CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Pentachlorophenol has been identified in at least 328 of the 1,867 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2019). However, the number of sites in which pentachlorophenol has been evaluated is not known. The number of sites in each state is shown in [Figure 5-1.](#page-0-0) Of these sites, 327 are located within the United States, and 1 is located in Puerto Rico (not shown).

Figure 5-1. Number of NPL Sites with Pentachlorophenol Contamination

• Due to its former widespread use, the general population may be exposed to pentachlorophenol via ingestion of drinking water and food, as well as inhalation of air.

• Professional wood treatment applicators applying pentachlorophenol as a wood preservative or employees involved in the manufacture and formulation of pentachlorophenol products are expected to have the greatest exposure, primarily through dermal and inhalation routes.

- Pentachlorophenol production results in the formation of a number of contaminants including CDDs, CDFs, other chlorophenols, hexachlorobenzene, and chlorophenoxy compounds. Technical- and commercial-grade formulations contain varying levels of these contaminants (see Table 2-1 for contaminant levels in several formulations). The formulations used and that people are exposed to are commercial-grade formulations typically consisting of 90% pentachlorophenol.
- The environmental fate of pentachlorophenol is dependent upon the pH of the soil or water. In water and soil, pentachlorophenol is not volatile except under acidic conditions. Pentachlorophenol has greater mobility in soils under neutral or alkaline conditions and has a greater tendency to bioconcentrate under acidic conditions.
- Pentachlorophenol volatilizes from treated wood surfaces.
- Pentachlorophenol is hydrolytically stable and is generally considered moderately persistent under aerobic and anaerobic conditions. It can undergo direct photolysis in sunlit surface waters.
- Pentachlorophenol is a persistent organic pollutant listed in the Stockholm Convention, Annex A.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Pentachlorophenol is produced by the stepwise chlorination of phenols in the presence of catalysts (aluminum trichloride or ferric trichloride) (Pommer and Jaetsch 2012). Outside of the United States, it is also produced by the alkaline hydrolysis of hexachlorobenzene. Typically, commercial-grade pentachlorophenol is 86% pure. Contaminants generally consist of other polychlorinated phenols, CDDs, CDFs, and hexachlorobenzene (HCB), which are formed during the manufacture process (EPA 2008).

Pentachlorophenol is a biocide that was previously broadly used as a fungicide, bactericide, herbicide, molluscicide, algaecide, and insecticide by agriculture and other industries including textiles, paints, oil drilling, and forestry (EPA 2008). It was first registered for use by the U.S. Department of Agriculture (USDA) on December 1, 1950, but is now a restricted use pesticide in the United States, meaning that it can only be applied for certain uses by certified pesticide applicators. According to the National Pesticide Information Retrieval System (NPIRS), only two U.S. corporations (KMG-Bernuth, Inc. and Arbor Preservative Systems, LLC) develop pentachlorophenol-containing products (NPIRS 2021); these products are shown i[n Table 5-1.](#page-2-0)

Table 5-1. Manufacturing Information of Pentachlorophenol-Containing Products

Source: NPIRS 2021

Pentachlorophenol is usually applied to wood as a mixture of pentachlorophenol and a hydrocarbon solution such as No. 2 fuel oil, kerosene, or mineral spirits (EPA 2008).

According to data from the EPA Chemical Data Reporting (CDR), the production volume of pentachlorophenol by KMG Chemicals was 8,434,248 pounds in 2012, 8,314,302 pounds in 2013, 7,633,241 pounds in 2014, and 13,507,112 pounds in 2015 (EPA 2021). This production volume includes domestically manufactured pentachlorophenol as well as imported pentachlorophenol.

[Table 5-2](#page-2-1) summarizes information on U.S. companies that reported the manufacture or processing of pentachlorophenol in 2020 to the Toxic Release Inventory (TRI) (TRI20 2021). TRI data should be used with caution since only certain types of industrial facilities are required to report. This is not an exhaustive list and it contains primarily companies involved in waste disposal or storage of chemicals.

Table 5-2. Facilities that Produce, Process, or Use Pentachlorophenol

Table 5-2. Facilities that Produce, Process, or Use Pentachlorophenol

aPost office state abbreviations used.

bAmounts on site reported by facilities in each state. cActivities/Uses:

- 1. Produce
- 2. Import
- 3. Used Processing
- 4. Sale/Distribution
- 5. Byproduct

7. Formulation Component 8. Article Component

9. Repackaging

6. Reactant

10. Chemical Processing Aid

- 11. Manufacture Aid
- 12. Ancillary
- 13. Manufacture Impurity
- 14. Process Impurity

Source: TRI20 2021 (Data are from 2020)

5.2.2 Import/Export

In 1982, 121,000 pounds of pentachlorophenol were imported to the United States (328,000 pounds were imported in 1980). According to data from the EPA CDR system, 13,507,112 pounds of pentachlorophenol were imported to the United States and 887,551 pounds of pentachlorophenol were exported by KMG Chemicals, Inc. in 2015. These data have not been made available for years 2016– 2020 (EPA 2021).

