# Pentachlorophenol: Toxicology and Environmental Fate

By Brett Fisher

Pentachlorophenol (penta or PCP) was first introduced for use as a wood preservative in 1936 by Dow Chemical Company and Monsanto Chemical Company.<sup>1</sup> Penta has since been used as an herbicide on ornamental lawns, golf courses, aquatic areas, and rights-of-way; for control of subterranean termites; as an anti-microbial agent in cooling towers, adhesives, latex paints, paper coatings, cements used with food can ends and seals, coatings in reusable bulk food storage containers, photographic solutions, leather tanneries, and pulp and paper mills; and, as a disinfectant.<sup>2</sup> It is marketed under the trade names Santophen, Penchlorol, Chlorophen, Pentacon, Penwar, Sinituho and Penta among others.3

As of 1977, about 50 million pounds of penta were produced annually in the United States.<sup>2</sup> In 1985, 35 million pounds of penta were manufactured in the U.S.<sup>4</sup> Vulcan Chemicals, located in Wichita, Kansas, is penta's sole U.S. producer.<sup>5</sup> In 1988, the U.S. Environmental Protection Agency (EPA) cancelled all uses of penta except for its use as a wood preservative.<sup>6</sup>

There are two manufacturing processes used to produce penta: (1) the direct chlorination of phenol, the Boehringer process; and (2) the alkaline hydrolysis of hexachlorobenzene, the Dow process. In Europe, approximately equal use is made of both methods. In the US, penta is produced solely by the Boehringer process.<sup>7</sup>

Chlorination of phenol in the Boehringer process occurs in two stages. In stage one, chlorine is bubbled through phenol at 105° F to yield tri- and tetrachlorophenols (phenols with three and four chlorine atoms respectively). In stage two, the temperature is gradually increased to 130° F to keep the reaction mixture molten and to further chlorinate the tri- and tetrachlorophenols to form pentachlorophenol. The process,

however, is incomplete. Technical grade penta contains from 4 to 12 percent tetrachlorophenols, which are toxic in their own right. In addition, the high temperatures used in manufacturing penta produce several contaminants including hexachlorobenzene, dioxins, and furans (see Figure 1).<sup>2</sup>

There are two general methods for preserving wood, the pressure process and the non-pressure process. The pressure-treating process involves placing the wood in a pressure-treating vessel where it is immersed in the preservative and then subjected to applied pressure. The excess penta is vacuumed from the vessel and the treated wood is removed, inspected, stored, and shipped. In the non-pressure process, penta is applied to the surface of wood by spraying, brushing, dipping, and soaking. This process is used for short-term wood protection in construction where the wood will be protected from exposure to soil or weather through brick or cement barriers. This process is also used to control sapstain fungi (fungi which leave a blue stain on wood) by passing green lumber through a spray tunnel or by dipping the wood.<sup>7</sup>

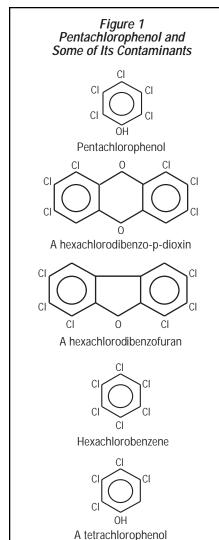
#### **Human Exposure**

People are exposed to penta in the workplace, in treated homes, indoor and outdoor air, drinking water, and food. Penta can enter the body through inhalation, ingestion of contaminated food or water, and skin contact with treated wood.

Workers in wood preserving facilities, sawmills and other workplaces who handle penta or treated wood receive the most significant exposures primarily through skin contact and secondarily through air. 6.7.8.9.10.11 Based on limited data from animal studies, EPA has estimated that human skin absorbs 50 percent of the amount of penta it is exposed to from oil-based formulations and 1 percent from water-based formulations. 12

Researchers from the University of Washington, however, who applied amounts of penta to skin from human cadavers to simulate levels at which people are exposed found more penetrated the skin than had been estimated by EPA: 62 percent of the penta in oil was absorbed and 16 percent of the penta in water. 13 Two recent studies of sawmill workers exposed to water-based penta support these findings. 10,14 These findings suggest that workers and others, such as those living in treated homes or children who play on treated playground structures, may be at greater risk from exposure through skin contact than estimated by EPA.

