

REVIEW

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Pentachlorophenol and its effect on different environmental matrices: the need for an alternative wood preservative

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Abstract

Wood is considered to be one of the most important materials in the global economy. Wood loses shelf life in countries with severe winters. Pentachlorophenol (PCP) was predominantly used as a wood preservative because of its efficacy in controlling wood decay. This study discussed the overall impact of PCP across various environmental matrices, including soil, plants, water, air, and humans. Pentachlorophenol is a phenol substituted with five chloro-groups. High chlorination levels and stability of PCP make it hazardous to the environment, and persistent, and it also interferes with human, aquatic, and soil microbial health. PCP is volatile; thus, it is constantly discharged into the atmosphere and ingested by the human population. Owing to its hazardous nature, it was added to the Stockholm Convention's list of persistent organic pollutants (POPs) and phased out of the industry in 2023. This review has summarized PCP properties, usage, production volume, different transformation pathways, and its harmful effects on different environmental matrices such as air, water, soil, crops, and human health which have helped to outline the expected features of the new chemical compared with PCP. The improved chemical is intended to have quick degradability, fewer chlorine atoms, no aromatic structure, be non-toxic, environmentally benign, and efficient against wood deterioration while also penetrating the wood better.

Keywords Pentachlorophenol, Wood preservatives, Toxicity, Environmental impact, Wood treatment

Introduction

Wood is an economically important and inevitable commodity throughout the world. Global wood products trade increased by 143%, worth US\$244 billion, between 1990 and 2019 [71]. Wood preservation is unavoidable in cold nations, such as Canada, where wet climatic conditions encourage wood degradation [78]. Wood

preservation companies are a large part of the economy and are striving to use more environmentally friendly protection techniques to meet the high standards in the competitive industry. They produce utility poles, railway ties, bridge construction, building frames, decks, flooring, and other products [15]. There are different ways to preserve wood, such as brushing, spraying, dipping, and immersing the wood in baths with changing temperatures, or using one of the different pressure treating cycles [96]. Brushing and spraying are the simplest but less effective than the pressure-treating cycles because the life-span is only slightly extended to a maximum of 3 years [114]. Wood preservation, especially using chemical wood preservatives, provides 6–8 times longer life than untreated wood [114].

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There are two categories of wood preservatives: water-borne and oil-borne. Water-borne preservatives are soluble in water and are mainly used in residential settings because of their dry and paintable surfaces [92]. Chromated copper arsenate, copper azole, and micronized copper azole are the three most important water-borne preservatives in use. The oil-borne wood preservative is insoluble in water and must be dissolved in petroleum or other organic solvents to penetrate the wood [92]. Pentachlorophenol (PCP) and creosote are two common oil-borne preservatives that can be applied by brush, dip, or pressure treatment [122]. However, creosote production declined in Canada by the 1950s, and in the 1970s, PCP mostly replaced it [17].

Pentachlorophenol is an organochlorine compound that has been used as a pesticide and disinfectant. It is a manufactured chemical created through the catalytic chlorination of phenol at a temperature of 191 °C [94]. Pentachlorophenol and its sodium salt were first manufactured as a wood preservative in the 1930s and have been extensively used to preserve industrial wood products since 1941 [26, 77]. It has proven to be an excellent preservative for industrial wood products used in ground contact and above-ground applications. The wood preservative can be either placed in a pressure vessel or sprayed onto the wood. Studies have shown that pressure treatment is more efficient because it provides homogeneous protection of wood through deeper penetration and higher preservative retention [111].

However PCP has health effects, it is effective against wood-decaying pests, it is carcinogenic and extremely persistent, with reported toxicological effects including pancreatitis, jaundice, acute renal failure, intravascular hemolysis, and pulmonary edema [29, 93, 105]. According to Vani et al. [126], PCP is extremely toxic to fungi, insoluble in water, resistant to leaching, and non-corrosive to metals. It is ubiquitous in the Canadian environment. Due to its toxicity potential and endocrine disruptive tendencies, PCP was added to the Stockholm Convention's list of persistent organic pollutants (POPs), and its production has drastically reduced in North America [28]. The European Union (EU) ceased its production in 1992, and the EU has set a new limit value for PCP and its salts and esters that was published in the EU 2021/277 article, and it became effective from 15th March 2021 [36, 85]. Countries such as Sweden in 1978, Indonesia in 1980, Switzerland in 1988, Austria in 1991, India in 1991, and New Zealand in 1991 completely banned PCP usage [118]. Approximately 94 of 104 countries voted in favor of the global prohibition of PCP [14]. However, this ban was not endorsed in North America, as PCP was still considered a vital provision of infrastructures such as utility poles and railroad ties, and it was restricted to only industrial use outdoors by 1990 [43,

116]. In Canada, according to the Pest Control Act [21(5) (a)], the last date for the authorized sale of pest control products containing PCP was October 4, 2022, and the last date for the authorized use of PCP to treat wood was October 4, 2023. During this one-year phase-out period, the manufacture, sale, or import of canceled products containing PCP to treat wood was prohibited [90].

Therefore, it becomes important to identify a PCP alternative that offers superior defense against pests without environmental toxicity. In order to do this, it is important to first understand the characteristics of PCP. Thus, this review will describe the physical and chemical characteristics of PCP, as well as its various uses and production volumes worldwide. It will also cover the environmental risks related to PCP use in various matrices, including the air, water, soil, crops, and human health, as well as the different transformation pathways in these matrices. This review aims to understand the properties and toxicity of PCP which will provide an idea of what needs to be done in the future to reduce environmental toxicity caused by PCP. The expected features of PCP alternatives are noted based on this information.

Background to pentachlorophenol

Pentachlorophenol is considered to be one of the most widely used wood preservatives and is currently considered a possible contaminant. This section will describe the physical and chemical properties of PCP, its various uses, and its production volume worldwide. Understanding its physical and chemical properties will help to determine the intended properties of new oil-borne preservatives.

Physicochemical properties of pentachlorophenol

Pentachlorophenol is a phenolic compound substituted with five chlorine atoms and does not have isomers (Fig. 1). It is produced by the stepwise chlorination of phenols in the presence of catalysts, namely aluminum trichloride or ferric trichloride. However, it has also been produced by the alkaline hydrolysis of hexachlorobenzene, especially outside the USA [91]. The physicochemical properties are given in Table 1. Technical grade PCP is 86% pure and is primarily used as a wood preservative, whereas petroleum oil is typically used as a carrier [3, 123]. Impurities or contaminants in technical grade PCP contribute to the compound's toxicity. These impurities include tetrachlorophenol, trichlorophenol, hexachlorobenzene, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and chlorinated phenoxyphenols [123]. Impurities in the technical grade PCP makes it 10 times more potent than the purified one [20]. The degree of toxicity and other properties vary with the degree of chlorination, and the most toxic congener is 2,3,7,8 tetrachlorodibenzo-p-dioxin [123]. It