5.2.3 Use

Pentachlorophenol was one of the most widely used biocides in the United States. It was registered for use by EPA as an insecticide (termiticide), fungicide, herbicide, molluscicide, algicide, and disinfectant, and as an ingredient in antifouling paint (Cirelli 1978), but it has been a restricted-use pesticide since July 1984 (EPA 1984a). Most non-wood preservative uses were cancelled in 1987 (EPA 2008). The only current registered use for pentachlorophenol is as a "heavy-duty" wood preservative (meaning that it is applied via high-pressure cylinders instead of being brushed on); however, its use to treat wood contained in interior settings is prohibited with a few exceptions (e.g., support structures in barns, stables, etc. that

are in direct contact with soil). It is used primarily on treated industrial products such as utility poles, pilings, and railroad ties.

Pentachlorophenol treated wood is not available for sale to the general public. Pentachlorophenol is no longer contained in wood-preserving solutions or insecticides and herbicides available for home and garden use since it is a restricted-use pesticide.

5.2.4 Disposal

As discussed in the EPA Registration Eligibility Decision (RED) for pentachlorophenol, there are two different waste products associated with this substance: wood treated with pentachlorophenol and industrial waste generated by its production and application (EPA 2008). Wood that is to be discarded that was treated with pentachlorophenol is typically land disposed in either construction and demolition landfills, municipal solid waste landfills, or industrial non-hazardous waste landfills. Disposal of wastewaters generated from the production or application of pentachlorophenol are regulated by the Resource Conservation and Recovery Act (RCRA) and are subject to certain restrictions (EPA 1991). For example, many of the reported releases for pentachlorophenol in the TRI are to RCRA Subtitle C landfills which are special landfills under the RCRA that are authorized to accept hazardous waste for disposal and must follow very stringent guidelines for their design and operation (see Section 5.4).

5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ \geq 10 full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes

≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005).

5.3.1 Air

Estimated releases of 102 pounds (~0.0463 metric tons) of pentachlorophenol to the atmosphere from 36 facilities domestic manufacturing and processing facilities in 2020, accounted for about 1% of the estimated total environmental releases from facilities required to report to the TRI (TRI20 2021). These releases are summarized in [Table 5-3.](#page-5-0)

Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use Pentachlorophenola

Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use Pentachlorophenola

^aThe TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

bData in TRI are maximum amounts released by each facility.

cPost office state abbreviations are used.

dNumber of reporting facilities.

eThe sum of fugitive and point source releases are included in releases to air by a given facility.

f Surface water discharges, wastewater treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

9Class I wells, Class II-V wells, and underground injection.

hResource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

i Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

j The sum of all releases of the chemical to air, land, water, and underground injection wells.

kTotal amount of chemical transferred off-site, including to POTWs.

 $RF =$ reporting facilities; $UI =$ underground injection

Source: TRI20 2021 (Data are from 2020)

5.3.2 Water

Estimated releases of 863 pounds (~0.39 metric tons) of pentachlorophenol to surface water from

36 domestic manufacturing and processing facilities in 2020, accounted for about 9.6% of the estimated total environmental releases from facilities required to report to the TRI (TRI20 2021). This estimate includes releases to wastewater treatment and publicly owned treatment works (POTWs) (TRI20 2021). These releases are summarized in [Table 5-3.](#page-5-0)

5.3.3 Soil

Estimated releases of 7,987 pounds (~3.62 metric tons) of pentachlorophenol to soil from 36 domestic manufacturing and processing facilities in 2020, accounted for about 89% of the estimated total environmental releases from facilities required to report to the TRI (TRI20 2021). These releases are summarized in [Table 5-3.](#page-5-0)

5.4 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 pKa 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 et al. 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 or transformation processes for pentachlorophenol in soils.

5.4.1 Transport and Partitioning

The moderately long persistence and its presence in atmospheric samples at remote locations with no known local sources of pentachlorophenol suggests that this substance is susceptible to long-range atmospheric transport (Cessna et al. 1997; Waite et al. 1998). A reported pKa of 4.7 indicates that pentachlorophenol will exist almost entirely as the conjugate base form at typical pH levels found in the environment, and volatilization is expected to be negligible for ionic substances. Pignatello et al. (1983) reported that volatilization loss of pentachlorophenol as vapor and aerosol from treated river water in outdoor manufactured channels was $\leq 0.006\%$ of the initial test concentration. The pH of the water was 7.4–7.6, indicating that >99% was present in the form of the anionic species. 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

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evaporated water) from water (pH unreported), sand (pH 6.8), loam (pH 6.1), and humus (pH 6.9) 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.

Although pentachlorophenol does not volatilize significantly from water or soil surfaces except under acidic (≤pH 5) conditions, it is volatilized from treated wood surfaces. Walls in a closed room that were treated with pentachlorophenol released the chemical into the air, with concentrations reaching 1 μ g/m³ on the first day after treatment and $160 \mu g/m^3$ on the fifth day (Gebefugi et al. 1976). Ingram et al. (1986) studied the volatilization of pentachlorophenol under different temperature, air flow rates, and humidity levels from treated wood formulated with three commercially important solvents (methylene chloride, mineral spirits, and P9 Type A oil). The highest levels monitored occurred in the methylene chloride solvent at elevated temperature and high air flow rates. For example, at a flow rate of 1 L/minute and at 35 $^{\circ}$ C, the average air level of pentachlorophenol in the test chamber was 1,050 µg /m³ using methylene chloride as a solvent, 509 μ g /m³ using mineral spirits, and 74 μ g /m³ using P9 oil (Ingram et al. 1986).

