences constructed with treated wood products, inhalation of contaminated indoor air may also be an important source of exposure. A reduction in volatilization of pentachlorophenol by coating the treated wood surfaces with varnishes and epoxy coatings was demonstrated by Ingram et al. (1986). In past years, pentachlorophenol has been detected in human adipose tissue, blood, and urine.

Data have been collected on pentachlorophenol levels in human urine, blood, adipose tissue, and cerebrospinal fluid for both occupational and nonoccupational groups. While levels are much higher in occupationally exposed groups, tests on the general population consistently show evidence of low-level exposure. In an FDA study in Florida, Cranmer and Freal (1970) found an average pentachlorophenol urine level of 4.9 µg/L in the general population, compared with 119.9 µg/L in carpenters, boat builders, and spraymen. A range of 1,100–5,910 µg/L in the urine of Japanese pest control operators exposed to pentachlorophenol, compared with 10–50 µg/L in nonexposed workers was cited by Bevenue and Beckman (1967). A comparison of results from a study in Hawaii on pentachlorophenol in urine of three groups (occupational, nonoccupational, and a mixed population) was done by Bevenue et al. (1967). The pentachlorophenol level of 1,802 µg/L in the occupationally exposed population was almost 50 times higher than the nonoccupational group level of 40 µg/L. Hill et al. (1989) detected pentachlorophenol in

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100% of urine samples taken from 197 children in Arkansas at a median concentration of 14 µg/L. Ninety-seven of these children lived in the vicinity of a herbicide plant while the remaining one hundred were part of a control group of children who lived elsewhere. No difference was observed in the amount of pentachlorophenol detected in the urine samples of these two groups. Pentachlorophenol was also found in 100% of urine samples taken from 50 members of the general population of Barcelona, Spain, at a mean concentration of 25 µg/L (Gómez-Catalán et al. 1987).

An analysis of the urine samples of 1,000 adults residing in the United States detected pentachlorophenol in 64% of the samples (Hill et al. 1995). The adults tested were a subset of those participating in the National Health and Nutrition Examination Survey (NHANES III). The median pentachlorophenol concentration in urine was found to be 1.5 ng/mL. A Canadian study compared results from urine analysis studies of nonoccupationally exposed individuals residing in Saskatchewan, Canada, a region with little lumber industry. In the first study with normal healthy individuals, performed in September 1992, 100% of the samples analyzed were found to contain detectable amounts of pentachlorophenol with a median concentration of 1.3 ng/mL (Thompson and Treble 1994). A subsequent study, performed in January 1995, also detected pentachlorophenol in 100% of the urine samples (Thompson and Treble 1996). The median concentration in this latter study was 0.5 ng/mL. A third urinary analysis study of nonoccupationally exposed individuals residing in Saskatchewan also detected pentachlorophenol in 94% of the urine samples at a median concentration of 0.5 ng/mL (Treble and Thompson 1996).

Among a group of 16 patients with neurological symptoms, pentachlorophenol was detected in blood serum and cerebrospinal fluid using a gas chromatograph with electron capture detection technique. Mean concentrations in these media were 22 µg/L (range, 4–60 µg/L) and 0.75 µg/L (range, 0.24–2.03 µg/L), respectively. Three people in the study group who reported contact with wood preservative products had the highest serum levels of pentachlorophenol. Cerebrospinal fluid levels were not correlated with serum levels or cerebrospinal protein levels (Jorens et al. 1991).

The National Health and Nutrition Examination Survey II (NHANES II) and the National Human Adipose Tissue Monitoring Survey (NHATS) analyzed blood and urine specimens from approximately 6,000 persons between the ages of 12–74 years in 64 communities throughout the United States for the presence of a number of compounds, including pentachlorophenol, during the period of 1976–1980. The initial results of the survey indicated that pentachlorophenol was detected in about 79% of urine samples tested (Murphy et al. 1983), and that pentachlorophenol-related phenols were also detected at lower frequencies. The mean pentachlorophenol value in urine samples tested during 1976–1979 was 6.3 µg/L

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with the maximum level of 193  $\mu\text{g/L}$  (Kutz et al. 1978). Pentachlorophenol measured in urine was considered to be the result of exposure to pentachlorophenol, lindane, and hexachlorobenzene. More recent results of NHANES II indicate that pentachlorophenol was found in 71.6% of the urine samples collected from the general population at an estimated geometric mean concentration of 6.3  $\text{ng/mL}$ . These results suggest that, during 1976–1980, almost 119 million individuals from the general population were exposed to pentachlorophenol. Males were found to have higher percentage quantifiable levels of pentachlorophenol and higher geometric mean concentrations in urine than females (Kutz et al. 1992). In a study of workers exposed to pentachlorophenol in the wood-preserving industry, Arsenault (1976) reported pentachlorophenol levels of 120–9,680  $\mu\text{g/L}$  in urine, with a mean concentration of 1,683  $\mu\text{g/L}$ . In another study, Ferreira et al. (1997) compared the concentration of pentachlorophenol in the urine and blood of a group of workers occupationally exposed to pentachlorophenol at a wood-transformation unit to those of a control group with no known exposure to pentachlorophenol. The mean level of pentachlorophenol in the occupationally exposed group was found to be 1,197 and 1,273  $\mu\text{g/L}$  in urine and blood, respectively. The mean concentration of pentachlorophenol in the control group was considerably lower at 6.4 and 15.3  $\mu\text{g/L}$  in urine and blood, respectively. The urine samples of wood workers from a wood factory in northern Italy were monitored before work at 8 a.m. and after the work shift at 5 p.m (Colosio et al. 1993a). The results indicated that a greater amount of pentachlorophenol was excreted in the morning (175  $\mu\text{g/L}$ ) than in the evening (106  $\mu\text{g/L}$ ). A subsequent study by Barbieri et al. (1995) obtained similar results from which a half-life of about 10 days was estimated for pentachlorophenol excretion in urine.