Although most people are not occupationally exposed to penta, researchers for the national Health and Nutritional Examination Survey II of the National Center for Health Statistics found

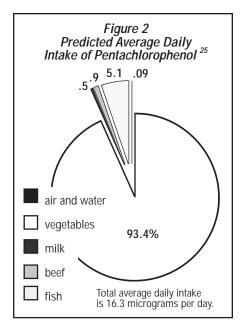


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penta in 79 percent of urine samples from the general population. <sup>15</sup> In a study of 179 Arkansas children, 100 percent of the urine samples tested positive for penta with an average level of 14 parts per billion (ppb). <sup>16</sup> Penta is also present in human fat tissues and human breast milk. <sup>17,18</sup> In fact, surveys of the literature on human exposure to penta indicate that people living in industrialized societies will generally be contaminated with penta at concentrations of 1 to 100 ppb. <sup>19</sup>

One source of exposure to penta in the general population is from indoor air and dust. Residents of log homes treated with penta in Kentucky were found to have elevated levels of penta in their blood (580 - 1,750 ppb) and urine (47 - 216 ppb). The source of the exposure was continuous vaporization of penta from factory-treated logs. The youngest children had the highest blood levels of penta, even though they spent as much time in the home as older children and adults.<sup>20</sup>

Researchers measuring levels of penta in humans reported an average 40 ppb in the blood of the general population and an average of 420 ppb in 143 residents of log homes in nine states. The children residing in penta treated log homes were found to have 1.8 times more penta in their blood than adults. Because the primary route of exposure to penta in homes is through the air, the researchers concluded that children could be expected to have more penta in their blood than adults because they have



a higher metabolic rate and therefore breathe more often relative to body weight and blood volume than adults. They also suggested that skin contact with treated walls could raise blood levels of penta in very young children.<sup>21</sup>

In a 1976 spot survey of selected foods, penta residues ranging from 1 to 100 ppb were found in powdered dry milk, soft drinks, bread, candy bars, cereal, noodles, rice, sugar, and wheat."

Penta, and other toxins, accumulate in household dust and can contribute to the total exposure of children and adults. Because of their lower body weight, greater dermal contact with dust, and frequent hand-to-mouth activity, young children ingest at least 2.5 times more dust than adults.<sup>22</sup> In a study of German homes, penta has been found in house dust at levels that remained relatively high over time while levels in indoor air decreased.<sup>23</sup> In a study of Seattle homes, penta was found in house dust at an average level of 3.4 parts per million (ppm). In two of these homes, the penta may have been tracked in from decks that had been treated with penta three and five years before the samples were collected.24

Because an estimated 96.5 percent of the penta in the environment will end up in soil, researchers looking at environmental sources of human exposure to penta have calculated that the food chain, especially fruits, vegetables, and grains, accounts for 99.9 percent of human exposure to penta (Figure 2).25 In a 1976 spot survey of selected foods, penta residues ranging from 1 to 100 ppb were found in powdered dry milk, soft drinks, bread, candy bars, cereal, noodles, rice, sugar, and wheat. The residues in the grain and sugar items were attributed to the storage of these foods in pentatreated containers.<sup>16</sup>

In addition, use of penta treated wood that comes in contact with livestock can contaminate animal products with penta or its contaminants.<sup>26</sup> In a study of pork and chicken in Canada, 60 percent of 144 samples contained penta while half of 26 chicken fat samples with high levels of penta also contained hexa-, hepta-, or octa-dioxins (those with six, seven, and eight chlorine atoms per dioxin molecule).<sup>27</sup> In a survey of cow milk in Ontario, Canada, 57 percent of 359 samples contained penta at an average of 29 ppb. The exposure of dairy cattle to penta was attributed to penta contaminated wood shavings or sawdust used as litter; direct contact between the cows and treated wood; and contact between feed and treated wood.28