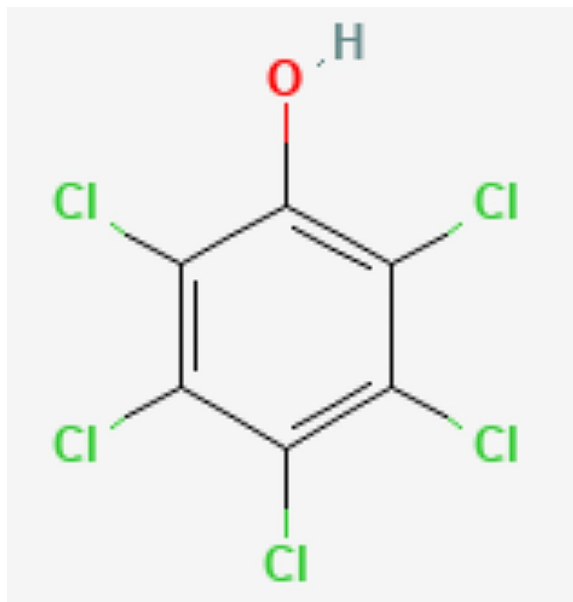


Fig. 1 Structure of the pentachlorophenol

Table 1 Physiochemical properties of PCP

Property	Value
Pure PCP color	Colorless white crystalline solid
Impure PCP color	Dark gray to brown and exists as dust, beads, or flakes
Molecular weight	266.35 g/mol
Density	1.978 g/ml
Dissociation constant (K_a) at pH 4.99	1.6×10^{-14}
Sublimes	$54 \pm 2^\circ\text{C}$
Melting point	$190\text{--}191^\circ\text{C}$
Boiling point	309°C
Vapor pressure	1.1 104 mm Hg at 25°C
Log octanol/water partition coefficient ($\log K_{ow}$) at 25°C	5.05
Odor threshold in water	0.86 mg/L at 30°C
Solubility at 20°C	14 mg/L in water, 1.7 g/g in methanol, and 0.014 g/g in benzene
pK_a	4.74 at 25°C
Henry's law constant	$5 \times 10^{-7} \text{ atm} \cdot \text{m}^3/\text{mol}$

Sources [121, 43, 95]

is slightly soluble in water but dissolves in organic solvents such as alcohol, ether, and benzene [95]. It is solid at room temperature. Pentachlorophenol is a weak acid, and its ionic form dominates in the aqueous solution [79]. Volatilization from water is pH-dependent, and the unionized form is more volatile. Chlorine compounds are harmful, and in fact, PCP has five chlorine atoms, making it a much more harmful pollutant [22]. Therefore, it is critical to find a substitute wood preservative with a lower chlorine atom count while preserving the intended level of overall antimicrobial activity.

PCP use

Pentachlorophenol is predominantly used as a wood preservative, but it has a variety of other applications, such as a biocide, fungicide, herbicide, algicide, herbicide, disinfectant, defoliant, anti-sapstain, and anti-microbial agent. The wood industry was looking for suitable toxic chemicals in the 1930s when PCP was introduced as a new preservative. The performance, color, odor, and aesthetic effects of older treatment chemicals like creosote were inadequate, and they had negative consequences on the treated product [19].

Owing to their great availability and affordable price, they were the most chosen impregnation products and are mostly used to treat telephone and power line poles, as well as railroad ties. It was also applied to guardrail posts, signposts, and retaining walls. Furthermore, PCP is an active ingredient in exterior stains and paints. It has also been used in leather and textile applications. Pentachlorophenol has been used as an antimicrobial agent in industrial cooling systems, food packaging, dental products, antimicrobial soaps, and dermatological medicinal treatments, in addition to being a wood preservative [27, 62]. It has also been used in agriculture as herbicides and desiccants for forage seed crops, non-food vegetation, as biocides for post-harvest washing of fruit, and as insecticides in beehives, seed plots, and greenhouses [43].

Production volume of pentachlorophenol

The worldwide production of PCP as of 1981 was estimated to be 90,000 tons per year. Canada has the second largest wood industry in the world, next to the USA and in the same position as the UK. In 1999, nearly 3.5 million m^3 of treated wood was produced in Canada, of which 143,520 m^3 of wood products were PCP treated. As of 2021, the PCP-containing products are Dura-Treet 40 wood preservative with 34% PCP, whereas KMG-B Penta OL technical Penta, KMG-B Penta OL Penta Blocks, and Stella Jones Penta contain 86% PCP [80]. According to EPA Chemical Data Reporting (CDR), as of 2012, the production volume of PCP, including both domestically manufactured and imported by KMG chemicals, was 3825.71 tons, which became 6126.73 tons in 2015 [33]. Approximately 6126.73 tons of PCP were imported to the USA and 402.59 tons of PCP were exported by KMG Chemicals, Inc. in 2015 [33]. However, in most European countries, the production of PCP ceased in the mid-1990s. Spain stopped its production in 2003 and Finland in 2000. After the cessation of production, PCP was imported from the US to the European market [125]. It is estimated that the total amount of PCP used in Canada as of 2002 was 147 tons, which was imported from the U.S., and it was much higher in the U.S. where 5000 tons was used [125]. Data on the production volume of PCP are not available for recent years (2016–2023) since most

of countries and companies ceased their production and due to changes in the industry brought about by environmental restrictions.

Environmental issues associated with PCP use

Pentachlorophenol is considered to be one of the most widely used wood preservatives and is currently considered a possible contaminant. It is hazardous to both the environment and human health. To develop a substitute for PCP, it is necessary to understand its chemical attributes and toxicity. Therefore, the findings of many papers on the toxicity of PCP in various environmental matrices, including the atmosphere, soil, microbial communities, and their enzymatic activities, crops, and aquatic systems, are reviewed below. Similarly, it is critical to evaluate how PCP in the environment influences human health.

PCP in the air

Pentachlorophenol easily evaporates from treated wood surfaces because of its high vapor pressure, and loss may be as high as 30–80% but its sodium salt is non-volatile [134]. It has been measured that the exposure to PCP from the indoor pressure-treated wood logs brushed with PCP was 0.0005 to 0.01 parts per billion (ppb), and about 0.034 to 0.0104 ppb has been measured from the air due to the industrially dipped, non-pressure treated log homes [7]. About 0.063 mg/day of PCP is estimated to be inhaled by the general population, whereas the workers at the wood treatment facilities and lumber mills are estimated to breathe 10.5 to 154 mg/day and can absorb about 35 mg/day via the skin [7]. Volatilization from aqueous systems is not a significant method of transfer into the atmosphere due to its low Henry's Law constant [43]. In the atmosphere, volatilized PCP may undergo photolytic degradation or react with photochemically produced hydroxyl radicals [123]. The impact and toxicity of PCP reduce as it degrades. Its reaction with photochemically produced hydroxyl radicals induces dechlorination in PCP, which helps in its degradation and reduction in its toxicity [37]. The estimated rate of PCP loss by vapor-phase photolysis in the atmosphere based on the quantum yield of 254 nm in the laboratory, molar absorptivity values, and solar intensity values for mid-day in summer at 40°N was 6.2% per hour [18]. At a peak noon summer hydroxyl radical concentration of 6.2×10^6 radicals/cm³, the estimated loss rate of PCP was 1.5% per hour with a half-life of 66 h from an estimated rate constant of 4.7×10^{-13} cm³/molecule-second [18]. However, photolysis is the dominant degradation process for PCP in the atmosphere. Pentachlorophenol in the atmosphere associated with particulate matter or moisture is lost through wet deposition [8]. However, contaminants of PCP, such as trichlorinated dibenzodioxin (CDDs) and

dibenzofuran (CDFs), which are inherently toxic, may be released into the environment via volatilization and leaching during pressure treatment of utility poles or when utility poles are removed from service and disposed of by landfills [123]. Inhalation of PCP from the atmosphere is one of the main routes of exposure for humans and animals. Inhalation and dermal exposure of PCP in production workers, herbicide sprayers, wood treatment workers, and infants through contaminated diapers and bed liners have resulted in porphyrin excretion [23, 56] and liver enlargement [4, 42, 99, 108], increased serum liver enzyme levels [25, 66], and centrilobular degeneration [12]. Detailed human and animal health impacts are provided later sections.

