

Fate and Toxicity of Chlorinated Phenols of Environmental Implications: A Review

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Abstract

Chlorophenols are ubiquitous contaminants in the environment. They are used as intermediates in manufacturing agricultural chemicals such as biocides, fungicides, herbicides, insecticides, and precursors in the synthesis of other pesticides; pharmaceuticals and dyes since the 1930s. Chlorophenols are released into the environment from several sources such as industrial waste effluent discharge, application of pesticides, insecticides, or by degradation of complex chlorinated hydrocarbons. Thermal, biological and chemical degradation of chlorophenols is responsible for the harmful metabolites which constitute public health problems. These compounds may cause histopathological alterations, genotoxicity, mutagenicity, and carcinogenicity amongst other health problems in humans and animals. Furthermore, the recalcitrant nature of chlorophenolic compounds to degradation is responsible for its persistence, and a comprehensive understanding of the fate and mobility of these compounds and their metabolites is needed for environmental monitoring and risk assessment of their pathogenicity to humans and animals. This review explores research on mobility of chlorophenols in different media, and the health implication and toxicity of chlorophenols with regards to animal, humans and the environment.

Keywords: Chlorophenol; Metabolites; Carcinogenicity; Mutagenicity; Genotoxicity; Environment; Chemicals

Abbreviations: CPs: Chlorophenols; PCP: Pentachlorophenol; SOM: Soil Organic Matter; DOC: Dissolved Organic Carbon; NOM: Natural Organic Matter; 4-MCP: 4-Monochlorophenol; TCE: Trichloroethene; PCDD/F: Polychlorinated dibenzodioxins and-furans; US-EPA: United States Environmental Protection Agency; ISIRI: Institute of Standard and Industrial Research of Iran; PAHs: Polycyclic Aromatic Hydrocarbons.

Introduction

Chlorinated phenols are chlorinated aromatic compound commonly found in pesticide preparations as well as industrial wastes which are commonly resistant to biological degradation. Chlorophenols and their derivatives is one of the most general pollutants in effluents discharged from diverse industries producing various products including resins, plastics, adhesives,

iron, steel, aluminum, leather etc. Additionally, chlorophenol is used as a solvent, as an antiseptic and as an additive in disinfectants. They are recalcitrant to biodegradation thus, they are persistent in the environment. A variety of chlorophenols derivatives compounds are highly toxic, mutagenic and carcinogenic for living organisms [1,2].

Chlorophenols are group of pollutants attracting global attention because of their toxicity and ubiquity. Chlorophenols (CPs) include mono-, di-, tri-, tetra-, and penta-chlorinated phenols (CP, DCP, TCP, TTCP, and PCP, respectively). Among the 19 possible forms of chlorophenols, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) made the list Priority Pollutant List of the US Environmental Protection Agency [3]. The 2-CP, 2,4-DCP and 2,4,6-TCP are precursors for the production of chlorophenol products and 2,4-DCP, 2,4,6-TCP and PCP are used as pesticides, herbicides, fungicides, bactericides, and inhibits several biological agents [4].

Fate in Soils

Phenolics are the most abundant plant metabolites and are believed to decompose slowly in soils compared to other soil organic matter (SOM). Thus, they have often been considered as a slow carbon pool in soil dynamics models [5]. The release of phenolic compounds to the soil can be by leaching from treated wood products, atmospheric deposition in precipitation (such as rain and snow), herbicidal application, and spills at industrial facilities and at hazardous waste sites. However, adsorption of these chlorophenols in soils is pH dependent because it increases under acidic conditions and it decreases in neutral and basic conditions [6]. In soil, soluble phenols face four different fates. They might undergo degradation and mineralization as a carbon source by heterotrophic microorganisms; they can be transformed into insoluble and recalcitrant humic substances by polymerization and condensation reactions (with the contributions of soil organisms); they might remain in dissolved form, leached by percolating water and finally leave the ecosystem as part of dissolved organic carbon (DOC) [7].