## **Human Toxicology**

**Acute Toxicity:** The acute toxicity of penta is believed to derive from its ability to interfere with the production of energy at the cellular level. This interference (uncoupling of oxidative phosphorylation) causes increased cell metabolism resulting in increased heat production.<sup>3,7,19</sup>

A person may have up to about 100 ppb of penta in their blood and urine before they begin to experience adverse effects. Levels of penta found in various organs and fluids after fatal poisonings range from 20 to 145 ppm in adults. Levels of penta in children and infants after fatal poisonings are lower, indicating children are more susceptible to penta than adults. Surveys of poisonings reported in the literature suggest that the largest single dosage that produces no illness is little less than the fatal dosage. <sup>29</sup>

The most common symptoms of those experiencing penta poisoning include stuffy nose, scratchy throat, and tears in the eyes. Skin contact can lead to contact dermatitis and, more rarely, chloracne. The chloracne is possibly a result of the contaminants in penta. A person experiencing systemic poisoning by penta would show symptoms of profuse sweating and intense thirst, rapid breathing and heart rate, fever, abdominal pain, nausea, weakness, dizziness, anorexia, and nausea.<sup>3</sup>

Once in the body, penta is distributed throughout and accumulates in the liver, kidney, brain, spleen and fat. Although penta is not readily metabolized in the body, it can attach (conjugate) to glucuronic acid and break down to tetrachlorohydroquinone. Most penta, however, is eliminated from the body.<sup>4</sup> In 1986, researchers at the Institute of Toxicology in Switzerland have found that humans eliminate half of the penta they are exposed to in 17 days as penta or penta conjugated to glucuronic acid. Their findings were supported by reported cases of penta poisonings but contrasted with previous findings of a 33 hour elimination half life in humans.<sup>30</sup> Penta may therefore have a greater potential for accumulation and persistence in the human body than previously indicated.

**Reproductive Effects:** Penta has been found in the semen of exposed workers and a significantly increased incidence of chromosomal aberrations in exposed worker's peripheral lymphocytes (one of the cells found in blood) has been documented. Although reproductive dysfunctions have not been reported, these findings suggest a high priority for future investigations of penta's reproductive effects.<sup>31</sup>

**Teratogenicity:** EPA has concluded that penta and possibly its hexachlorodibenzo-p-dioxin (HxCDD) contaminants cause birth defects and fetotoxic effects in test animals.<sup>32</sup> Reported adverse effects in fetuses from penta exposure include distorted sex ratios, increased incidences of resorbed embryos, skeletal anomalies, subcutaneous edema (excessive fluid), reduced survival, and reduced growth.<sup>7,29</sup> Reported no observable effect levels (NOELs) for teratogenicity range from 3 to 5.8 milligrams per kilogram (mg/ kg) per day for penta and .001 mg/kg per day for HxCDD.<sup>4,29,33</sup>

Mutagenicity: The majority of tests in yeast, bacteria, or mammalian cells have reported penta not to be genetically active. Questions have been raised as to the validity of this research since controls, doses, and statistical data were not reported in every study. Other tests have indicated that penta, and tetrachlorophenol, can damage genes. Penta's metabolite, tetrachlorohydroquinone, has also been shown to damage genes. Additional testing of penta in mammalian systems is necessary to determine whether penta is mutagenic.