Effect on soil and agriculture

Pesticides such as PCP are rapidly emitted into the environment. Upon the application of PCP either directly as a pesticide or indirectly as a wood preservatives, it penetrates into the soil and causes physical, chemical, and biological changes in the soil. Volatilization, adsorption, and infiltration are examples of abiotic processes that modify the physical nature of PCP, whereas hydrolysis and photodegradation alter the chemical structure of PCP. The biotic changes occur as a result of adsorption and metabolism by microorganisms in the soil. However, these activities are influenced by the physicochemical properties of PCP, soil, and other environmental variables (Fig. 2) [3, 104]. Photolysis is not a major transformation process in the soil but may be increased in near-saturated soils. When 1500 µg/L of PCP was applied to the near-saturated loamy sand soil, degradation was observed 55% more in the irradiated samples than in the dark controls in 14 days because the near-saturated condition in the loamy sand soil increased the evaporative flux and translocated the compound to the surface (0.5 mm of soil depth) where photodegradation occurred [31]. Pentachlorophenol has low volatility when it is solid, but once dissolved, it volatilizes slowly in the soil and adsorbs strongly to the organic matter. On the other hand, alteration could be biotic through the act of absorption and metabolism by various microorganisms in the soil (Fig. 2) [3, 104]. These processes depend on the physicochemical properties of the soil and pesticide.

Soil is capable of either degrading or immobilizing pollutant compounds, which reduces the leaching and volatilization of PCP. However, if the pollutant concentration exceeds the soil storage capacity, the soil fails to prevent PCP leaching and volatilization, resulting in a change in environmental conditions. Pentachlorophenol is persistent in the environment, especially in the soil, due to its stability in structure and a high degree of chlorination [137]. The half-life is generally less than 10 weeks in the soil [58]. However, it may persist in the soil for many

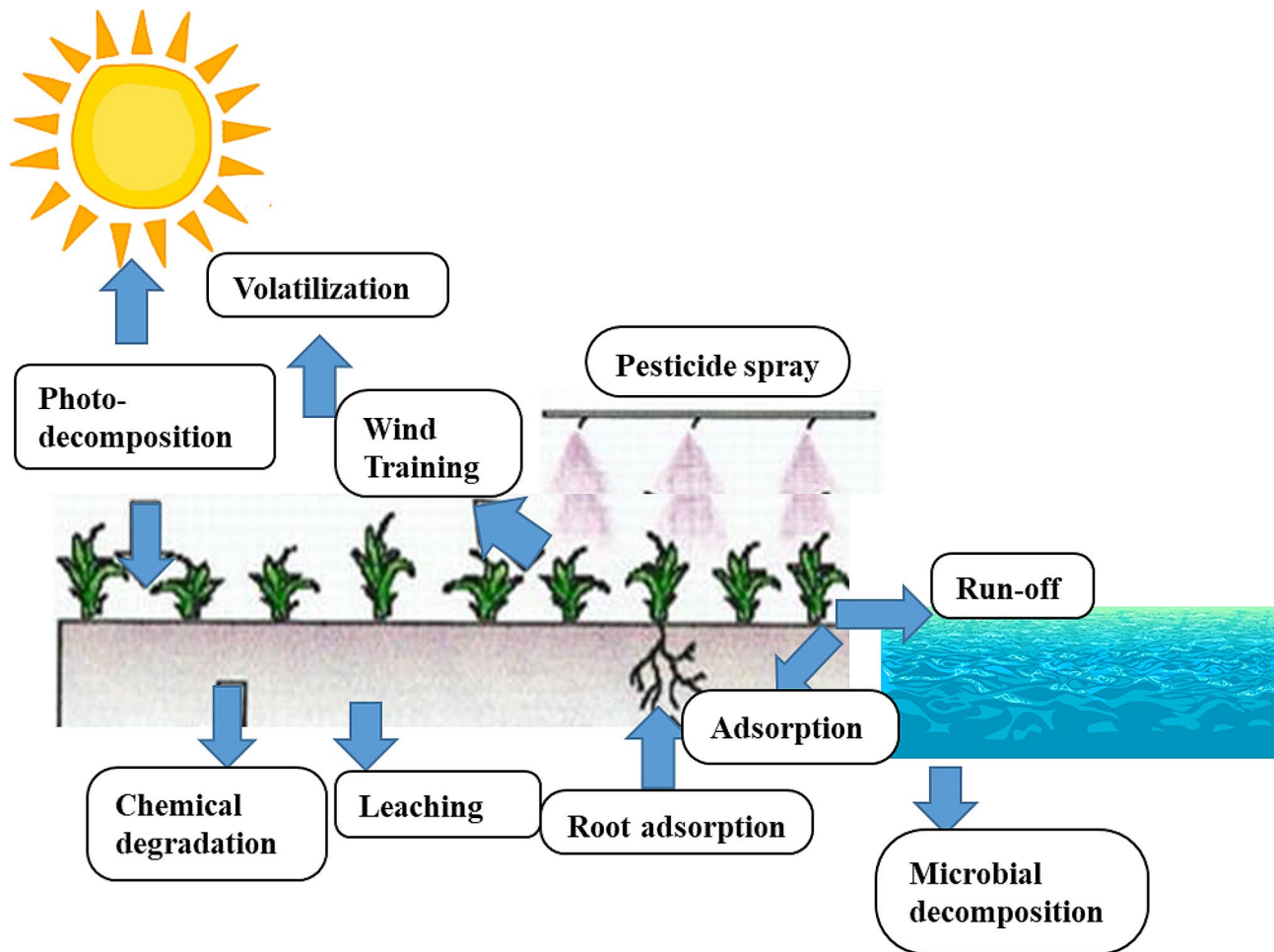


Fig. 2 The figure depicts the fate of pesticides such as PCP after its application into the soil. PCP applied to the soil is subject to relocation or alteration of its chemical structure, which may be abiotic, where a change in its physical nature is observed due to volatilization, adsorption by the soil, and leaching processes and/or change in its chemical nature by hydrolysis and photodegradation. The information and pictures were adapted from Siampiringue [104]

years in heavily contaminated soil because the higher concentration of PCP in the soil reduces its efficiency to break down. And also in cold northern climates as temperature might not be conducive for the degradation under such harsh climate. However, it may be degraded, thereby increasing the mobility of its derivatives in water and potentially contaminating drinking water [44]. Adsorption of PCP in the soil is influenced by soil pH and organic carbon content, where decreased pH increases adsorption, and as adsorption increases, its bioavailability decreases, thereby reducing its biodegradation [24]. Sorption of PCP will be greater in soil with a higher proportion of organic content therefore, poorly absorbed in neutral and alkaline soil, which makes it more mobile in them [9, 55]. PCP degradation was more rapid in the soil with low humic acid content, high moisture content, low soil granular size, enhanced soil pH, and at soil temperature conducive for microbial activity [131]. High PCP input, high soil moisture, alkaline soil conditions, and low organic matter content in the soil are factors that lead to

an increase in PCP leaching [46]. According to the Canadian Council of Ministers of the Environment's (CCME) Canadian soil quality guidelines, soil quality guidelines for human health and environmental health are 7.6 and 28 mg/kg dry weight of PCP, respectively [20].