A mean pentachlorophenol blood serum level of 420  $\mu\text{g/L}$  was reported for residents of log homes, whereas a mean level of 40  $\mu\text{g/L}$  was reported for members of the general public with no known exposure to the compound. For residents of the log homes, pentachlorophenol serum levels of children were found to average 1.8 times those of their parents. Pentachlorophenol urine concentrations for residents of log homes averaged 69  $\mu\text{g/L}$ , whereas urine levels for the general population were found to be 3.4  $\mu\text{g/L}$ . Inhalation was believed to be the most likely route of exposure to pentachlorophenol in log homes (Cline et al. 1989). Pentachlorophenol was also found in serum samples taken from members of the general population of Barcelona, Spain, at a mean concentration of 21.9  $\mu\text{g/L}$  (Gómez-Catalán et al. 1987). In a separate study of 66 residents of log homes treated with pentachlorophenol in Kentucky, Hosenfeld et al. (1986) reported a geometric mean pentachlorophenol blood serum level of 47.6  $\mu\text{g/L}$  and a geometric mean urine concentration of 21  $\mu\text{g}$  per gram urinary creatinine. Pentachlorophenol was detected in blood and urine of all 66 residents.

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Mean pentachlorophenol blood serum levels in workers using pentachlorophenol or pentachlorophenol-treated materials were found to range from 83 to 57,600  $\mu\text{g/L}$  by Cline et al. (1989). This upper limit is approximately 100 times the value expected from exposure to the threshold limit value (TLV) (Braun et al. 1979). Workers were involved in the construction of log homes, repair of telephone lines, custodial care of log cabin museums, and in various operations in wood-preserved and chemical-packaging facilities. One worker from a chemical-packaging facility, with a whole blood pentachlorophenol level of 23,000  $\mu\text{g/L}$ , died of pentachlorophenol poisoning (Cline et al. 1989).

A mean level of 26.3  $\mu\text{g/kg}$  was found in adipose tissue from the general U.S. population and it was concluded that humans are continuously exposed to low levels of pentachlorophenol from the environment, food supplies, and disinfectants (Shafik 1973). The distribution and bioconcentration of pentachlorophenol in different tissues of humans was investigated by Geyer et al. (1987). By comparing daily intake of pentachlorophenol with tissue concentrations, bioconcentration ratios of 5.7, 3.3, 1.4, 1.4, and 1.0 were obtained in liver, brain, blood, spleen, and adipose tissue, respectively. Pentachlorophenol has also been found in human milk samples from West Germany at 0.03–2.8  $\mu\text{g/kg}$  (Gebefugi and Korte 1983). In a study of human tissues removed at autopsy, including testes, kidney, prostate glands, livers, and adipose tissue, pentachlorophenol was found in all tissues examined at a range of 7 ppb in subcutaneous fat to 4,140 ppb in testes (Wagner et al. 1991).

Based on the pentachlorophenol levels in their 1977 food survey, FDA estimated an average dietary intake of 0.76 mg/day for a typical 15–20-year-old male, and EPA (1978a) calculated an average dietary intake of 1.5 mg/day and a maximum dietary intake of 18 mg/day. However, the actual intake will be lower than estimates because average dietary intakes were based on mean concentration of positive samples. Considering pentachlorophenol levels in fish, peanut butter, food packaging materials, jar lids, etc., the average intake of pentachlorophenol in food has been estimated to be 1.5 mg/day (EPA 1980f). Daily dietary intake of pentachlorophenol from contaminated food has been estimated by another source to be 0.1–6  $\mu\text{g/day}$  (WHO 1987). Using a six-compartment environmental partitioning model, Hattemen-Frey and Travis (1989) reported that the food chain is the most important source of exposure to pentachlorophenol for the general population. They estimated average daily dietary intake of the compound to be 16  $\mu\text{g/day}$  from ingestion of contaminated food, primarily root vegetables.

Pentachlorophenol was detected in 15% of the foods collected in eight market basket surveys from different regions of the United States during the period of April 1982 to April 1984 (Gunderson 1988). Foods representative of the diets of eight different age/gender population groups were prepared for consumption prior to analysis in a revision to FDA's Total Diet Study methodology. Estimated mean



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daily intakes (ng/kg/day) of pentachlorophenol for these groups in 1982–1984 were as follows:

(1) 6–11-month-old infants, 59.0; (2) 2-year-old children, 48.5; (3) 14–16-year-old females, 16.2; (4) 14–16-year-old males, 20.7; (5) 25–30-year-old females, 15.9; (6) 25–30-year-old males, 18.2; (7) 60–65-year-old females, 13.9; and (8) 60–65-year-old males, 15.5. In a later survey of the Total Diet Study, Gunderson (1995a) estimated mean daily intakes (ng/kg/day) of pentachlorophenol for these same eight age/gender population groups during a 1986–1991 study as follows: (1) 6–11-month-old infants, 0.9; (2) 2-year-old children, 1.4; (3) 14–16-year-old females, 0.5; (4) 14–16-year-old males, 0.5; (5) 25–30-year-old females, 0.8; (6) 25–30-year-old males, 0.7; (7) 60–65-year-old females, 0.8; and (8) 60–65-year-old males, 0.8. A substantial reduction in the amount of pentachlorophenol in the estimated mean daily intake has been observed since the 1982–1984 study. In a monitoring program conducted by the Danish National Pesticide Monitoring Program from 1995 to 1996, no pentachlorophenol was detected in the samples of fruits, vegetables, cereals, bran, fish, or animal products such as meats, butter, cheese, fat, and eggs.