The soil pH plays a significant role in particular for the adsorption of ionic pesticides such as chlorophenol [8]. Depending on the charge of the compound, the adsorption will increase (or decrease) with pH [9]. For example, sorption of 2,4-DCP decreased with increasing in pH and increases as the pH decrease because a greater

proportion of 2,4-DCP is in molecular form relative to anionic form [9,10-12]. It was reported that the adsorption of chlorophenols was highly dependent on pH since it has strong influence on the surface charge of the soils [6]. In general, the adsorption of chlorophenols decreases as their water solubility increases because of their high affinity for the water phase, and conversely, the adsorption increases with the hydrophobicity of compounds. However, the hydrophilic/hydrophobic balance of the soils must be put into consideration. The adsorption of polar compounds does not always decrease with increasing water solubility [9,13].

Sorption studies are essential for evaluating the mobility of herbicides/pesticides in soils. The distribution coefficients are used in mathematical modeling of chlorophenol transport in soils [14]. Desorption is of high importance as well because it determines the amount of herbicide that can be released back to aqueous solution and thus controls the final distribution of the chlorophenol in soil [15,16]. The sorption-desorption behavior of a soil-applied herbicide is one of the most important factors governing its environmental impacts such as degradation, transition, and leaching [17]. The sorption behavior of 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol, chlorotriazine atrazine, methylthitriazineametryn, methoxytriazineatratone, hydroxyatrazine and diakylated atrazine in a topsoil and an aquifer sediment before and after removal of sorbent organic matter and in humic acid. Freundlich isotherm coefficients K_f and $1/n$ and free energy change (ΔG°) were calculated for all compounds in all sorbents. According to sorbent pH values, chlorophenolate anions and uncharged triazine species dominated in all sorption experiments with topsoil and aquifer sediment. In experiments with humic acid, chlorophenols, atrazine and dialkylated atrazine existed almost completely as neutral species, whereas protonated species dominated for hydroxyatrazine, atratone and ametryn. In addition to a hydrophobic partition, sorption of all compounds in native soil and sediment sorbents include specific, more polar interactions, which greatly matter and of mineral surface, as well as on the system pH. A significantly greater sorption intensity of all compounds in 'organic-free' than in the native aquifer sediment confirmed the importance and possible dominance of mineral surface in the sorption process. Sorption intensity of chlorophenol and triazine compounds in humic acid was closely related to compound hydrophobicity [18].

The role of natural organic matter (NOM) on sorption of chlorinated hydrophobic organic pollutants. The desorption of 1,3,5-TCB under the influence of different

concentrations of NOMs were studied and it was reported that increasing the natural organic matter (NOM) in solution led to higher desorption for all types of sorbents. It is generally accepted that natural organic matter (NOM) plays a crucial role in the adsorption to and desorption from sorbent for all organic compounds [19]. The roles NOMs play are often contradictory in terms of their effect on the adsorption and desorption process. On the one hand, natural organic matter (NOMs) could facilitate the dispersion of sorbent in water and make more adsorption sites available for adsorbates, thus increasing the adsorption. Similarly, NOM would compete with organic compounds for the same adsorption sites or physically block some available adsorption sites for organic compounds, resulting in reduced adsorption. Even though NOMs adsorbed on the sorbent surface can function as a new adsorbent, their affinity with organic compounds appears to be smaller than the affinity between natural sorbents and organic compounds. Both of these competing effects are expected to occur during the adsorption and desorption process [6]. Literatures suggest that adsorption of chlorinated phenols to the soil is the key process that affects their ecotoxicological impact, environmental mobility and the rate of degradation [20]. The desorption process of herbicides is also important since it determines the release rate and the potential mobility of herbicides in the soil [21].

Biodegradation and Decomposition of Chlorophenols in Soils

The extent and rate of biodegradation depend on numerous factors, including soil pH, organic carbon content, biomass, and the chlorophenol isomer and its concentration. In neutral clay-loam soil at 20°C under aerobic conditions, 2-CP was degraded the fastest. Decomposition rates were as follows: 100% of the 2-CP in 1.5 days, 95% of the 2,4,6-TCP in 3 days, 83% of the 4-CP in 20 days, 81% of the 2,4-DCP in 40 days, and 72 and 31% of the 2,4,5-TCP and 2,3,4,5-TeCP, respectively, in 160 days [22].