Microbial communities are the most important part of the soil and perform several activities, including detoxification of the terrestrial ecosystem [124]. Pentachlorophenol in the soil alters the biology of the soil, which includes changes in the microbial community structure and activity over time [21, 74, 137]. It also affects the diversity of the soil's microbial community and diminishes microbial resilience against natural and anthropogenic disturbances, thereby posing a significant risk to the ecosystem. PCP influences soil activities such as respiration, nitrification, and ammonification. At 2 mg/kg of PCP in the soil, the respiration process remained unaltered; however, at 20 mg/kg of PCP, it decreased by 10–20% [139]. In a comparison of the three processes, the effect of PCP on nitrification is the most sensitive with the No

Observed Effect Concentration (NOEC) between ≥ 10 and < 100 mg/Kg ww, less sensitive on respiration with NOEC of ≥ 100 and < 1000 mg/Kg ww, and the least sensitive on ammonification process with ≥ 1000 mg/Kg ww [129]. Biodegradation is the major transformation mechanism for PCP in soil, with half-lives varying between 2 and 4 weeks [63].

In a microcosm study, a change in the microbial community was observed when members of the bacterial phylum proteobacterial, such as Xanthomonadaceae, Burkholderiaceae, and Enterobacteriaceae, and fungal phyla, such as Ascomycota and Basidiomycota, were stimulated [21]. Further evaluation of the study revealed an increase in the activity of the manganese peroxidase enzyme, which is primarily responsible for degrading lignin, dyes, organic pollutants, and emerging contaminants in wastewater, in the first 14 days of exposure [21]. However, it reduced laccase enzyme activity, which is a copper-containing enzyme that catalyzes the oxidative conversion of various chemicals, such as mono-, oligo-, polyphenols, and aromatic amines [30]. Pentachlorophenol lowered the beta-glycosidase enzyme activity and reduced the dehydrogenase enzyme activity, thereby decreasing the respiration and degradation capacity of microorganisms [119]. It reduces the abundance of Fe^{2+} - and SO_4^{-2} -reducing bacteria thereby increasing the acidity of the soil [69]. Pentachlorophenol affects the carbon utilization efficiency of microbes, thereby making them inefficient in metabolizing amines, amides, and carboxylic acid [133]. Pentachlorophenol increases the rate of phosphorous (P) transformation, which inhibits its degradation as PCP degrades at a low P concentration of 1 mmol/L [100].

The harmful effects of PCP in contaminated soil on plants include a decrease in root length, plant biomass (aerial and root), and germination (%) in different laboratory studies [59, 119]. At the lowest soil PCP concentration of 3.2 mg/kg, phytotoxic effects were occurred in lettuce, which reduced 25% of its growth, and at 4.8 mg/kg it reduced 50% of the growth, and 23% reduction in seedling emergence at 11 mg/kg [129]. About a 50% reduction in turnip growth was observed when the soil was spiked with 11.32 mg/kg of PCP [47]. It also affects root exudates, decreases citric acid, and increases malic and succinic acids in ryegrass roots [119]. In legumes, it inhibits the luteolin-induced nod gene expression by 90% and reduces the activity of enzymes connected with the nitrogen (N) cycle, such as protease and urease enzymes, in the rhizosphere, thereby inhibiting its N-fixation ability [40]. The concentration of PCP between 50 and 250 mg/kg did not affect the microbial biomass of the ryegrass rhizosphere [119]. A study has shown that corn plants exposed to PCP-treated soil accumulated 6.30 mg ^{14}C -PCP/kg in 14 days; 16% of this was PCP itself, 40% consisted of unidentified chemicals, and 44% was PCP

conjugate [73]. When 1 mg/kg of PCP was applied to the soil with carrots during one growing season, 57.6% was recovered in the soil, 42% was lost in the atmosphere, 0.1% leached to groundwater, and 0.1% was taken by carrots [101]. However, rapid metabolization occurs in plants where PCP derivatives are detected, whereas little PCP is intact in plant tissues [73]. In Canada, about 881 pork liver tissue samples were tested for PCP in which 6.6% of samples contained 0.1 mg/Kg of PCP with the highest level being 0.72 mg/Kg. In 51 beef liver samples, 2% had 0.1 mg/Kg of sample and the maximum level was 0.35 mg/Kg. About 214 chicken and 68 turkey liver tissue samples were analyzed and only one showed a level above 0.1 mg/Kg where wood shavings were used as a bedding material [2].

Effects on aquatic ecosystems

As a general environmental concern, the aquatic environment is particularly sensitive to PCP and its derivatives. The toxicity of PCP depends on environmental factors such as concentration, pH, adsorption to suspended solids, temperature, biodegradation rate, and photodecomposition rate [1]. Pentachlorophenol is not considered a persistent contaminant at low concentrations due to the photochemical degradation and microbial breakdown at the surface water, soil media, and sewage [1]. It is hydrolytically stable at pH 4–9 because it prevents hydrolysis, a major degradation process [123]. As pH and salinity decrease, the compound dissociates and rapidly photodegrades in surface water [1].

Pentachlorophenol photodegrades in surface water, where its concentration drops by 5–28% in three weeks. It has a half-life of 0.70 h at 0.5 cm depth and 9.63 h at 13.8 cm depth [89]. In a laboratory analysis, PCP in aqueous solution was photolyzed under UV light irradiation at 100 mg/L with estimated half-lives of approximately 100 h at pH 3.3 and 3.5 h at pH 7.3 [135]. In a laboratory experiment, when the PCP in an aqueous solution was exposed to sunlight, the concentration of PCP decreased from 9.3 mg/L to 0.4 mg/L in 24 h and finally reached zero at the end of 48 h [6]. Tetrachlorophenols, three tetrachlorodiols, and respective quinones, chloranilic acid, and eventually 2,3-dichloro maleic acid are the derivatives of photolyze PCP, which also undergo photodegradation but at a slower rate than the PCP [8]. Biodegradation of PCP occurs by acclimated microorganisms mainly at the surface water with a half-life ranging from hours to days [55]. Pignatello et al. [88, 89] conducted a follow-up study that demonstrated that the main method for removing PCP added to river water and outdoor constructed channels is biotransformation. It reduced PCP levels by 26–46% after 3 weeks of the acclimation period and 55–74% after 3–5 weeks of the adaptation period. Biotransformation occurs at a greater rate under aerobic

conditions above sediments than under anaerobic conditions. The microbes responsible for the mineralization of PCP are associated with rock and macrophyte surfaces or surface sediments rather than existing in the water phase [88].

Due to their high toxicity levels and relatively high water solubility, their bioaccumulation potential in marine organisms is relatively high [79]. Aquatic organisms exposed to PCP can experience both acute and chronic toxic effects. The lethal concentration 50 (LC₅₀) values are 68 µg/L in chinook salmon, 52 µg/L in rainbow trout, 205 µg/L in fathead minnow, 68 µg/L in channel catfish, and 32 µg/L in bluegill sunfish [61]. The lethal concentration of 50 is the amount of substance required to kill the organism during a predetermined period. PCP affects the energy metabolism of fish by partially uncoupling phosphorylation and increasing oxygen consumption by altering several enzymes involved in glycolysis and the citric acid cycle [16, 132]. However, pure PCP was quickly eliminated from the fish after absorption as a metabolite, having a short biological half-life of just 10 h [120].