In earlier surveys of pentachlorophenol exposure, food was found to be the most important source of intake for members of the general population (Coad and Newhook 1992; Wild and Jones 1992). In a multimedia analysis of pentachlorophenol exposure for the general population of Canada, food sources (mostly dairy products, grains, and cereals) accounted for an estimated 74–89% of the total daily intake of pentachlorophenol. Inhalation exposure, especially of indoor air, accounted for an estimated 10–25% of total daily intake, whereas water and soil/household dust were found to be negligible sources. Daily exposure of recreational fishermen consuming about twice as much fish as members of the general population was estimated to be only about 2% higher than that of the general population. However, lifetime dietary intakes of pentachlorophenol for aboriginal subsistence fishermen, relying on traditional diets of fish and fish products were estimated to be about twice those of members of the general Canadian population (Coad and Newhook 1992). In the United Kingdom, dietary sources are believed to account for greater than 90% of the estimated total daily intake of 5.7  $\mu\text{g}$  pentachlorophenol/day by members of the general population. This value is considerably smaller than the 39  $\mu\text{g}/\text{day}$  estimate for occupationally-exposed individuals. Inhalation is believed to be the most important route of exposure in workplace settings (Wild and Jones 1992). In a study that used the clearance concept to estimate net daily intake (i.e., net daily intake=clearance times average steady state concentration in plasma), the net daily intake of pentachlorophenol for members of the general U.S. population not specifically exposed to the compound was estimated to be 12.3–135.9  $\mu\text{g}/\text{day}$ . For members of the general U.S. population residing in log homes, net intake was estimated to be 140–157  $\mu\text{g}/\text{day}$ . Daily intake estimates for occupationally-

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exposed individuals varied widely depending on the type of work involved; estimates ranged from 35 to 24,000  $\mu\text{g}/\text{day}$  (Reigner et al. 1992a).

The National Organic Monitoring Survey conducted in 1976 found pentachlorophenol residues in 86 of 108 drinking water samples, with a mean of 0.07  $\mu\text{g}/\text{L}$  and a maximum of 0.7  $\mu\text{g}/\text{L}$  (EPA 1978a); however, the median concentration was less than 0.01  $\mu\text{g}/\text{L}$ , the minimum detectable limit. In another survey, pentachlorophenol was detected at 1.3–12.0  $\mu\text{g}/\text{L}$  in 8 out of 135 systems surveyed (EPA 1980a, 1980c). Assuming an intake of 2 L of drinking water/day, exposure for most people would be less than 0.02  $\mu\text{g}/\text{day}$ , while the maximum exposure would be 24  $\mu\text{g}/\text{day}$ .

Inhalation of estimated ambient levels of pentachlorophenol in the atmosphere has an associated exposure level of 6  $\mu\text{g}/\text{day}$  for the general population (EPA 1980f). Subpopulations in the vicinity of pentachlorophenol sources and workers may be exposed to significantly higher levels. For example, workers in the vicinity of a cooling tower may have been exposed to 14.4 mg pentachlorophenol/day, and those in wood-treatment plants may have been exposed to 0.9–14 mg pentachlorophenol/day (EPA 1980f). Pentachlorophenol levels in the air of an experimentally treated room varied greatly (1–160  $\mu\text{g}/\text{m}^3$ ) with temperature and ventilation (Gebefugi et al. 1976).

Pentachlorophenol was detected at a geometric mean concentration of 0.080 ng/L in 62 of 63 air samples taken in 21 log homes treated with the compound. The homes, all located in Kentucky, were categorized into six treatment types: (1) "never treated"; (2) external treatment; (3) manufacturer treated; (4) treated and sealed; (5) treated, sealed, and neutralized; and (6) treated and neutralized. Concentrations in "never treated" homes, which were lower than those in treated homes, were believed to be the result of the application of pentachlorophenol to logs during storage to prevent fungal growth. Treated logs were found to be the source of pentachlorophenol in indoor air; air concentrations were highly correlated with pentachlorophenol concentrations in wood cores (geometric mean, 15,900 ng/g wood) and log surface wipes (geometric means, 89.6 and 187 ng/100  $\text{cm}^2$ ) (Hosenfeld et al. 1986). Concentrations of pentachlorophenol in older structures built with pressure-treated wood brushed with pentachlorophenol were reported to range from 0.5 to 10  $\mu\text{g}/\text{m}^3$  (EPA 1984b). Use of sealers decreased this concentration by 85%. Indoor air interiors of structures built with industrially dipped nonpressure-treated wood were reported to contain levels of pentachlorophenol that ranged from 34 to 104  $\mu\text{g}/\text{m}^3$  (EPA 1984b). Logs used for home construction are no longer treated with pentachlorophenol. Pentachlorophenol in air samples taken from 75 rooms in 30 buildings with suspected use of pentachlorophenol-containing wood

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preservatives in Germany ranged from <0.03 to 576 ng/m<sup>3</sup>. Pentachlorophenol in the dust samples taken from the same sites ranged from 0.083 to 79 ng/kg (Schnelle-Kreis et al. 2000).