The observation of 2,3,4,6-Tetrachlorophenol in soil (157-338 µg/g dry soil) at a sawmill 28 years after it closed provides evidence that this compound can persist in soil. Soil concentrations of 2,3,4,6-Tetrachlorophenol when the mill was closed were not stated. In general, degradation or complete mineralization to carbon dioxide (CO₂) is greater in soils with low organic carbon content [23], slightly alkaline pH [24], increased temperatures [22,23], and increased inoculum concentrations [23]. Microbial degradation of chlorophenols in soil under anaerobic conditions has not been observed consistently. For 2-CP, 4-CP, 2,4-DCP, 2,4,5-TCP, 2,4,6-TCP, and 2,3,4,5-

TeCP, no statistically significant differences in degradation rates between non-sterile and sterile clay loam soils occurred when both soil samples were incubated under anaerobic conditions [22].

Chlorophenol isomers undergo biodegradation in soils under aerobic conditions. Aerobic microorganisms that can degrade chlorophenols have been isolated from soil bacterial cultures. *Pseudomonas picketti* DTP0602, which used 2,4,6-trichlorophenol as the sole source of carbon and energy, was isolated from mixed cultures of soil bacterial populations that had been acclimatized to 2,4,6-TCP [25]. This bacterial species dechlorinates the chlorine atom at position four (4) of various CPs to yield their corresponding hydroquinones.

Dehalobacter species strain TCP1 was isolated from a digester sludge sample, which is able to dechlorinate 2,4,6-trichlorophenol (2,4,6-TCP) to 4-monochlorophenol (4-MCP) with H₂ as the sole electron donor and acetate as the carbon source. Strain TCP1 also distinguishes itself from other Dehalobacter species with its capability to dechlorinate tetrachloroethene or trichloroethene (TCE) to both cis- and trans-dichloroethenes in a ratio of 5.6 (±0.2):1. The growth yields of strain TCP1 on TCE and 2,4,6-TCP were 4.14 × 10¹³ and 5.77 × 10¹³ cells mol⁻¹ of Cl-released, respectively. Both the culture-dependent and housekeeping *rpoB* gene-based approaches indicate the purity of the culture. Strain TCP1 can serve as a promising candidate for the bioremediation of 2,4,6-TCP contaminated sites, and its discovery expands our understanding of metabolic capabilities of Dehalobacter species [26].

Fate in Water

The majority of known environmental releases of chlorophenols were to surface water [27]. The principal point source of water pollution by chlorophenols is industrial waste discharge; another point discharge is the leaching of chlorophenols from landfills. In general, increasing chlorination increases the tendency of these compounds to partition into sediments and lipids and to bioconcentrate. Concentration of phenol in surface water of Netherlands were of 2.6-5.6 µg/L. River water polluted with sewage derived from petrol processing plants contained the concentration of phenol over 40 mg/L [28].

Chlorophenols are subject to abiotic and biotic degradation and transformations. The general population may be exposed to chlorophenols through ingestion of chlorinated drinking water and food contaminated with the compounds and inhalation of contaminated air.

Exposure to 4-CP could also occur through its use as a root canal packing. Populations with potentially unusually high exposure to chlorophenols generally include employees of facilities that manufacture or use chlorophenols and their derivatives and those who live in the vicinity of chlorophenol-containing waste disposal sites and waste incinerators. Relative fast degradation of phenol causes its concentration in waters exposed to strong anthropogenic pollution incomparable. Phenol was also found in domestic water supply in the USA at a level of 1 $\mu\text{g/L}$. In high concentrations phenol is determined near factories that impregnate wood and its value reaches 9.7 $\mu\text{g/m}^3$ [29].

The photolysis rates of 2-CP in natural waters depend on pH, season, and dissolved organic material [30]. In all cases the reaction rate is first order. Based on empirical data, these investigators proposed that direct photolysis of 2-CP may only occur in natural waters at pH between 7 and 9. Indirect photolysis in lake waters was only significant in summer months; in sea waters, indirect photolysis has a more significant role in the spring and fall. It was found that the dissolved organic matter in pond water does not contribute to indirect photolysis as significantly as a humic acid solution. The photo catalytic degradation process with titanium dioxide particles has been shown to be feasible for achieving a high degree of removal of 2-chlorophenol in water with almost complete disappearance in only a few hours of illumination time. However, the demineralization of reaction intermediates requires a longer time, and was found to be more effective for acidic solutions. Increasing the light intensity would significantly increase the decomposition rate of 2-chlorophenol at pH 3, but not pH 11 [31].