The adsorption or mobility of pentachlorophenol in soils is also pH dependent. 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). The amount of pentachlorophenol adsorbed at a given pH also increases with increasing organic content of the soil (Chang and Choi 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 $K_{\rm oc}$ of 32,900 was measured for pentachlorophenol in lake sediment, river sediment, and aquifer materials.

However, normalized partition coefficients (i.e., K_{∞}) 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 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

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lower concentrations (<40 μ g/L) than at higher ones (>1,000 or 10,000 μ g/L), indicating that pentachlorophenol will move at rates closer to that of the groundwater when present at higher concentrations $(>10,000 \mu g/L)$. 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 $1,000-10,000 \mu g/L$, 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 mg/L. However, mobility in soil was limited, as indicated by the average soil concentration of 3.4 mg/L pentachlorophenol at a distance of 12 inches from the poles.

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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 and Wallnofer 1986).

Veith et al. (1985) demonstrated that chemicals with a log K_{ow} value >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 µg/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 and Grantham1977). 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; polychaeta, 3,830; bluegill sunfish, 13; blue mussel, 324; and eastern oyster, 78 (EPA 1986a). The Japanese Chemicals Inspection Testing Institute (CITI) determined the BCF of pentachlorophenol in carp at two nominal concentrations over the course of an 8-week incubation period (JCHECK 2021).

At an exposure level of 3 μ g/L, the BCF was in the range of 39–116 after 8 weeks and at an exposure level of 0.3 µg/L, the BCF was 45–99. The overall weight of evidence would suggest that pentachlorophenol does not bioconcentrate in aquatic organisms as much as other hydrophobic, chlorinated pesticides and that bioconcentration is expected to be pH dependent with greater accumulation under acidic conditions where the free acid is the dominant species instead of the conjugate base.

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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 μ g/kg, maximum concentrations of the compound in fish tissues were 40 μ g/kg after 50 days and 20 μ g/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).

5.4.2 Transformation and Degradation

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°N; the estimated loss of pentachlorophenol to vapor-phase photolysis was 6.2% per hour. This rate represents the maximum rate at 40°N; 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 $4.7x10^{-13}$ cm³/molecule-second, assuming a peak noon summer hydroxyl radical concentration of $6.2x10^6$ radicals/cm³. Based on the estimated relative rates of photolysis and degradation by hydroxyl radicals, it was concluded that the former process

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would likely be the dominant of the two. It is noted that the estimate by Bunce and Nakai (1989) did not take into account the adsorption of the compound to particulates in the atmosphere. Using the method of Meylan and Howard (1993), a half-life of 9.7 days for the vapor-phase reaction of pentachlorophenol with hydroxyl radicals can be obtained from an estimated rate constant of $5.5x10^{-13}$ cm³/molecule-second and an average hydroxyl radical concentration of $1.5x10^6$ molecule/cm³. Adsorption of pentachlorophenol to particulate matter, however, will attenuate the rate of this process in the atmosphere.

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 1979). 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°C 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. Chi and Huang (2004) found differences in the photodegradation rates of pentachlorophenol between the surface microlayer and subsurface water. The difference in the first-order

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rate constants under natural sunlight was correlated with the dissolved organic carbon enrichment in the surface microlayer. The photodegradation rate decreased with increasing salinity and increased with increasing pH.

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°C. 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 flasks 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. Screening tests indicate pentachlorophenol is not readily biodegradable. Pentachlorophenol at a concentration of 100 mg/L achieved 0% of its theoretical biochemical oxygen demand using an activated sludge inoculum at 30 mg/L and the Japanese MITI test (Organisation for Economic Cooperation and Development [OECD] 301C guideline), indicating that it is not readily biodegradable (JCHECK 2021). Using a standard OECD 301B guideline, pentachlorophenol was not degraded, nor was it degraded using what Martin et al. (2017) considered a more environmentally relevant biodegradation screening test that used a higher inoculum concentration.

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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 hydrosoil (i.e., pond soil/sediment) on the transformation of pentachlorophenol (applied as the sodium salt). The persistence of pentachlorophenol was associated with three 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.

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 and Wallnofer 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 the rate is greater when moisture content is high and soil temperature approaches the optimum for microbial activity (Young and Carroll 1951).

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Biodegradation is considered the major transformation mechanism for pentachlorophenol in soil. Halflives 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°C, 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°C), while losses from inoculated plots were 50–85%.

Pseudomonas biotransformed [14C]-pentachlorophenol rapidly and released radiolabeled carbon dioxide as well as the intermediate metabolites, tetrachlorophenol and TCHQ. 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°C 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-,

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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 and Wallnofer 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 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 that 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 laboratoryscale, 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 that was preexposed to pentachlorophenol at various levels. At concentrations ranging from 10 to 20,000 μ g/L, the acclimation periods were reduced from 8.6–21.1 to 0.1–3.2 days when sediments were amended with preexposed activated sludge compared with activated sludge that 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 \leq 2.2 days; at 74,000 μ g/L, the postacclimation half-life decreased from 80 days to >51.6 days.

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Other Media. Laboratory studies were conducted to determine the effect of artificial light and sunlight on concentrations of pentachlorophenol and CDDs in wood treated with pentachlorophenol (Lamparski et al. 1980). Although CDDs are known to be present in pentachlorophenol products as impurities, formation of OCDD, as well as 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.

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to pentachlorophenol depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of pentachlorophenol in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on pentachlorophenol levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

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.