Dermal absorption is another potential exposure pathway. Pentachlorophenol is readily absorbed through skin (Qiao et al. 1997; Wester et al. 1993). EPA (1984) has assumed a dermal absorption efficiency in humans of 50% for pentachlorophenol in organic solvents and 10% for an aqueous solution of sodium pentachlorophenate. Dermal exposure is potentially an occupational problem; the general public is not expected to be exposed to pentachlorophenol via dermal contact. Santodonato (1986) suggested that dermal contact is the most important route of occupational exposure to pentachlorophenol because of the manner in which the compound is used (i.e., manual handling of solutions and treated materials) and its low vapor pressure. Workers such as carpenters, lumberyard workers, and loading-dock laborers who handle treated materials could be exposed continually via this route as well as by inhalation. The potential for dermal exposure to pentachlorophenol at hazardous waste sites is unknown.

The National Occupational Hazard Survey (NOHS), conducted by the National Institute for Occupational Safety and Health (NIOSH), estimated that 179,243 workers in 22,347 plants were potentially exposed to pentachlorophenol in the workplace in 1970 (NIOSH 1976). The largest numbers of exposed workers were employed in the following fields: general building contractors; special trade contractors; chemicals and allied products industries; electric, gas, and sanitary services; and medical and other health services industries.

Preliminary data from a second workplace survey, the National Occupational Exposure Survey (NOES) conducted by NIOSH from 1980 to 1983 indicated that 26,463 workers (including 3,916 women) in 1,490 plants employed in lumber and wood products, business services, wholesale trade, general building contractors, and chemicals and allied products industries were potentially exposed to pentachlorophenol in the workplace in 1980 (NIOSH 1984a). Most of these workers were pest controllers, electrical power installers and repairers, laborers, assemblers, carpenters, miscellaneous precision workers, janitors, engineers, and engineering technicians.

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**6.6 EXPOSURES OF CHILDREN**

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in 3.7 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Children are likely to be exposed to pentachlorophenol via the same routes that affect adults, such as inhalation of contaminated air, ingestion of contaminated groundwater used as a source of drinking water, ingestion of contaminated food, and dermal contact with contaminated soils or products treated with the compound. In addition, small children are more likely than adults to come into intimate contact with yard dirt, lawns, and house (carpet) dust. Dislodgeable pesticide residues in carpets or on uncovered floors may present a relatively important exposure route for infants and toddlers through dermal contact and oral ingestion. The tendency of young children to ingest soil, either intentionally through pica or unintentionally through hand-to-mouth activity, is well documented. These behavioral traits can result in ingestion of pentachlorophenol present in soil and dust. Though pentachlorophenol is known to: (1) adsorb to soil, especially at lower pH (Chang and Choi 1974; Choi and Aomine 1974; Kuwatsuka and Igarashi 1975); (2) have an insignificant rate of volatilization from soil (Kilzer et al. 1979); and (3) biodegrade at a moderately rapid rate, very little data are available on the actual measurements of pentachlorophenol in soil. No studies are available that describe the dermal absorption of pentachlorophenol in children. Two studies are available, however, that show that absorption of pentachlorophenol occurs in both Rhesus monkeys and swine when dermally exposed to soil amended with pentachlorophenol (see Section 3.4.1.3). Therefore, it is possible that children may absorb pentachlorophenol dermally when exposed to soil contaminated with pentachlorophenol.

Hill et al. (1989) compared the amounts of chlorinated phenols and phenoxy acids found in the urine of 97 children living in the vicinity of a herbicide manufacturing plant to those found in the urine of a

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control group of 100 children living away from the herbicide plant. There was no significant difference in the amounts of pentachlorophenol or other herbicide residues detected in the two groups with the median pentachlorophenol concentration of 14 µg/L. This insignificant difference in the amounts of pentachlorophenol between the two groups indicated that the children living in the vicinity of the herbicide plant were not at a greater risk of exposure. Cline et al. (1989) measured the pentachlorophenol in the serum and urine of adults and children living in pentachlorophenol-treated log houses. The pentachlorophenol serum levels of children were found to average 1.8 times those of their parents. The mean concentrations were: (1) 2–5-year-old children, 600 µg/L; (2) 6–10-year-olds, 490 µg/L; (3) 11–15-year-olds, 370 µg/L; and (4) adults, 310 µg/L. The higher concentration of pentachlorophenol detected in children was attributed to their greater body surface-to-weight ratio and a higher respiratory rate as compared to adults. An East German study (Rehwagen et al. 1999), comparing urban versus rural exposure, detected a lower concentration of pentachlorophenol in the urine of children from the city of Leipzig than in the urine of children from the towns of Hettstedt, Wippra, Roitzsch, and Greppin. Although the inhalation of house dust was a possible source of exposure to pentachlorophenol, no correlation could be established between the amount of pentachlorophenol detected in the urine and the amount of pentachlorophenol in the house dust.

Pentachlorophenol was used extensively in treating wood. Today, though no longer used in treatment of wood products in residences and agricultural buildings, pentachlorophenol is still widely used in the treatment of utility poles and railroad ties. Playing near a utility pole such as a telephone or an electrical pole may pose a risk of dermal exposure. Pentachlorophenol is also known to volatilize from treated wood (Bunce and Nakai 1989) with emissions expected to be highest in the hottest months of the summer (Ingram et al. 1986). Therefore, low-level inhalation exposure may occur for children playing nearby. The soil samples, within a distance of 8 inches from the utility poles, were found to have a higher concentration of pentachlorophenol relative to those further away, indicating that leaching is occurring from their bases (Weinberg 1997). This indicated a downward migration of pentachlorophenol down the poles, which would result in a higher concentration in the lower sections. Higher than expected dermal exposure of children may, therefore, also occur since children may touch the lowest sections of utility poles while playing. Old and unpainted playground equipment constructed with pentachlorophenol-treated wood may be another mode of dermal exposure for children.