Carcinogenicity: Based on studies that report negative results for carcinogenicity, researchers prior to 1988

concluded that penta does not cause cancer.<sup>4</sup> However, these studies are not considered adequate by present standards that would make a negative response for carcinogenicity valid.<sup>7</sup> The International Agency for Research on Cancer has classified penta as a Group 3 chemical for carcinogens (inadequate data in humans and animals). EPA had originally classified penta as a Class D carcinogen (inadequate animal evidence), but reclassified it as a Class B<sub>2</sub> carcinogen (probable human carcinogen) based on a 1988 National Toxicology Program study.<sup>35</sup> The hexachlorobenzene and hexachlorodibenzo-p-dioxin contaminants in penta are known carcinogens.<sup>4</sup> Agriculture Canada concludes that the combined evidence from epidemiological studies on human with mixed exposures to chlorophenols, dioxins, or pesticides contaminated with these chemicals suggest that occupational exposure to chlorophenols or phenoxy herbicides increases the risk of three kinds of cancer: soft tissue

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sarcoma, Hodgkin's lymphoma, and non-Hodgkin's lymphoma.<sup>33</sup>

Other Health Effects: Exposure to penta has also been associated with aplastic anemia, leukemia, and other blood disorders. The People exposed to penta have reported peripheral neuropathy and other problems related to nerve damage (neurotoxicity) that may also be due to exposure to penta's contaminants. The Commercial grade penta has also been demonstrated to suppress the immune system in mice, an effect that may also be due to

penta's contaminants since pure penta was not immunotoxic.<sup>38,39</sup>

Health Standards: The American Conference of Governmental Industrial Hygienists has established a threshold limit value (TLV) of 0.5 milligrams per cubic meter for maximum daily exposure to penta in the air in the workplace. EPA has established a lifetime health advisory for exposure to penta in drinking water of 220 ppb. The World Health Organization has recommended a drinking water criterion of 10 ppb for penta. Development of these standards did not take into account the potential adverse health effects of penta's contaminants.

# Environmental Fate and Effects on Nontarget Organisms

Penta is a significant contaminant of soil, surface water, and groundwater especially around sawmills and wood preserving facilities.<sup>33,40</sup> Researchers using a mathematical model for partitioning of penta in the environment calculated that 96.5 percent of penta is in soil, 2.5 percent in water, 1 percent in air, and less than 1 percent in suspended sediments and organisms in aquatic environments.<sup>25</sup>

In a study of movement of penta from treated wood posts that were in direct contact with soil, 95 percent of the penta remained in the wood posts after 2.5 months. Most of the penta that moved into the soil remained in the upper layer immediately surrounding the posts.41 Penta can persist in the soil from 14 days to 5 years depending on the soil microbes present.<sup>32</sup> Researchers in Finland found no clear decrease of soil levels of penta one year after a sawmill with a wood preserving facility on site stopped using penta.<sup>42</sup> A study of the effect of penta on the soil ecosystem reported that levels of 20 ppm inhibited activity of the microbes in soil and continued to inhibit activity over the 48 day period of the study.<sup>43</sup>

Because penta can move from soil to surface and ground water, effects of penta on aquatic environments are also of concern. Researchers at St. Olaf College in Minnesota applied penta to outdoor experimental water channels stocked with fish and other aquatic organisms at the aquatic criterion level for penta (48 micrograms per liter), three times this level, and nine times this level. Their study found adverse ecosystem effects at all levels tested sug-

gesting that criteria levels set to be protective of the environment were failing to do so.<sup>44</sup> Researchers in British Columbia have found penta in the nearshore waters of the lower Fraser River at levels which would be toxic to salmon species after 24 and 48 hours. Additional studies in the area have found substantial bioconcentration of penta in tissues of starry flounder and Dolly Varden trout. Agriculture Canada has concluded that use of penta and other chlorophenols pose a significant hazard to fish and fisheries in Canada, particularly in British Columbia.<sup>33</sup>

### **Summary**

As a result of over 50 years of use as a pesticide, pentachlorophenol residues are ubiquitous in the environment and in humans. Humans who are occupationally exposed to penta, or who live in homes constructed from treated wood, have the highest amounts of penta in their bodies, but a large majority of people with no obvious exposure also have measurable residues. In addition to its acute effects, exposure to penta is known to cause cancer and birth defects in laboratory animals, as well as chromosome abnormalities, blood disorders, and nerve damage in humans. Penta has contaminated soil, surface water, and groundwater and affected fish populations. As of 1989, penta was banned in ten countries and severely restricted in nine.45

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