[Table 5-4](#page-18-0) shows the lowest limit of detections that are achieved by analytical methods in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in [Table 5-5.](#page-18-1)

Table 5-4. Lowest Limit of Detection Based on Standardsa

aDetection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

bDetection limits in air are dependent upon sampling times and volumes.

Table 5-5. Summary of Environmental Levels of Pentachlorophenol Media **Low** High For more information Outdoor air (ng/m³) <LOD 136 Section 5.5.1 Indoor air (ng/m³) <LOD 104,000 Section 5.5.1 Surface water (µg/L) \langle < LOD \langle \rangle < LOD Section 5.5.2 Groundwater (µg/L) \leftarrow LOD 2,060 Section 5.5.2 Drinking water (µg/L) \lt LOD 2,060 Section 5.5.2 Soil (μg/kg) <LOD 654,000 Section 5.5.3 Sediment (µg/kg) \leq LOD \leq 1,480 Section 5.5.3 Food (ppb) \leq LOD 40 Section 5.5.4

 $LOD =$ limit of detection

Detections of pentachlorophenol in air, water, and soil at NPL sites are summarized in [Table 5-6.](#page-18-2)

Table 5-6. Pentachlorophenol Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

aConcentrations found in ATSDR site documents from 1981 to 2019 for 1,867 NPL sites (ATSDR 2019). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

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5.5.1 Air

Limited information is available on the levels of pentachlorophenol in ambient air. EPA (1980b) estimated atmospheric concentrations of pentachlorophenol using air models. A cumulative concentration estimate based on all emission sources was $0.15-136$ ng/m³. 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/m³) where pentachlorophenol has been used extensively as an herbicide and wood preservative.

In a study designed to evaluate the potential exposure of pre-school children to environmental pentachlorophenol, Wilson et al. (2007) measured the levels of pentachlorophenol in the 257 children's homes and daycare centers in North Carolina and Ohio (Wilson et al. 2007). For more than a 2-day period, each child's home, daycare center, indoor air, outdoor air, house dust, soils, food, beverages, hand surfaces, and urine were sampled for pentachlorophenol. Inhalation was presumed to be the predominant route of pentachlorophenol exposure. Pentachlorophenol was detected in >50% of indoor air, outdoor air, and dust samples. The 50th percentile indoor air concentrations of pentachlorophenol were 1.50 ng/m³ in North Carolina homes and 2.14 ng/m³ in Ohio homes. The 50th percentile indoor air concentrations of pentachlorophenol for daycare centers studied in North Carolina and Ohio were 1.1 and 1.32 ng/m³, respectively. The 50th percentile pentachlorophenol air concentrations for outdoor air samples obtained from near North Carolina and Ohio homes were 0.91 and 0.43 ng/m³, respectively. The 50th percentile pentachlorophenol concentrations in outdoor air samples from near the selected North Carolina and Ohio daycare centers were 0.77 and 0.22 ng/m³, respectively (Wilson et al. 2007). Thus, the children were exposed to higher levels of airborne pentachlorophenol in and around their homes than the levels to which they were exposed in their daycare centers (Wilson et al. 2007).

Pentachlorophenol was detected at a geometric mean concentration of 0.080 ng/L (80 ng/m³) in 62 of 63 air samples (range $1-904$ ng/m³) taken in 21 log homes treated with the compound (EPA 1986b). 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 cm2)

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(EPA 1986b). Concentrations of pentachlorophenol in older structures built with pressure-treated wood brushed with pentachlorophenol were reported to range from 0.5 to 10 μ g/m³ (500–10,000 ng/m³) (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 μ g/m³ (34,000–104,000 ng/m³) (EPA 1984b). Logs used for home construction are no longer treated with pentachlorophenol.

Air concentrations ranged from 15 to 30 μ g/m³ (15,000–30,000 ng/m³) at a wood treatment facility in Georgia (ATSDR 2007). The levels in the surrounding residential area ranged from <1.3 to 8.1 μ g/m³ $\left($ <1,300–8,100 ng/m³ $\right)$ (ATSDR 2007).

SPECIATE is EPA's repository of speciation profiles of air pollution sources containing information on the species makeup or chemical composition of organic gases, particulate matter, and other pollutants emitted from these sources. SPECIATE can be used for site assessments and health studies. For additional information, see https://www.epa.gov/air-emissions-modeling/speciate.

5.5.2 Water

Recent water monitoring data can be accessed at EPA's Water Quality Exchange (WQX) through the Water Quality Portal (WQP) (https://www.epa.gov/waterdata/water-quality-data-wqx). These data are provided by submissions from over 400 federal, state, tribal agencies, and other organizations. A search of the national water quality database for STORage and RETrieval (STORET) and National Water Information Systems databases indicated that there were 488 surface water and groundwater samples collected and tested for pentachlorophenol at 244 unique sites in 10 states in 2020–2021. There were no positive detections in groundwater monitoring results, and the only positive detections in surface water monitoring were below the limit of quantification ranging from 0.1 to 0.5 μ g/L (WQP 2021). Thirty-eight U.S. streams were monitored from 2012 to 2014 for 719 compounds; pentachlorophenol was found in 10 streams at $\sim 0.1 \mu g/L$ (Bradley et al. 2017).