Wastewater containing phenols, chlorophenols and other toxic compounds require careful treatment before release into the receiving water sources. The treatment processes of phenolic effluents into two main categories: destructive process such as destructive oxidation with O_3 , H_2O_2 , or manganese oxides, and recuperative processes such as adsorption and membrane separation. Adsorption process is presently being used broadly for organic and inorganic micro pollutants removal from aqueous environments [32]. This procedure is the easiest, the fastest, the most efficient and cost-effective option for removal of phenolic compounds. Among different materials, activated carbon has high affinity to phenolic compounds. Nevertheless, the high cost of activated carbon has stimulated interest in investigating the possibility of using low cost adsorbents. Substitute materials experienced consist of straw, automobile tires, fly ash, coal reject, biosolids, pistachio nut shell Phenol

and its derivatives are one of the most common pollutants in effluents discharged from diverse industries producing various products including herbicides, resins, plastics, adhesives, iron, steel, aluminum, leather, and disinfectants ash, palm seed coat, fertilizer waste and sawdust [32,33]. The concentrations of phenol in surface water are different. In natural waters its amounts are between 0.01 - 2.0 $\mu\text{g/L}$ [34].

The risk of chlorophenols entering the surface water and groundwater mainly comes from the adsorbed herbicide present in the soil. To protect surface and groundwater from pesticide contamination and evaluate their impact, extensive knowledge concerning degradation and sorption-desorption processes in the environment is required. The adsorption-desorption process of chlorinated phenols is influenced by several factors such as organic matter content, soil texture, pH, temperature, etc. [35].

Fate in Atmosphere

Chlorophenols enter the atmosphere through volatilization, with mono- and di-chlorophenols being the most volatile. Once released to the environment, chlorophenols are subject to a series of physical, chemical, and biological transformations. Sorption, volatilization, degradation, and leaching are the primary processes governing their fate and transport. PCP ingresses into the atmosphere on account of its volatility. Volatility increases considerably with increasing temperature, but is likewise dependent on possible additives and e.g. the nature of the treated wood. Burning wood treated with PCP liberates polychlorinated dibenzodioxins and -furans (PCDD/F).

Chlorophenols are found in the atmosphere as vapors coming from the manufacturing of these compounds or from by-products resulting mainly from combustion processes. Generally, concentration levels of chlorophenols are the result of local emission sources. There is little or no report of data of ambient air concentrations of chlorophenols but pentachlorophenol (PCP) was measured in mountain air sampled in the La Paz region (5200m above ground) at concentrations between 0.25 and 0.93 ngm^{-3} while in urban air, PCP was detected at higher concentrations at Antwerp in Belgium (5.7 to 7.8 ng.m^{-3}) and in Canada (1 lg.m^{-3}) [36].

Toxicity of Chlorinated Phenols

Phenol toxicity is related with two main processes; unspecified toxicity related with hydrophobicity of the

individual compound and formation of free radicals [37]. Microbiological transformation of chlorophenols, mainly PCP used in finishing materials, leads to the formation of other toxic compounds – trichloroanisole and tetrachloroanisole [38]. Therefore, phenol and its compounds are grouped as priority pollutants by the United States Environmental Protection Agency (US-EPA), which takes the 11th place under the 129 chemicals with a discharge limit of ≤ 1 mg/L in the treated effluent. In Iran, a maximum phenol level of 1.0 mg/L is permitted in wastewater for discharge to surface water resources by the Institute of Standard and Industrial Research of Iran (ISIRI). Short-term exposure to large amounts of PCP can cause harmful effects on the liver, kidneys, blood, lungs, nervous system, immune system and gastrointestinal tract [39]. Elevated temperature, profuse sweating, uncoordinated movement, muscle twitching and coma are additional side effects. Contact with PCP (particularly in the form of vapor) can irritate the skin, eyes and mouth.

Long-term exposure to low levels such as those that occur in the workplace can cause damage to the liver, kidneys, blood and nervous system. Also, exposure to PCP is also associated with carcinogenic, renal and neurological effects. The U.S. Environmental Protection Agency Toxicity Class classifies PCP in group B2 (probable human carcinogen). Since phenol is absorbed through the skin relatively quickly, systemic poisoning can occur in addition to the local caustic burns [40]. The transformation or degradation of chlorophenols could lead to the formation of more toxic intermediates or end products due to the electrophilic nature of metabolites that may bind and damage DNA or genes. The harmful impact of chlorophenols and their metabolites on the ecobiota may lead to acute toxicity, histopathological changes, mutagenicity, and cancer. These severe health problems make it sacrosanct not only to control chlorophenols in the environment but also carry out risk assessments, controlled by their fate in the environment with a view to ensure environmental safety and preserving the public health communities.