Stocks and pools of PCP in air, water, and soil

According to the study conducted by Environment Canada in 1992, PCP levels were found to be higher in utility and railway ditches, with the amount of PCP averaging about 1060 mg/kg at the base of the poles [121]. After service, the PCP-treated wood is either incinerated, disposed of in landfills, recycled, or reused. Different countries have different discarding regulations. In the case of burning PCP-treated wood, toxic contaminants such as dioxins and difurans are released. Therefore, PCP-treated wood is buried in landfills in Canada and the US. On- and off-site disposal and releases of PCP from wood products, hazardous wastes, or other means from 36 domestic manufacturing and processing facilities are listed in Table 2. From Table 2, approximately 89% of PCP goes into the soil, 1% into the air, and 9.6% into the water, and a higher amount of PCP is found in the soil than in the atmosphere or aquatic system [115]. The cost for state budgets on PCP ban is difficult to estimate in Canada and the U.S. The cost may be involved with adopted control measures, monitoring, and communication. The treatment of hazardous wastes involves governmental costs for monitoring and control. These costs will

Table 2 Estimated release of pentachlorophenol into environmental matrices such as air, water, and soil in 2002, 2008, and 2020 [41, 115]

Environment matrices/Year	2002	2008	2020
Atmosphere (Kg/year)	60	171	46.26
Water (Kg/year)	407	513	391.4
Soil (Kg/year)	5152	1865	3622.84

be dropped significantly when treated poles are replaced by alternatives.

Public health impacts

The route of exposure to PCP is either inhalation, oral, or dermal with three exposure periods acute (≤14 days), intermediate (15–365 days), and chronic (>365 days). Approximately tens of thousands of people from Canada and many other countries continue to be exposed to PCP through its use as a wood preservative for telephone poles, pilings, and fence posts and as a pesticide in leather tanneries [90]. The higher toxicity of PCP in mammals is because it decouples oxidative phosphorylation, making cell membranes permeable to protons and thus dissipating the gradient transmembrane permeable protons. This in turn also dissipates the gradient transmembrane of H⁺ ions and electric potential, which eventually alters the functionality of the membranes [106]. In laboratory animal oral studies, acute [11, 117], intermediate [13, 45, 64, 117], and chronic [103] exposure to pure, technical-grade, and commercial-grade PCP resulted in alterations in serum liver enzyme levels, increase in liver weight, and hepatocellular hypertrophy, degeneration, fibrosis, and necrosis.

The acute, intermediate, and chronic exposure of either animals or humans may lead to body weight reduction [102], respiratory challenges [81], cardiovascular diseases [67], gastrointestinal problems [65], hematological [67], musculoskeletal [81], hepatic [117], renal [65], endocrine [60], immunological [53], neurological, and other non-cancer diseases [81]. Experimental studies on animals have demonstrated the embryotoxic and fatal effects of PCP. Experimental rats were fed with 3 and 30 mg/kg of PCP, with female rats administered the highest dose before mating, during mating and gestation, and throughout lactation. The PCP-fed rats showed a drop in mean adult body weight, significantly decreased neonatal survival, and mild signs of toxicity, including decreased body weight (females), impaired liver function (both sexes), and impaired kidney function (females) [103].

Because of increased liver cancers and unusual tumor forms in several oral animal trials, the EPA has categorized PCP as a potential human carcinogen (category B2) [122]. Aplastic anemia, red-cell aplasia, thrombocytopenic purpura, several types of leukemia, Hodgkin's disease, non-Hodgkin lymphoma, cardiomyopathy, nerve injury, soft-tissue sarcomas, severe inflammation of the upper and lower respiratory systems, fetal damage, congenital deformities, and infertility secondary to sperm destruction are the diseases caused by PCPs and their contaminants [83, 98].

Cooper and Jones [26] extracted data on three different types of cancer risks, namely non-Hodgkin, soft-tissue sarcoma, and multiple myeloma, concerning PCP

exposure from different case studies conducted between 1970 and 1995 (Table 3). A meta-analysis was performed and data obtained from Cooper and Jones [26] study was used to make a forest plot to see the effect of and the correlation between PCP exposure and cancer risk (Table 3). The effect of the studies are shown as the odds ratio (OR). The odd ratio in the forest plot denotes the likelihood of new cases occurring where values of more than 1 are at risk. The results of the statistical test of heterogeneity for the above meta-analysis are shown in the text “Test for heterogeneity: $\chi^2=12.761$, $df=11$, $P=0.228$, $I^2=21\%$ (Fig. 3; Table 4).” The P -value for the test of heterogeneity was 0.228, indicating that there was no evidence to reject the null hypothesis in favour of the alternative. Therefore, homogeneity existed between the sample estimates. The value for χ^2 is the test statistic resulting from the statistical test used to derive the P -value. The value for degrees of freedom (“ df ”) equals the number of trials minus one and is used along with the test statistic to calculate the P -value. Higgins I^2 statistic, simply referred to as I^2 , is often also used as an alternative test for heterogeneity.

This statistic represents the percentage of variation between the sample estimates that is due to heterogeneity. It can take values from 0% to 100%, with 22% indicating that statistical homogeneity exists. Significant statistical heterogeneity is often considered to be present if I^2 is 50% or more. The value of I^2 in our study is approximately 22% and lower than the threshold of 50% which corroborates the inference from the statistical test of the hypotheses that statistical homogeneity existed among the studies used in our study. (Fig. 3; Table 4)

Case-control studies on non-Hodgkin lymphoma such as [87, 136], a study on soft-tissue sarcoma [136] and a study on multiple myeloma [86] analyzed occupational exposure to chlorophenols with limited data and especially included those jobs and activities with high exposure of pentachlorophenol. From these studies it was observed that there was a strong association between jobs generally associated with PCP such as fencing work and wood preservation and chlorophenols as OR values are closer to or higher than 1.5 (Table 3; Fig. 3). However, these studies have shown a weak association with

Table 3 Case-control studies of non-Hodgkin lymphoma, soft-tissue sarcoma, and multiple myeloma risk concerning PCP exposure

The type of cancer	Chemical and test methods	Number of exposed cases	Number of exposed controls (C)	Odds ratio (OR)*	Confidence interval (CI 95%)*	Reference and subjects
Non-Hodgkin lymphoma	Chlorophenols (Structured interview)	83	168 Cancer Control (CC) 228 Population Control (PC)	1.3 (Chlorophenol) 2 (Fencing work)	0.6–2.7 (Chlorophenol) 1.3–3.01 (Fencing work)	[86] New Zealand Male, age < 70 years
	Chlorophenol (Structured interview)	576	694	0.99 (Chlorophenol); >1.5 (wood preserver and manufacturers); 0.94 (lumber grader)	0.8–1.2	[136] USA (Washington state) Male-age 20–79
	Pentachlorophenol (PCP) Self-administered questionnaire with telephone interview	105	355 PC	8.8	3.4–24	[49] Sweden Males, aged 25–85 years
	Pentachlorophenol (PCP) Company records and industrial hygienist review	32 death (7 countries)	158	2.75 (PCP) 4.19 (high PCP)	0.45–17 (PCP) 0.59–29.6 (high PCP)	[68] Europe primarily male (31 of 32)
Soft-tissue Sarcoma	Chlorophenols Structured interview	128	694 PC	0.99 (Chlorophenol) 2.7 (lumber grader)	0.7–1.5 (Chlorophenol) 1.1–6.4 (lumber grader)	[136] USA (Washington state) Males aged 20–79
	Chlorophenols Self-administered questionnaire with follow-up telephone interview	434	948 PC	2.8	1.5–5.4	[50] Meta-analysis of four studies. Sweden Male, ages 25–80 years
	Chlorophenols Structured interview	82	92	1.5	0.5–4.5	[107] New Zealand male, age 20–80
Multiple myeloma	Chlorophenols	76	315	1.6 (Fencing work) 1.4 (Sawmill merchant)	0.9–2.7 (Fencing work) 0.5–3.9 (Sawmill merchant)	[87] New Zealand Male, age < 70 years