Lewis et al. (1994) conducted a nine-home pilot study to monitor the potential exposure of small children to pesticides in the residential environment. Pentachlorophenol was found to be one of the most frequently occurring pesticides and was detected in all of the samples in all nine houses irrespective of the

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age of the house (year of construction ranged from 1930 to 1989). The mean concentration of pentachlorophenol reported by the authors at various sites around a house is as follows: entryway soil, 0.03 µg/g; walkway soil, 0.02 µg/g; and play area soil, 0.02 µg/g. It was also detected in house dust, 0.83 µg/g; child hand rinse, 0.02 µg; and air, 0.05 µg/m<sup>3</sup>. No attempts were made by the authors to estimate the amounts of carpet dust or soil that the children who participated in the study may have ingested. The authors concluded that dust ingestion could constitute a substantial portion of a child's exposure to pesticides along with dermal absorption from house dust or yard soil.

A potential source of exposure in infants is the presence of pentachlorophenol in breast milk or formula. No data were located on the presence of pentachlorophenol in breast milk in the United States. However, in a study from Upper Bavaria, Gebefugi and Korte (1983) detected pentachlorophenol in 100% of the samples of breast milk, with a median concentration of 1.43 µg/kg. No significant sources of pentachlorophenol exposure were identified. In a more recent study from Bratislava, Slovakia (a city with a highly concentrated chemical industry and intensive agriculture), human milk obtained from 50 mothers was analyzed for the presence of chlorophenols (Veningerova et al. 1996). The median concentration of pentachlorophenol was found to be 2.21 µg/kg. The main source of pentachlorophenol exposure was through the ingestion of contaminated foods. No pesticide residues (including pentachlorophenol) were detected in ready to serve milk-based infant formula, with and without iron (Gunderson 1995b; Yess et al. 1993).

Van Langeveld (1975) reported levels of pentachlorophenol ranging from 10 to 270 µg/L in 9 out of 65 samples of children's paints in the Netherlands. It is not known whether these paints are imported into the United States. No data were available about the presence of pentachlorophenol in children's paints made in the United States.

Percutaneous pentachlorophenol absorption from the pentachlorophenol used in the laundry can be a significant source of pentachlorophenol exposure in infants. Smith et al. (1996) reported an occurrence of pentachlorophenol poisoning in newborn infants in St. Louis, Missouri during April–August 1967. The infants were exposed to pentachlorophenol through the diapers, which were rinsed in the hospital laundry room with an anti-mildew agent containing 22.9% sodium pentachlorophenate. Pentachlorophenol has, since then, been regulated as a restricted-use pesticide. It is not likely to be used in the laundry today.

Foods representative of the diets of eight different age/gender population groups, including children (6–11-month-old infants, 2-year-old children, and 14–16-year-old males and females), were prepared for

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consumption prior to analysis in a revision to the FDA's Total Diet Study methodology (Gundersen 1988). Estimated mean daily intakes (ng/kg/day) of pentachlorophenol for children in 1982–1984 were as follows: (1) 6–11-month-old infants, 59.0; (2) 2-year-old children, 48.5; (3) 14–16-year-old females, 16.2; and (4) 14–16-year-old males, 20.7. In comparison, the intake for adults ranged from 15.5 to 18.2 ng/kg/day. In a later survey of the Total Diet Study during 1986–1991, Gundersen (1995a) estimated mean daily intakes (ng/kg/day) of pentachlorophenol for these population groups as follows: (1) 6–11-month-old infants, 0.9; (2) 2-year-old children, 1.4; (3) 14–16-year-old females, 0.5; (4) 14–16-year-old males, 0.5; and (5) 25–30-year-old females, 0.8. In comparison, the intake for adults ranged from 0.7 to 0.8 ng/kg/day. A substantial reduction in the amount of pentachlorophenol in the estimated mean daily intake has been observed since the 1982–1984 study. No data are available for the exposure to and the effect of pentachlorophenol through specific food sources such as fish, animal products, cereals, etc. FDA also tested the presence of pesticide residues in a variety of infant and adult foods eaten by infants and children (Yess et al. 1993). Since whole and unpeeled fruits and vegetables were tested, the results were not indicative of pesticide residues in foods as consumed. Pentachlorophenol was found in plain milk (6.5% of the samples, maximum residue of 100 ppb), vitamin D milk (3% of the samples, maximum residue of 20 ppb), pork (7% of the samples, maximum residue of 6 ppb), grape jelly (4% of the samples, maximum residue of 4 ppb), raw pears (4% of the samples, maximum residue of 7 ppb), and in canned, evaporated milk (7% of the samples, maximum residue of 7 ppb). No data are available on children and their weight-adjusted intake of pentachlorophenol.

The children of pesticide applicators who use pentachlorophenol may potentially be exposed to elevated levels from contact with their parents' skin, hair, work clothes, and/or other workplace objects. In addition, pentachlorophenol adsorbed onto the parent or the parent's clothing may contaminate household objects when they come in contact with them, potentially exposing children to pentachlorophenol. Although pentachlorophenol is a restricted-use pesticide and is only supposed to be used by an EPA-certified applicator for specified uses, there have been instances in which children were exposed to pesticides (methyl parathion) from the illegal application of pesticides. No monitoring data are available on this route of exposure to pentachlorophenol.

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**6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES**

Pentachlorophenol levels in human tissues are much higher in occupationally exposed groups than in the general public. Populations with potentially high exposure include individuals involved in the manufacture and use of the compound. Residents near pentachlorophenol manufacturing plants and waste water treatment sludge disposal sites may also be exposed to the chemical at higher concentrations than the general public. Residents around the 313 NPL sites known to have pentachlorophenol contamination may also be exposed to the chemical at higher levels ( $>1,000 \mu\text{g}/\text{kg}$ ) in contaminated environmental media.