Phenol and its derivatives like pentachlorophenol are widely used as insecticides and often as herbicides. Phenol is a general protoplasmic poison with corrosive local effects that denature proteins. Poisoning with phenol compounds may occur by ingestion, inhalation and absorption through skin [41]. Acute poisoning can cause strict gastrointestinal disturbances, kidney malfunction, and circulatory system failure and also lung edema. Deadly doses can be absorbed through the skin. Key organs injured by chronic exposure to phenol consist of spleen, pancreas and kidneys [3,41]. This review

addresses the incidence and fate of chlorophenolic compounds in the environment with emphasis on the role of sorption processes.

The experiments under sunlight proved applicability of photosensitive chitosan for aqueous solution of single as well as mixture of phenol, 2-chlorophenol, and 2,4-dichlorophenol degradation. The contribution of photolysis in photosensitized oxidation (mostly via 1O_2 mechanism) of the pollutants was negligible. The fastest degradation was achieved for 2,4-DCP. The results of toxicity investigation show that toxicity of reaction mixture towards *V. fischeri* has significantly decreased in photo oxidation progress. The EC_{50} was found to increase over the irradiation time; however, this increase was not directly related to the transformation of the parent compounds. The photo degradation of the phenol compound mixture depends on water matrix. In all water matrixes, 2,4-DCP is the fastest degraded, while the increased concentrations of 2CP as well as PhOH were detected. The higher 2,4DCP photo degradation efficiency in the natural water was probably due to the dissolved organic as well as inorganic matter [42].

Analytical Method for Determination of Chlorophenols in Biological and Environmental Medium

The analytical techniques employed determination of concentration levels and monitoring of chlorophenol are many and they depend on the nature of sample matrix. Analytical techniques mainly used in chlorophenol analysis for both environmental and biological samples are gas chromatography with electron-capture detector or flame ionization detector or mass spectrometer detectors (GC-ECD/FID/MS)]. High performance Liquid chromatography or Liquid chromatography coupled with UV detector (LC or HPLC-UV), electrochemical detection or capillary electrophoresis [43-49], has also been used. EPA employs techniques that are based on liquid-liquid or solid phase extraction of chlorophenols followed by derivatization with diazomethane, methylene chloride or pentafluorobenzyl bromide and GC-ECD/FID/MS detection. Analytical procedures for chlorophenols involve the use of solvent extraction, solid-phase extraction, solid-phase micro extraction, or supercritical fluid extraction [50-53]. Immunoassays were developed for urinary biomarkers of exposure to chlorophenols, and other environmental pollutants, such as triazines, organophosphorus insecticides, carbaryl, naphthalene, and polycyclic aromatic hydrocarbons (PAHs) [44].

Conclusion and Future Research Study

The vast industrial applications and production of chlorinated phenolic compounds has resulted to the release of xenobiotics into the environment. Sorption processes are established means for transport, mobility and distribution of these chemicals in the environment and environmental variables such as pH, temperature, intensity of sunlight, availability of organic matter, salinity etc., have all been proven to influence the distribution of the pollutants in ecosystems. Chlorophenols are recalcitrant to biodegradation and these accounts for their persistence in the environment. However, microbes exposed to these priority environmental pollutants have evolved the ability to degrade some of these contaminants. Thus, biological degradation can be exploited as a bioremediation tool to solve the challenge of environmental pollution.

There is need to further study to understand the genetic basis of catabolism of chloroaromatic compounds, which has the potential of enhancing the potentials and efficacy of naturally occurring microbes, genetically improved microorganism or construct new microorganisms capable for degrading pollutants in soil and aquatic environments more efficiently.

The scientific quest to develop novel and environmentally safe compounds/materials for remediation processes, either for mineralization of organic pollutants and/or immobilization of inorganic and organic compounds has not yet been fully realized, but examples of both types of strategies have been reported in form of biological mineralization and bio-immobilization with the aid of microorganisms.

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