Pentachlorophenol was detected in drinking water samples of log homes that were treated with pentachlorophenol and used cisterns as the sole water source at levels ranging from 0.0002 to 0.001 µg/L (EPA 1986b). In 2001, pentachlorophenol was detected in 33% of sampled stream and raw water that supply a U.S. water treatment facility at concentrations ranging from 0.1 to 0.3 μ g/L prior to treatment. After treatment, pentachlorophenol was not detected in finished water (Stackelberg et al. 2004).

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Pentachlorophenol is currently a regulated contaminant under the Safe Drinking Water Act (SDWA) and as a consequence, a 6-year review for its occurrence in public water systems is mandated by law. Data from the third 6-year review collected from 2006 to 2011 showed that 40,322 public water systems (PWS) servicing over 234 million people were included for the study of occurrence of pentachlorophenol in PWS (EPA 2016). Pentachlorophenol was detected above its minimum reporting level of $0.04 \mu g/L$ in 226 out of the 40,322 PWS tested (0.56%). The range of the $5th-95th$ percentile concentrations of pentachlorophenol in all the PWS tested was 0.01–0.98 µg/L (EPA 2016). There were also 11 systems out of 40,322 (0.027%) that had at least one measurement in which the concentration of pentachlorophenol exceeded the maximum contaminant level (MCL) of 1 µg/L (EPA 2016). High levels of pentachlorophenol have been observed in private wells that may become contaminated via leaching from utility poles or after an accidental spill. Pentachlorophenol was detected at levels of 2,060 and 1,150 µg/L in private wells in Vermont due to leaching of pentachlorophenol from utility poles that were in contact with the water table providing potable water to homes using these wells (Karlsson et al. 2013).

5.5.3 Sediment and Soil

Arsenault (1976) reported pentachlorophenol concentrations of 3.4–654 ppm (3,400–654,000 µg/kg) 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 woodtreatment facility, an NPL site, in Louisiana (ATSDR 1995). It was also found in soil at an inactive landfill in Florida, also an NPL site, at a maximum concentration of $21,000 \mu g/kg$ (ATSDR 1993). Pentachlorophenol was found in on-site (up to $13,000 \mu$ g/kg) and off-site (up to $1,300 \mu$ g/kg) soil samples from the Camilla Wood Preserving Company in Camilla, Georgia (ATSDR 1999). Davis et al. (1994) reported soil levels of pentachlorophenol prior to remediation of >100,000 µg/kg at a former wood treating facility located in Florida. The shuttered Gas Works Park located near Seattle, Washington (closed in 1959) had pentachlorophenol levels measured at 2 of 14 sampling locations at concentrations of 52 and 460 µg/kg (Turney and Goerlitz 1990).

Recent sediment monitoring data can be accessed at the EPA Water Quality Data WQX (https://www.epa.gov/waterdata/water-quality-data-wqx). A search of the STORET and National Water Information Systems databases indicated that there were 25 sediment samples collected and tested for pentachlorophenol at 23 unique sites in the United States in 2020. There were no positive detections at or above the method detection limit of 1,480 ug/kg (WQP 2021). No data were available for 2021.

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). FDA Total Diet Study market basket surveys from 1991–1993 through 2003–2004 collected between September 1991 and October 2003 showed that pentachlorophenol was detected in 1 out of 44 samples of cured ham at a concentration of 20 ppb and 1 out of 44 chicken breast samples at a level of 10 ppb (FDA 2006). 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 $(1.8-62 \mu g/kg)$ and chicken (6–12 µg/kg) (Farrington and Munday 1976). Recent food concentration data in the United States were not located; however, in a survey conducted from 2012 to 2015 in the United Kingdom for 120 retail foods, pentachlorophenol was found at $\langle 0.01 - 1.90 \mu g/kg$ whole wet weight basis. Pentachlorophenol was detected infrequently, or not at all, in poultry, fish and shellfish, and milk and dairy products, with the highest concentration found in eggs (Fernandes et al. 2019). Monitoring data from 2015 to 2018 in China of 3,100 animal source foods showed that average pentachlorophenol concentrations declined from 17.42 to 2.39 μg/kg wet weight over the time period (Zhou et al. 2021).

No biological data were located in a search of the STORET and National Water Information Systems databases for 2020–2021. Lake trout collected from Lake Ontario and Lake Superior between May and August of 2000 and 2001 had pentachlorophenol maximum blood plasma residues ranging from 105 to 658 pg/g (0.000105–0.000658 mg/kg) (Campbell et al. 2003). Pentachlorophenol was not detected in fish from Lake Superior or Lake Michigan in a study conducted in 2014–2015 (Baygi et al. 2021).

Pentachlorophenol was detected in the plasma of nestling peregrine falcons from 34 active nests across Ontario and western Quebec collected in 2004 and 2005 (Fernie and Letcher 2010). The geometric mean pentachlorophenol level was 3.16 ng/g (wet weight) with a range of values of 0.46–24.44 ng/g (weight weight).

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Levels of pentachlorophenol ranging from 10 to 270 µg/L were reported in 9 out of 65 samples of children's paints in the Netherlands (Van Langeveld 1975). Wang et al. (2021) studied the concentration of wood preservatives in 90 wooden toys manufactured in China; pentachlorophenol was found in 1 of 33 building block toys and 1 of 20 jigsaw toys.