Pentachlorophenol is found as a residue in treated wood that has been preserved with this chemical. Examples of consumer items containing pentachlorophenol-treated wood have included boats, furniture, and log homes. In fact, some families living in homes historically treated with pentachlorophenol have been reported to have symptoms of chronic exposure (Jagels 1985). Since the compound is no longer used in the treatment of wood products for log homes, outdoor furniture, or playground equipment, human exposure from these sources is probably limited to contact with materials treated in the past.

**6.8 ADEQUACY OF THE DATABASE**

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of pentachlorophenol is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of pentachlorophenol.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.



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**6.8.1 Identification of Data Needs**

**Physical and Chemical Properties.** The physical/chemical properties of pentachlorophenol are well characterized and allow the prediction of the environmental fate of the compound (see Chapter 4). Estimates of the distribution of pentachlorophenol in the environment based on available constants (e.g., water solubility, Log  $K_{ow}$ , Log  $K_{oc}$ , vapor pressure) are generally in good agreement with experimentally determined values. No additional studies are required at this time.

**Production, Import/Export, Use, Release, and Disposal.** Pentachlorophenol is currently being produced by only one manufacturer (SRI 1998). Current production volume data are not available; however, it is known that production volumes steadily decreased from 45 million pounds in 1983 (Mannsville 1987) to 9.1 million pounds in 1996 (IARC 1999). No recent data are available on the production, export, and use volumes of pentachlorophenol. In the past, pentachlorophenol was one of the most heavily used pesticides in the United States but is now regulated as a restricted use pesticide (CELDS 1992; EPA 1984b). The compound is found in all environmental media (air, soil, and water) as a result of its past widespread use. The only disposal method located in the literature is incineration, which releases polychlorinated dibenzo-*p*-dioxins and dibenzofurans at unspecified levels (Karasek and Dickson 1987). Disposal of pentachlorophenol is subject to EPA restrictions (EPA 1991, 1992).

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The TRI, which contains this information for 1999, became available in 2001. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

**Environmental Fate.** Information on environmental fate of pentachlorophenol is sufficient to permit a general idea of transport and transformation of the chemical in the environment. Atmospheric or vapor-phase pentachlorophenol is expected to photolyze at an estimated (midday in summer at 40 EN) maximum rate of 6.2% per hour, and to degrade through reactions with hydroxyl radicals at an estimated (midday in summer) loss rate of 1.5% per hour (Bunce and Nakai 1989). Meylan and Howard (1993) estimated a half-life of 58 days for the vapor-phase reaction of pentachlorophenol with hydroxyl radicals. However, the data need still exists for actual rates of vapor-phase photolysis and atmospheric degradation due to hydroxyl radical attack. Volatilized pentachlorophenol may also be lost from the atmosphere through deposition. The compound is expected to partition to soils and sediment (Kuwatsuka and Igarashi 1975), and to be transported in surface water and groundwater (Davis et al. 1994; Mohammed et al. 1998).

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Pentachlorophenol is transformed by photolysis in water, with half-lives of 3.5 hours (pH 7.3) to 100 hours (pH 3.3) under UV light and a half-life of 48 hours (pH 7.3) in sunlight (Wong and Crosby 1981). Aqueous photolysis of the compound occurs more rapidly at the water surface (half-life of 0.7 hours at 0.5-cm depth), with attenuated rates occurring at greater depths in the water column (half-life of 9.6 hours at 13.8-cm depth; Pignatello et al. 1983). Pentachlorophenol does not photolyze to a significant extent in soils, but may be photolyzed at the soil surface (top 0.5 mm) when near-saturated conditions exist; total degradation in near-saturated irradiated soils was 55% greater than in the dark controls (Donaldson and Miller 1997). Additional information on soil photolysis rates at various soil moisture contents may be helpful in determining the potential for degradation of the compound at sites with pentachlorophenol-contaminated areas which are flooded intermittently. A more important mechanism for the transformation of pentachlorophenol in soils is the adsorption of the compound to soil mineral particles and soil organic matter. Pentachlorophenol is a weakly acidic compound (pKa of 4.74) that is adsorbed to the largest extent under acidic soil conditions (where it is present in the unionized form which it is less soluble in water), and has greater mobility in neutral or alkaline soils where it is present as the phenolate anion (Kuwatsuka and Igarashi 1975). Maximum adsorption has been reported at soil pH values of 4.6–5.1, with no adsorption above pH 6.8; at a given pH, adsorption increases with increasing organic matter content (Choi and Aomine 1974). In aquifers, the retardation or decreased mobility of the compound has been observed to be greater in areas of lower pentachlorophenol concentrations (<0.04 mg/L) than in areas of high concentrations (>1 or 10 mg/L; Davis et al. 1994). Although it was determined in previously conducted studies of natural sediments and aquifer materials that the adsorption of pentachlorophenol was highly dependent on the organic matter content of the adsorbent, with an average  $K_{oc}$  of 32,900 measured (Schellenberg et al. 1984), the use of normalized partition coefficients ( $K_{oc}$ ) do not accurately predict the adsorption of ionizable compounds such as pentachlorophenol since the adsorption of such does not increase linearly with the increasing concentration of the compound (Christodoulatos et al. 1994). For this reason, the need exists for a more accurate means of measuring and/or interpreting the potential mobility of pentachlorophenol in aquifers and in surface soils which are either intermittently subjected to flooding or are in contact with overland runoff. Because the presence of alcohols and petroleum compounds such as oils and kerosene (all of which are utilized as cosolvents in the application of pentachlorophenol) may decrease the adsorption of pentachlorophenol in soils (Christodoulatos et al. 1994; Jackson and Bisson 1990), and because pentachlorophenol has also been observed to desorb more readily from contaminated soils in the presence of compounds such as methanol (You and Liu 1996), there is a need for data that indicate the potential mobility of pentachlorophenol when it is present in the soil or water in combination with such cosolvents. Additionally, data are necessary on the adsorption of pentachlorophenol when it is present in combination with other