*OR at a confidence interval (CI) of 95% OR-Odds ratio effect of PCP exposure on cancer (value > 1 at high risk). Data obtained from Cooper and Jones [26]

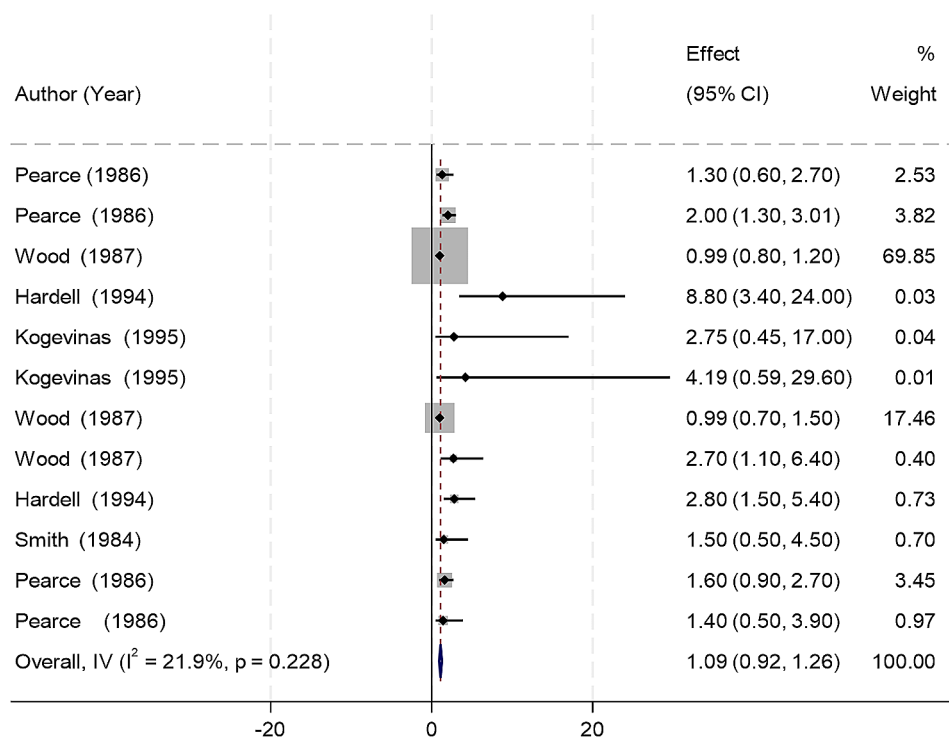


Fig. 3 Forest plot for effect of PCP exposure on (OR) non-Hodgkin lymphoma, soft-tissue sarcoma, and multiple myeloma risk at a CI of 95% from Table 3; *Effect OR-Odds ratio; CI-Confidence Interval at 95%; * I^2 - Higgins I^2 statistic

Table 4 Results of the statistical test of heterogeneity for the metaanalysis of case-control studies of non-Hodgkin lymphoma, soft-tissue sarcoma, and multiple myeloma risk concerning PCP exposure

Measure	Value	df*	p-value
Cochran's Q	14.08	11	0.228
H	1.131	1	1.585
I^2 *(%)	21.90%	0.00%	60.20%
Test of overall effect=0: z=12.761 p=0.000			

*df - degrees of freedom; I^2 - Higgins I^2 statistic

chlorophenol with OR value <1.5. A stronger risk of non-Hodgkin lymphoma was observed due to high exposure to pentachlorophenol with the OR of 8.8 and 95% CI=3.4–24 [49] (Table 3; Fig. 3). The meta-analysis of four soft-tissue sarcoma studies [34, 35, 48, 51] has shown a higher association between high PCP exposure and soft-tissue sarcoma with OR of 2.8 and 95% CI=1.5–5.4 (Table 3; Fig. 3). Therefore, the meta-analysis indicates that there is a strong association between PCP exposure and cancer and it could be a possible cause for the three important cancers such as non-Hodgkin lymphoma, soft-tissue sarcoma, and multiple myeloma. In 2016, an international Working Group of 18 scientists convened by the International Agency for Research on Cancer (IARC), the cancer agency of the World Health Organization, classified PCP as carcinogenic to humans (Group-1), as there was

sufficient evidence available on PCP causing non-Hodgkin lymphoma in humans [57].

Transformation pathways of the PCP

Pentachlorophenol, a phenolic compound with five chlorine atoms, degrades majorly through photodegradation commonly called as photolysis and biodegradation. The transformation pathways of PCP through photolysis and biodegradation pathways are explained in detail below.

Photolysis

PCP upon the addition of hydroxyl radicals and less chlorinated phenols is converted into catechol, hydroquinone, or trihydroxylated forms via photolytically reductive dechlorination [10, 70, 76]. The lower the number of chlorine atoms, the lower the toxicity [32]. Although dechlorination reduces the toxicity of PCP, environmental metabolism may lead to genotoxicity [130]. In a previous study, the photolytic transformation products of PCP detected using gas chromatography-mass spectrometry in water were 3,5-dichlorophenol, 2,3,5-trichlorophenol, 3, chlorodroquinone, pentachlorobenzene, pentachloronitrobenzene, trichlorohydroquinone, pentachlorophenol, tetrachlorophenol, tetrachlorohydroquinone, 1,2,4-trihydroxy-trichlorobenzene, hexachlorohydroxydiphenylether, heptachlorohydroxydiphenylether, octachlorohydroxydiphenylether, nonchlorodiphenylether, heptachlorodibenzo-p-dioxin,

nonchlorohydroxydiphenylether, decachlorodiphenylether, and octachlorodibenzo-p-dioxin. PCP, tetra, tri, and di-chlorophenols are formed as major intermediates during photolysis through reductive dechlorination (Fig. 4) [54]. Hexa and penta-chlorobenzenes are formed during the photolysis of PCP during UV irradiation, where dechlorination of hexachlorobenzene and/or dehydroxylation of PCP forms pentachlorobenzene. Abstraction of the hydroxyl radical forming pentachlorobenzene followed by addition of the chlorine radical obtained from another dechlorination process form hexachlorobenzene (Fig. 5) [54]. Nonchlorohydroxydiphenylether formed by the self-condensation of PCP can be converted to octa-, hepta-, and hexa-chlorohydroxydiphenylethers by sequential dechlorination, where nonchlorohydroxydiphenylether acts as a precursor for octachlorodibenzo-p-dioxins, which further undergo dechlorination (Fig. 5) [54]. The formation of nonchlorinated hydroxydiphenylether by condensation of PCP and hexachlorobenzene is one of the major transformations in the photolysis of PCP (Fig. 5).