Pentachlorophenol was detected in 6 of 38 dust samples from homes in California tested over a 2-year period at a 95th percentile of 11,511 ng/g of dust (Shin et al. 2020)

5.6 GENERAL POPULATION EXPOSURE

Potential sources of pentachlorophenol exposure for the general population include air, dust, drinking water sources, food, soils, and dermal contact with contaminated products treated with the compound. In eight male anglers (50+ years) from the Lake Superior and Lake Michigan region, pentachlorophenol concentrations in serum were 0.07–0.3 ng/g (Baygi et al. 2021). Using data from spot urine samples collected from 31 participants in the United States, a daily pentachlorophenol intake of 0.34 μg/day was estimated (Honda and Kannan 2018).

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. 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 exposure. Pentachlorophenol is known to volatilize from treated wood products (Bunce and Nakai 1989) at a rate that is temperature-dependent (Ingram et al. 1986), and 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).

Inhalation of estimated ambient levels of pentachlorophenol in the atmosphere has an associated exposure level of 6 µg/day for the general population (EPA 1980b); however, it is likely that current exposure estimates are much lower. 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- to 20-year-old male, and EPA (1978) calculated an average dietary intake of 1.5 mg/day and a maximum dietary intake of 18 mg/day. However, the actual intake was lower than estimates because average dietary intakes were based on mean

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concentration of positive samples. Daily dietary intake of pentachlorophenol from contaminated food has been estimated by another source to be 0.1–6 µg/day (WHO 1987). Using a six-compartment environmental partitioning model, Hattemer-Frey and Travis (1989) reported that the food chain is the most important source of exposure to pentachlorophenol for the general population. The study authors estimated the average daily dietary intake of the compound to be $16 \mu g/day$ 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 daily intakes (ng/kg/day) of pentachlorophenol for these groups in $1982-1984$ were as follows: (1) 6- to 11-month-old infants, 59.0; (2) 2-year-old children, 48.5; (3) 14- to 16-year-old females, 16.2; (4) 1- to 16-year-old males, 20.7; (5) 25- to 30-year-old females, 15.9; (6) 25- to 30-year-old males, 18.2; (7) 60- to 65-year-old females, 13.9; and (8) 60- to 65-year-old males, 15.5. In a later survey of the Total Diet Study, Gunderson (1995) 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- to 11-month-old infants, 0.9; (2) 2-year-old children, 1.4; (3) 14- to 16-year-old females, 0.5; (4) 14- to 16-year-old males, 0.5; (5) 25- to 30-year-old females, 0.8; (6) 25- to 30-year-old males, 0.7; (7) 60–65-year-old females, 0.8; and (8) 60- to 65-year-old males, 0.8. These estimates demonstrate a substantial reduction in the amount of pentachlorophenol in the estimated mean daily intake since the 1982–1984 study. Given the fact that pentachlorophenol was rarely detected in food items from the FDA Total Diet Study collected between September 1991 and October 2003 (FDA 2006), it is therefore likely that current daily intakes are much lower.

Pentachlorophenol has been detected in human adipose tissue, blood, and urine. It is important to know that pentachlorophenol itself is a metabolite of other environmental contaminants (e.g., hexachlorobenzene, pentachlorobenzene, pentachloronitrobenzene), so its detection may also occur as a result of exposure to these substances. As part of the second National Health and Nutrition Examination Survey (NHANES II) and the National Human Adipose Tissue Monitoring Survey (NHATS), urine samples from approximately 6,000 persons between the ages of 12 and 74 years in 64 communities throughout the United States were analyzed for pentachlorophenol during the period of 1976–1980. Pentachlorophenol was detected in over 70% of the urine samples with a geometric mean concentration of 6.3 μg/L, 90th percentile concentration of 15.5 μg/L, and a maximum concentration of 193 μg/L (Kutz et al. 1978; 1992). Geometric mean concentration was higher in males (6.7 μg/L) than females (5.9 μg/L) and the highest geometric means were found among 12- to 19-year-olds, as compared to other age groups (Kutz

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et al. 1992). NHANES monitoring data in 1999–2000, 2001–2002, and 2003–2004 demonstrate a decrease in urinary pentachlorophenol levels in the U.S. population. As presented i[n Table 5-7,](#page-26-0) the geometric mean levels were not calculated because the proportion of results below the limit of detection was too high to provide a valid result. The creatinine-corrected urinary levels are presented in [Table 5-8.](#page-27-0)

The 90th percentile concentrations in 1999–2000, 2001–2002, and 2003–2004 (0.390, 1.23, and 2.57 μg/L, respectively) were much lower than the level in 1976–1980 (15.5 μg/L). Pentachlorophenol levels were measured in urine samples from pregnant women (n=361), as part of a multi-ethnic study conducted in New York City (Berkowitz et al. 2003). The 10th, 25th, 50th, 75th, and 90th percentile concentrations were 1.1, 2.4, 7.3, 28.4, and 76.0 μg/g creatinine, respectively. An analysis of global trends in pentachlorophenol levels found an exponential decrease in urinary pentachlorophenol levels with U.S. levels decreasing by 90% between the 1967–1978 and 1990–1995 time periods and by 44% between the 1990– 2005 and 1996–2003 time periods (Zheng et al. 2011).