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contaminants expected to occur in the same environment. Biodegradation is another major mechanism for the transformation of pentachlorophenol in the environment (Englehardt et al. 1986; McAllister et al. 1996; Pignatello et al. 1983). In water, pentachlorophenol may be biodegraded with observed first half-lives of less than 1 month following acclimation periods of 5–7 weeks; the presence of sediment generally decreases the acclimation period (Ingerslev et al. 1998; Pignatello et al. 1985). The biotransformation of pentachlorophenol in groundwater, and possibly in surface water may not be significant in the absence of nonacclimated microbial populations. Decreases in the observed aqueous concentration of the compound may be attributed to adsorption to sediment or particulate material rather than to degradation of the compound (Mohammed et al. 1998). Additional information, such as biodegradation half-lives in both surface water and groundwater, is necessary to evaluate the potential for the degradation of the compound in water that is not in contact with sediment, rock, or macrophyte surfaces and where acclimated microbial populations do not exist. In soils, biodegradation of pentachlorophenol is generally rapid, with half-lives of 2–4 weeks. The metabolism of the compound is more rapid in soils with acclimated microbial populations (Kaufman 1978). Biodegradation of pentachlorophenol and aged residues of the compound occurs in both aerobic and anaerobic soils, usually following an acclimation period, but may occur more completely and rapidly in aerobic soils (Frisbie and Nies 1997). In other studies, biodegradation of the compound was observed to be more rapid in anaerobic environments (Ide et al. 1972; Kuwatsuka and Igarashi 1975). McAllister et al. (1996) reported that there are multiple pathways for the biodegradation of pentachlorophenol, which differ according to the microbial populations present in the soil. While the biodegradation of pentachlorophenol has been studied extensively, there may still be a need for data that elucidate the effect of anaerobic environments (and alternating aerobic/anaerobic environments) on the rate and extent of the degradation of the compound and its metabolites. Additionally, information on the uptake and transformation of the compound in plants is necessary to improve the current understanding of pentachlorophenol's environmental fate; currently existing data on plant uptake and transformation are inconsistent between studies and are inconclusive with regard to the ability of specific plants to remove the compound from the soil (McAllister et al. 1996).

**Bioavailability from Environmental Media.** Pentachlorophenol is readily and completely absorbed following inhalation (Casarett et al. 1969; Cline et al. 1989; Hosenfeld et al. 1986; Jones et al. 1986), oral (Braun et al. 1979; Uhl et al. 1986), and dermal exposure (Hosenfeld et al. 1986; Qiao et al. 1997; Wester et al. 1993). Using Rhesus monkeys, Wester et al. (1993) demonstrated the dermal absorption from pentachlorophenol-treated soil. It was also shown that when [<sup>14</sup>C-UL]-pentachlorophenol in a soil-based mixture was applied occlusively or nonocclusively to a clipped 7.5-cm<sup>2</sup> abdominal site of 8 to 10-week-old female pigs, total radiolabel absorption was 29.08% under nonocclusive conditions and

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100.72% under occlusive conditions 408 hours after dosing (Qiao et al. 1997). Additional information on the bioavailability of pentachlorophenol adsorbed to soils would be helpful in assessing the relative importance of ingestion of contaminated soils as a potential route of human exposure. Additional information is also necessary on the desorption of the compound from soils when the soil pH is altered or when pentachlorophenol-contaminated soil comes into contact with cosolvents (such as alcohols or petroleum compounds), which may enhance desorption and/or increase the solubility of pentachlorophenol. Cline et al. (1989) detected elevated levels of pentachlorophenol in the urine of log-home residents. They believed inhalation to be the most likely route of exposure. Additional information is required to correlate the presence of pentachlorophenol in contaminated air and the exposure via inhalation.

**Food Chain Bioaccumulation.** The log  $K_{ow}$  of pentachlorophenol presented in Chapter 4 is 5.01, suggesting that pentachlorophenol is likely to bioaccumulate. However, the extent of bioaccumulation will depend on the pH of the medium since pentachlorophenol converts at higher pH levels to the more water-soluble pentachlorophenate anion. Pentachlorophenol is bioconcentrated by terrestrial and aquatic organisms (EPA 1986c; Makela et al. 1991; Smith et al. 1990). However, biomagnification of the compound in terrestrial and aquatic food chains has not been demonstrated as a result of the fairly rapid metabolism of the compound by exposed organisms (Niimi and Cho 1983). BCF values of 218 (whole fish) to 1,633 (fish lipid basis) for juvenile American flagfish were demonstrated by Smith et al. (1990). The half-life of pentachlorophenol in the tissues was reported to be about 16 hours. The food chain bioaccumulation potential of pentachlorophenol can currently be characterized without generating additional data.

**Exposure Levels in Environmental Media.** Pentachlorophenol has been detected in ambient air, surface water, drinking water, soils, and foods. Estimates of dietary intake of the compound have been made by the World Health Organization (WHO 1987), EPA (EPA 1978a), and FDA (FDA 1989; Gunderson 1988). In a comparison of the 1986–1991 study to the 1982–1984 study, Gunderson (1995a) observed a substantial reduction in the amount of pentachlorophenol in the estimated mean daily intake. Lewis et al. (1994) detected low levels of pentachlorophenol in air, dust and soil in a nine-home (year of construction ranged from 1930 to 1989) pilot study to monitor the potential exposure of small children to pesticides in the residential environment. Further monitoring is required to be able to evaluate the risk of exposure from pentachlorophenol-treated wood in homes. Limited information is available regarding the levels of pentachlorophenol in air in the United States. More ambient monitoring data of air is required to estimate the exposure of the general population via inhalation of pentachlorophenol in the 1990s.