Biodegradation

Biodegradation involves both aerobic and anaerobic bacteria for PCP breakdown. Pentachlorophenol is more resistant to biodegradation, especially aerobic degradation than low-chlorinated phenols due to the presence of five chlorine atoms on the phenolic ring. However, they can be reductively dehalogenated to phenols with

fewer chlorine atoms, which are further easy to mineralize [5]. Anaerobic conditions favor reductive dechlorination, which results in the displacement of chlorine atoms with hydrogen atoms [52]. Reductive dehalogenation that occurs metabolically by bacterial-triggered reductive dechlorination or catabolically, requiring the input of electron-donating substrates, utilizes halogenated compounds as terminal electron acceptors for energy-conserving anaerobic respiratory electron transport [39]. The reductive dehalogenation reactions result in the formation of phenol, which is further degraded to methane and carbon dioxide by bacterial genera such as *Desulfitobacterium*, *Dehalobacter*, *Anaeromyxobacter*, *Geobacter*, *Desulfomonile*, *Desulfuromonas*, *Desulfovibrio*, *Sulfurospirillum*, *Dehalogenimonas*, *Dehalobium*, and *Dehalococcoides* [97]. *Desulfitobacterium hafniense* strain PCP-1 was widely studied, which showed two enzymatic systems to dechlorinate PCP; one dechlorinates PCP at the ortho position to produce 3,4,5 tetrachlorophenol (TCP) and the second dechlorinates 3,4,5 TCP at the meta and para positions to produce 3-chlorophenol (CP) afterward to phenol, which is further degraded to carbon dioxide (CO₂) and methane (CH₄) (Fig. 6) [75, 112, 128]. *Sphingobium chlorophenolicu*, L-1 is an aerobic bacterium that converts PCP into tetrachlorohydroquinone (TCHQ) by removing chloride atoms, which is catalyzed by enzyme called PCP 4-monooxygenase (PcpB), a flavoprotein encoded by the pcpB gene [38, 84, 113, 138]. TCHQ is then sequentially halogenated

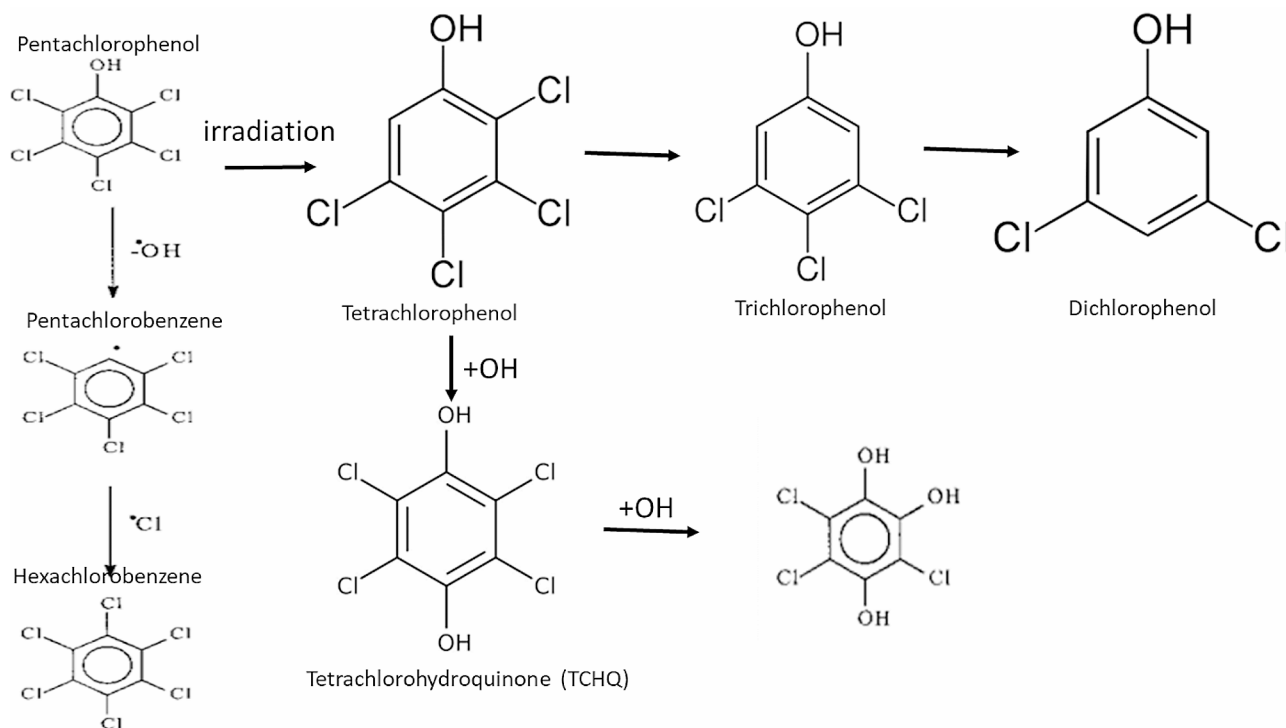


Fig. 4 Photolysis pathway of PCP in water. Modified from Hong et al. [54]

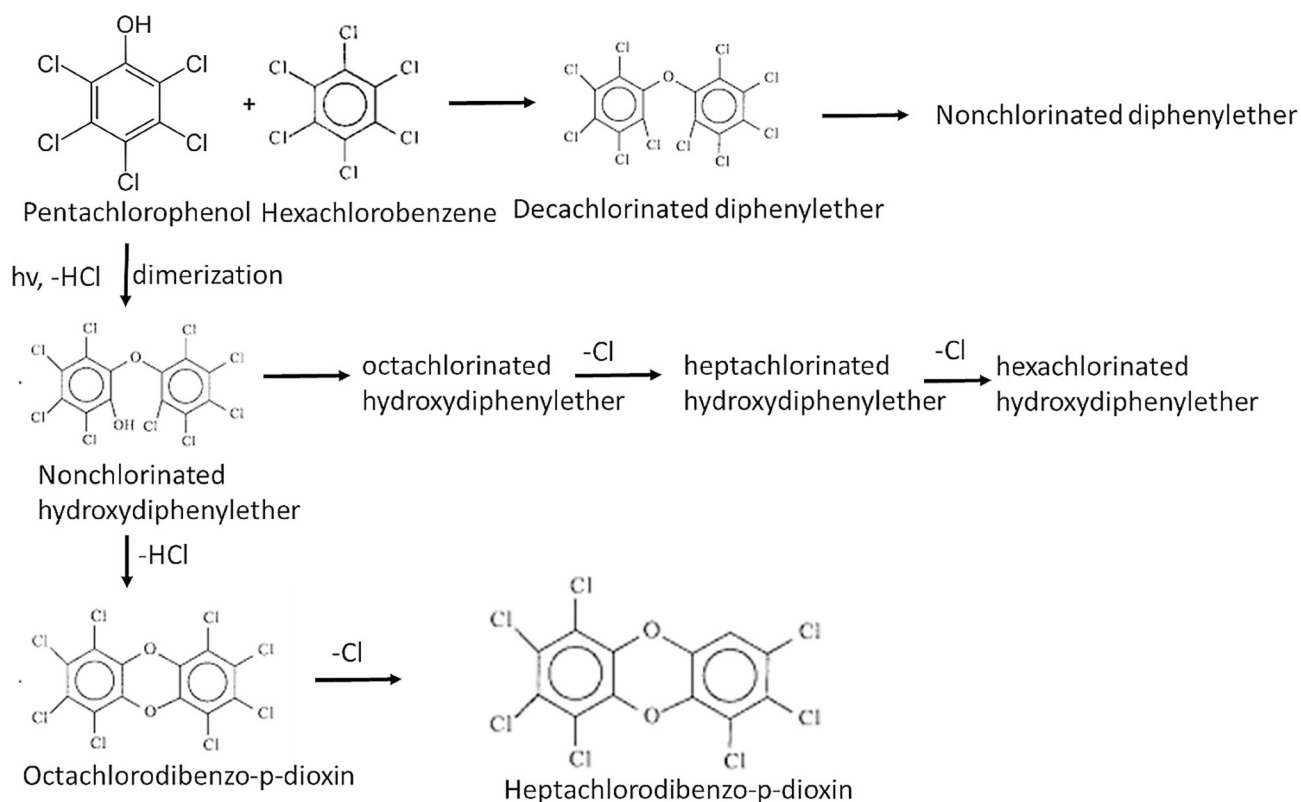


Fig. 5 Photodegradation pathway of PCP under UV irradiation and PCP dimerization. Modified from Hong et al. [54]