Historical data demonstrate the presence of pentachlorophenol in various human tissues. A mean level of 26.3 µg/kg was found in adipose tissue from the general U.S. population (Shafik 1973). 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 concentrations ranging from 7 μg/kg in subcutaneous fat to 4,140 μg/kg in testes (Wagner et al. 1991). Geyer et al. (1987) investigated the distribution and bioconcentration of pentachlorophenol in different human tissues 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 µg/kg (Gebefugi and Korte 1983). Hair and air samples from households in France/Luxembourg were compared; 27% of 78 hair samples had pentachlorophenol concentrations of $\langle 2.5-30 \rangle$ pg/mg and air concentrations of 1– 114 ng/sample. Exposure profiles varied from home to home and between residents in the same household, indicating that the two matrices were not necessarily associated (Raeppel et al. 2016).

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, toys, 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

Table 5-7. Urinary Pentachlorophenol Levels in the NHANES U.S. Population

*= geometric mean not calculated because the proportion of results below the limit of detection (0.25 µg/L in 1999-2000 and 0.5 µg/L in 2001-2002 and 2003-2004) was too high to provide a valid result; CI = confidence interval; LOD = limit of detection; NHANES = National Health and Nutrition Examination Survey

Source: CDC 2009, 2019 (https://www.cdc.gov/exposurereport/pdf/FourthReport_UpdatedTables_Volume1_Jan2019-508.pdf)

*= geometric mean not calculated because the proportion of results below the limit of detection (0.25 µg/L in 1999–2000 and 0.5 µg/L in 2001–2002 and 2003– 2004) was too high to provide a valid result; CI = confidence interval; LOD = limit of detection; NHANES = National Health and Nutrition Examination Survey

Source: CDC 2009, 2019 (https://www.cdc.gov/exposurereport/pdf/FourthReport_UpdatedTables_Volume1_Jan2019-508.pdf)

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and oral ingestion. The tendency of young children to ingest soil, either intentionally through pica behavior 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 3.1.1). Therefore, it is possible that children may absorb pentachlorophenol dermally when exposed to soil contaminated with pentachlorophenol. Another potential source of exposure for children is pentachlorophenol-treated wood. Wang et al. (2021) studied the concentration of wood preservatives in 90 wooden toys manufactured in China; pentachlorophenol was found in 1 of 33 building block toys and 1 of 20 jigsaw toys, indicating that dermal and oral exposures are possible. 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 or touching utility poles 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, inhalation exposure may occur for children playing nearby. Old and unpainted playground equipment constructed with pentachlorophenol-treated wood may be another mode of dermal exposure for children.

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- to16-year-old males and females), were prepared for consumption prior to analysis in a revision to the FDA's Total Diet Study methodology (Gunderson 1988). Estimated mean daily intakes of pentachlorophenol for children in 1982–1984 were as follows: 59.0 ng/kg/day in 6- to 11-month-old infants; 48.5 ng/kg/day in 2-year-old children; (3) 16.2 ng/kg/day in 14- to 16-year-old females; and 20.7 ng/kg/day in 14- to 16-year-old males. In comparison, the intake for adults ranged from 15.5 to 18.2 ng/kg/day. Much lower intakes were estimated in a later survey of the Total Diet Study during 1986–1991 (Gunderson 1995). Estimated mean daily intakes of pentachlorophenol were 0.9, 1.4, 0.5, and 0.5 ng/kg/day in 6- to 11-month-old infants, 2-year-old children, 14- to 16-year-old females, and 14- to 16-year-old males, respectively; the intake for adults ranged from 0.7 to 0.8 ng/kg/day.

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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 indirectly 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.

Potential exposures to pentachlorophenol and other pesticides from multiple environmental and personal media were examined in a study of 257 children selected randomly from households and daycare centers from selected counties in North Carolina and Ohio. The results suggested that the potential for children's exposures to pentachlorophenol is primarily via inhalation, while indirect ingestion may have made a modest contribution. The potential exposure doses of pentachlorophenol from inhalation exposure for these children were estimated to be 12 ng/day for North Carolina and 18 ng/day for Ohio. The potential exposure doses from indirect ingestion for the children were estimated to be 3.4 ng/day for North Carolina and 1.8 ng/day in Ohio. Furthermore, based on an assumption of 50% of chemical absorption in these children, the estimated potential absorbed doses of pentachlorophenol from inhalation were 0.34 ng/kg/day for North Carolina and 0.58 ng/kg/day for Ohio (Wilson et al. 2007). Pentachlorophenol was detected in 89% of the urine samples from the North Carolina children and in 99% of the urine samples from the Ohio children. The overall arithmetic means for urinary pentachlorophenol levels were 0.605 ng/mL for the children who lived in North Carolina and 1.27 ng/mL for the children who lived in Ohio. The level of pentachlorophenol excreted in urine by the children in this study over a 48-hour sampling period significantly exceeded the estimated intake based on environmental sampling, a finding that suggested that the children may have been exposed to other compounds that are biotransformed to pentachlorophenol (Wilson et al. 2007). However, these levels were lower than the 95th percentile values for children reported in the NHANES report (CDC 2009) and the authors noted that they were much lower than established reference levels (Wilson et al. 2007).

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

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pentachlorophenol concentration of $14 \mu g/L$, suggesting that 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- to 5-year-old children, 600 μ g/L; (2) 6- to 10-year-olds, 490 μ g/L; (3) 11- to 15-year-olds, 370 μ g/L; and (4) adults, 310 μ g/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.