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Contemporary monitoring studies demonstrating the presence or absence of pentachlorophenol in various sources of surface and drinking water are also needed.

Reliable monitoring data for the levels of pentachlorophenol in contaminated media at hazardous waste sites are needed so that the information obtained on levels of pentachlorophenol in the environment can be used in combination with the known body burden of pentachlorophenol to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Pentachlorophenol has been measured in blood (NHANES III) (Ferreira et al. 1997; NHANES II), urine (Barbieri et al. 1995; Bevenue et al. 1967; Colosio et al. 1993a; Ferreira et al. 1997; Hill et al. 1989, 1995; Thompson et al. 1994, 1996; Treble and Thompson 1996), cerebrospinal fluid (Jorens et al. 1991), and tissues of humans (Bevenue et al. 1967). Quantitative data that correlate varying levels in the environment with levels in body fluids and health effects are not available. One study exists for residents of log homes treated with pentachlorophenol; levels in blood and urine were highly correlated with levels in indoor air (Lewis et al. 1994). Additional information on exposure levels for populations living near hazardous waste sites would be helpful. Information regarding the exposure levels for populations near pentachlorophenol-treated utility poles would be useful. This information is necessary for assessing the need to conduct health studies on these populations.

**Exposures of Children.** No monitoring studies have been performed to investigate the exposure to and the body burden of pentachlorophenol in children. No studies are available on the dermal absorption of pentachlorophenol in infants and toddlers due to activities such as crawling, which will result in contact with the floor (carpet) and soil. Since pentachlorophenol is likely to be adsorbed to these materials, more information would allow the estimation of a child's exposure to pentachlorophenol to be more rigorously determined. A pilot study measured the amounts of pentachlorophenol in dust and soils that are found in areas where children may play, such as carpets and playgrounds (Lewis et al. 1994). As part of the FDA total diet study, mean daily intake of pentachlorophenol by 6–11-month-old infants, 2-year-old children, and 14–16-year-old males and females were determined (Gunderson 1995a). Studies dealing with the weight-adjusted intake of pentachlorophenol by children would help in assessing the effects of pentachlorophenol in children. No studies are available on the amounts of pentachlorophenol present in the breast milk of women in the United States. The estimation of the amounts of soil and house dust that are ingested by children needs to be determined. No information is available on the exposure of

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children to pentachlorophenol from the parent's body, work clothes, and other objects from work. Studies are required to identify childhood-specific means of decreasing exposure to pentachlorophenol.

Child health data needs relating to susceptibility are discussed in 3.12.2 Identification of Data Needs: Children's Susceptibility.

**Exposure Registries.** No exposure registries for pentachlorophenol were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

### 6.8.2 Ongoing Studies

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environment Health Laboratory Sciences Division of the National Center for Environmental Health, Centers for Disease Control and Prevention, will be analyzing human urine samples for pentachlorophenol and other phenolic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.

The U.S. Department of Agriculture is sponsoring several studies on the degradation, adsorption, and uptake of pentachlorophenol. At the Agricultural Research Service, Fargo, North Dakota, research is being conducted to identify and quantitate residues of chlorinated organics (congeners of dioxins, furans, and polychlorinated biphenyls) in beef, milk, and animal feeds, particularly forages. In another study at Ohio Agricultural Research and Development Center, Wooster, Ohio, models for the transport of dioxins that are contained in feed and in other environmental matrices to beef that is intended for human consumption are being developed. At Xenometrix, Inc., research is being focused on the microbial dehalogenation of pentachlorophenol by *Flavobacterium*. Researchers at University of Florida, Gainesville, Florida, are studying the soil processes that regulate the fate of chlorophenols in wetlands. Research is underway at Forest and Wildlife Research Center, Mississippi, to develop a rapid biological technique for cleanup of organic wood preservatives in groundwater using oxygen, surfactants, cofactors, and micronutrients; and to evaluate different commercial surfactants for enhancing the biodegradation of wood-preserving process water containing high concentrations of pentachlorophenol, polyaromatic

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hydrocarbons, oil, and grease. At Texas A&M University, College Station, Texas, research is being conducted to develop a method for dechlorinating pentachlorophenol from contaminated water and soil, and to refine the use of bioassays as monitoring tools to assess the changes in toxicity occurring as a result of remedial activities at Superfund waste sites. At Oregon State University, Corvallis, Oregon, researchers are working on determining the effects of estrogenic environmental pollutants on chemical carcinogenesis using rainbow trout as a model system.

In a study sponsored by the National Institute of General Medical Sciences, at University of Colorado, Boulder, Colorado, research is being performed to determine the mechanism of the enzyme, tetrachloro-hydroquinone dehalogenase, that plays a critical role in biodegradation of pentachlorophenol. A similar study, sponsored by National Science Foundation, investigating the role of tetrachloro-1,4-hydroquinone dehalogenase in the degradation of pentachlorophenol is underway at University of Colorado, Boulder, Colorado. The biochemistry of 2,4,5-trichlorophenoxyacetate and pentachlorophenol is being investigated in a National Science Foundation sponsored study at Washington State University, Richland, Washington.

In addition, ongoing remedial investigations and feasibility studies at NPL sites known to be contaminated with pentachlorophenol should add to the available database for environmental levels, environmental fate, and human exposure.