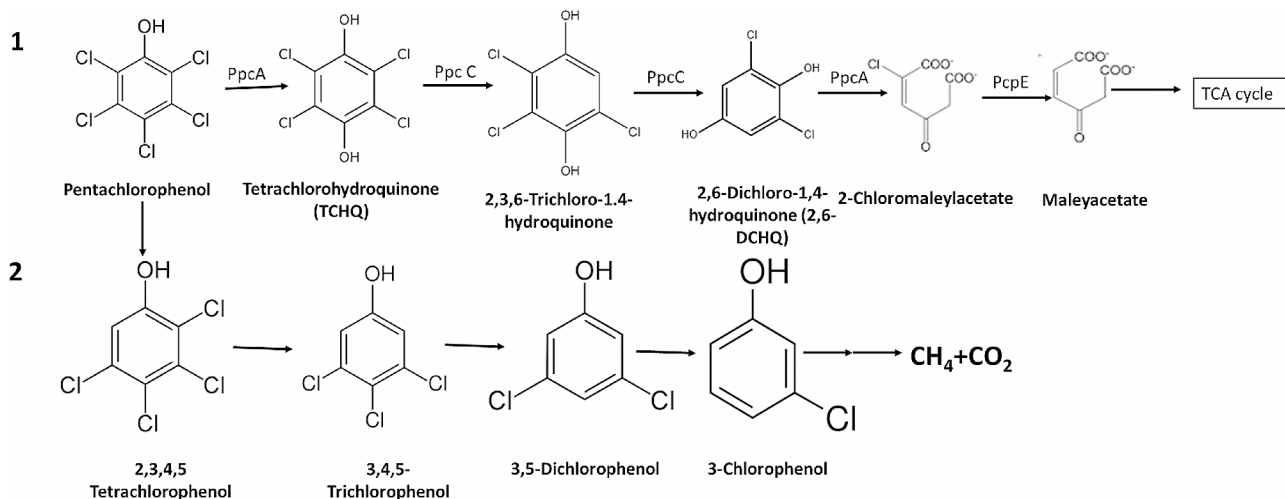


Fig. 6 1. Aerobic bacterial degradation pathway of PCP in *Sphingobium chlorophenolicum* L-1; gene, enzyme combination: PcpB, PCP 4-monooxygenase; PcpC, TCHQ-reductive dehalogenase (RDase); PcpA, 2,6-DCHQ-1,2 dioxygenase [5, 38, 110]. 2. Anaerobic bacterial degradation or dehalogenation pathway of PCP by *Desulfitobacterium habiense* strain PCP-1 [5, 75]. Modified from Lopez-Echartea et al. [72]

into 2,6-dichloro-1,4-hydroquinone (2,6-DCHQ) by a TCHQ-reductive dehalogenase (RDase) enzyme, and the reaction is encoded by the *pcpC* gene [84]. Degradation of 2,6-DCHQ into 2-chloromaleylacetate by the 2,6-DCHQ-1,2 dioxygenase enzyme [82]. Then 2-chloromaleylacetate further degrades into the tricarboxylic cycle (TCA) (Fig. 6) [5].

Need for a new oil-borne wood preservative

On October 4, 2023, PCP was phased out from the wood industry as a wood preservative in Canada because of its high toxicity. The company's sales of PCP in 2009 were \$26.2 million [125]. Due to this ban on PCP, the industry would no doubtfully face a major economic loss as industries will have to shift capacity from PCP treatment to

other treatments and upgrade equipment to accept new formulations. However clear quantitative cost data is not available because PCP has a small share in the lumber and timber market where the impact will not be as high as in the pole market [125]. The unavailability of potential alternatives for PCP will further incur economic loss to the industry. Therefore, it becomes inevitable to look for a chemical preservative that is not only effective against wood pests but also environmentally friendly and not as toxic as PCP. PCP is highly volatile, and its inhalation causes acute and chronic diseases in humans [134]. As a result, the new preservatives should be less volatile than chlorophenols and decay quicker in the atmosphere. PCP contains five chlorine atoms, and as discussed before, it is persistent in the soil due to its structural stability and the presence of chlorine atoms [137]. Owing to the environmental concerns and harmful effects of chlorine, an ideal chemical for wood preservation could preferably be devoid or contain a lesser number of chlorine atoms while maintaining its effectiveness against wood-decaying fungi. The burning of chemicals containing benzene rings in their structure, such as PCP, releases dreadful contaminants, such as PCDDs and PCDFs, into the atmosphere [127]. The new preservative should not contain an aromatic ring to prevent the release substances with carcinogenic effects. In addition, its derivatives should be less toxic.

The new preservative should not contain heavy metals that could accumulate and leak into various environmental matrices. Furthermore, the new wood chemical should be free of components that may generate hazardous derivatives during breakdown, which could be harmful to the environment. The preservative must not affect the number and diversity of microbial communities in the soil, thereby ensuring its resistance and resilience to anthropogenic and natural disturbances. Rather than being poisonous to the beneficial microbes engaged in degradation and enhancing plant growth, it should be toxic to wood-degrading microbial organisms. It must not harm aquatic life and should break down faster in aquatic systems. As discussed above, technical grade PCP contains contaminants that make it a potential wood preservative [20]. Nevertheless, the presence of these pollutants in technical grade PCP not only increases its environmental persistence but also has detrimental effects on human health. As with technical grade PCP, the new preservative must not include any hazardous pollutants or impurities. Lastly, neither it should have any carcinogenic qualities like PCP, nor should it result in acute or chronic human illnesses.

In addition to not being toxic and harmful to the environment, the new preservative should also have properties that might enable it to function effectively against wood-decaying fungi and wood insects. PCP and

creosote are more effective in penetrating and holding onto wood under pressure treatment because they are oil-borne preservatives that render them entirely soluble in petroleum and other organic solvents. Greater efficiency and water repellency can be readily achieved using oil-based preservatives [109]. These organic solvents aid in better penetration of chemicals into wood. Therefore, the new wood chemical should be preferably an oil-borne solution so that it can be soluble in organic solvents such as petroleum and oil for effective penetration and protection against decaying pests. There is a need for further studies to identify a new wood preservative with the aforementioned qualities.

Conclusions

This review discussed the effects of PCP in different environmental matrices such as air, soil, crops, microbial communities and enzymatic activities, aquatic systems, and mammals, including humans. Pentachlorophenol used to be the most preferred oil-borne preservative due to its effectiveness in penetrating wood and protecting against wood-decaying fungi. However, PCP is a hazardous substance that contaminates the environment and harms human health. It is quite persistent in environmental matrices such as air, water, and soil and eventually enters the human system. Its persistent presence in the environment allows humans to inhale it, come into contact with it through skin contact, or consume contaminated food. As a result, PCP can cause various illnesses in people, including cancer, because it has carcinogenic qualities. This review has provided insights on the characteristics of the potential alternative wood preservative: It should be both ecologically friendly and effective in protecting the wood. However, before applying any chemical as a wood preservative, further research on environmental assessment is needed.

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KK: Writing-Original draft preparations, methodology, software. ECU: Conceptualization, writing-reviewing and editing, validation, methodology, Software. SH: Conceptualization, writing-reviewing.

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