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 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 μ g/g; walkway soil, 0.02 μ g/g; and play area soil, 0.02 μ g/g. It was also detected in house dust, 0.83 μ g/g; child hand rinse, 0.02 μ g; and air, 0.05 μ g/m³. 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.

Maternal transfer during gestation and/or via breast milk is also a potential source of exposure for children. No data were located on the presence of pentachlorophenol in breast milk in the United States. Pentachlorophenol levels have been measured in breast milk of women living in Europe or Asia. Smallscale studies (\leq 50 women) have reported median breast milk pentachlorophenol levels of 1.43 μ g/kg in Upper Bavaria (Gebefugi and Korte 1983), 2.21 μg/kg in Bratislava, Slovakia (Veningerova et al. 1996), 0.020 μg/kg in Sweden (Guvenius et al. 2003), and 3.63 μg/kg in China (Hong et al. 2005).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Several populations with potentially high exposures have been identified; these include occupationally exposed groups, residents near pentachlorophenol manufacturing facilities, and families living in homes historically treated with pentachlorophenol.

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Pentachlorophenol exposure in occupational settings can occur through inhalation of contaminated workplace air and dermal contact with the compound or with wood products treated with the compound. Populations with potentially high exposure include individuals involved in the manufacture and use of the compound. EPA (2008) indicated that high levels of exposure are not expected due to mixing/loading operations because treatment plants utilize automated methods for chemical preservative delivery (metered feed/pump) and closed application practices (retorts). There is, however, the potential for workers near the treatment cylinder door to inhale treatment solution mist when treatment has been completed. NCI (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.

Pentachlorophenol levels in human tissues are much higher in occupationally exposed groups than in the general public. In an FDA study in Florida, Cranmer and Freal (1970) found an average pentachlorophenol urine level of 4.9 μ g/L in the general population, compared with 119.9 μ g/L in carpenters, boat builders, and spraymen. A range of $1,100-5,910 \mu g/L$ in the urine of Japanese pest control operators exposed to pentachlorophenol, compared with $10-50 \mu g/L$ 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 $1,802 \mu g/L$ in the occupationally exposed population was almost 50 times higher than the nonoccupational group level of 40 μ g/L.

In a study of workers exposed to pentachlorophenol in the wood-preserving industry, Arsenault (1976) reported pentachlorophenol levels of 120–9,680 μ g/L in urine, with a mean concentration of 1,683 μ 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 levels of pentachlorophenol in the occupationally exposed group were found to be 1,197 and 1,273 µg/L in urine and blood, respectively. The mean concentrations of pentachlorophenol in the control group were considerably lower at 6.4 and 15.3 µg/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 μ g/L) than in the evening (106 μ g/L). A subsequent study by Barbieri

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et al. (1995) obtained similar results from which a half-life of about 10 days was estimated for pentachlorophenol excretion in urine. Mean pentachlorophenol blood serum levels in workers using pentachlorophenol or pentachlorophenol-treated materials were found to range from 83 to 57,600 µg/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 various operations in woodpreservative and chemical-packaging facilities. One worker from a chemical-packaging facility, with a whole blood pentachlorophenol level of 23,000 μ g/L, died of pentachlorophenol poisoning (Cline et al. 1989). Bader et al. (2007) conducted a study in Germany and analyzed pentachlorophenol in post-shift urine samples of 189 painters and 148 bricklayers 1–4 years after the use of pentachlorophenol was banned. The results revealed a median pentachlorophenol urinary level of 2.4 μg/g creatinine in the painters, which was significantly higher than the median pentachlorophenol level of 1.8 μ g/g creatinine detected in urine samples from the bricklayers. The range of pentachlorophenol detected in urine samples from the painters was $\langle 0.2-52 \mu g/g$ creatinine, while the range of pentachlorophenol detected in urinary samples from the bricklayers was $\langle 0.2-25 \mu g/g$ creatinine (Bader et al. 2007). Continued exposure of painters to residual pentachlorophenol from contaminated wood surfaces may have accounted for the elevated pentachlorophenol levels observed in the painters in comparison to the bricklayers in this study (Bader et al. 2007).

Residents near pentachlorophenol manufacturing plants and wastewater treatment sludge disposal sites may also be exposed to the chemical at higher concentrations than the general public. Residents around NPL sites known to have pentachlorophenol contamination may also be exposed to the chemical at higher levels in contaminated environmental media. An investigation of residents living near a wood treatment facility in Georgia found elevated urinary pentachlorophenol levels in women compared to the U.S. general population; 22% of the women had urinary pentachlorophenol levels that were above the 95th percentile group in the NHANES (Zarus and Rosales-Guevara 2012).

Pentachlorophenol is found as a residue in treated wood that had previously 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). A mean pentachlorophenol blood serum level of 420 µg/L was reported for residents of log homes, whereas a mean level of 40 µg/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

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those of their parents. Pentachlorophenol urine concentrations for residents of log homes averaged 69 μ g/L, whereas urine levels for the general population were found to be 3.4 μ g/L. Inhalation was believed to be the most likely route of exposure to pentachlorophenol in log homes (Cline et al. 1989). In a separate study of 66 residents of log homes treated with pentachlorophenol in Kentucky, EPA (1986b) reported a geometric mean pentachlorophenol blood serum level of 47.6 µg/L and a geometric mean urine concentration of 21 µg/g urinary creatinine. Pentachlorophenol was detected in blood and urine of all 66 residents. 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.