# Review Article: A Review of Toxic Metals and & Hazardous Organics in Wood Treatment Sites and Their Etiological Implications

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#### ABSTRACT

Increased natural and human activities over the last century have led to excess levels of inorganic and organic pollutants into the environment and natural ecosystems. This review critically examines heavy metal and organic pollutants' role in wood treatment sites and their etiological consequences. These pollutants are not only recalcitrant but also tenacious to degradation under ordinary conditions. Although some heavy metals are essential to human health, they are toxic at elevated concentrations. Heavy metals feature carcinogenic properties and cause serious health risks to live systems and the environment because of their bio-accumulative, non-degenerative, and refractory characteristics. On the other hand, organic pollutants are readily introduced into the ecosystem from irresponsible use of detergents, volatile organic compounds, paints, pesticides, and wood preservatives. During the wood treatment process, various chemicals are used to enhance durability. Nevertheless, the use of wood preservatives such as chromated copper arsenate (CCA) and pentachlorophenol (PCP) potentially induces pollutants considered detrimental to human health and the ecological environment. Remediation of wood treatment sites using phytomanagement strategies and nanotechnologies has been presented in this review. Therefore, some challenges and recommendations for further research and applications are herein presented.

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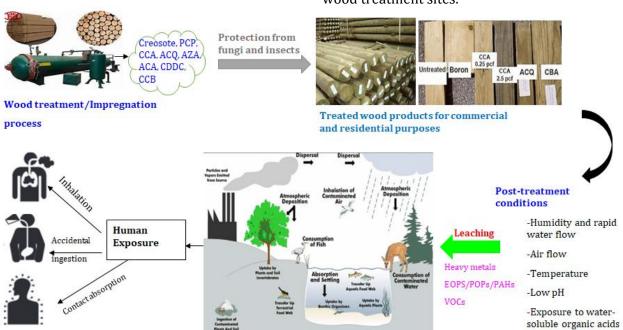
#### 1. Introduction

he by-products of toxic wood preservatives have been implicated in the etiology of various life-threatening human diseases, including cancer, stroke, rheumatoid, arthritis coronary heart diseases. The health hazards of heavy metals and organic pollutants have dominated research for many decades. There is, therefore, a good reason to understand that environmental pollution caused by untreated industrial effluent, pesticides, persistent organic pollutants (POPs), and solid waste disposal pose serious health risks not only to biological health but also to the natural environment [1]. When hazardous compounds are released into the environment, they contaminate water, air, and soil systems. Long-term anthropogenic activities have generally affected plant performance and communities because of elevated concentrations of toxic compounds in the soil and water [1-2]. These toxicities cause leaf discoloration, plant necrosis and chlorosis, inhibition of fine root development, oxidative stress, and changes in nutrient homeostasis [3]. Sub-surface soils contaminated with inorganic or organic pollutants and heavy metals bio-accumulate in food chains resulting in disastrous etiological risks on humans and wildlife [4]. Accordingly, studies have reported that heavy metal and hazardous organics decrease biodiversity, vitality, and soil productivity [4-6]. With the increasing awareness of these pollutants. environmental and human health hazards, such as toxic chemicals, have received mounting attention in research.

Currently, the production and use of wood and wood based products are ubiquitous [7]. Because of the rapid decline in forest resources, an increase in the durability of timber and wood by protection against marine borers, harmful conditions, insects, and rotting through wood modification and preservation methods has become indispensable [8]. Consequently, changing the disadvantaged features of wood by using preservatives and impregnating with chemicals is one of the feasible methods of enhancing its durability [9]. Nevertheless, numerous researchers have considered a wood treatment in the building industry and woodwork to be scientifically challenging because of the environmental and ecological concerns [3,10-11]. Despite their undesirable environmental effects, preservative-treated wood waste can be recycled as energy resources or other valuable products through pyrolytic thermochemical processes which convert these waste products into biochar, bio-oil, and noncondensable fuel gases such as hydrogen and methane [10]. Typically, pyrolysis is carried out under oxygen starved conditions at high temperatures of between 675 and 775 K [12-14]. Alkaline copper quaternary (ACQ) and chromated copper arsenate (CCA) treated wood wastes have been predominantly used as an alternative feedstock for biochar and bio-oil production [10]. Biochar, in particular, has gathered increasing interest in environmental management related to carbon sequestration and greenhouse gas reduction [15-16]. Moreover, biochar products find application in contaminant immobilization, water filtration, and soil fertilization [17]. Nonetheless, woodbased biochar produced through pyrolysis may lead to the release of trace amounts of arsenic (As) and organics which have been reported to volatilize during the thermochemical treatment of wood [10].

The fate of heavy metals and organic pollutants in the environment from wood preservative sites is often overlooked owing to the international motivation surrounding the prospects of wood preservation and the potentials of biochar from waste derived from wood preservatives [16, 18]. The environmental impacts of heavy metals and organic pollutants

have driven scientific research on heavy metal leaching, volatilization of trace heavy metals, and bioaccumulation of organic contaminants in the ecosystem to a new level [19-20]. Nevertheless, reviews on the presence of hazardous emerging organics, pollutants such as nitrated polyaromatic hydrocarbons, and heavy metals in wood treatment sites and their health impacts on humans and wildlife are not only significant but necessary. **Figure 1** summarizes possible routes through which hazardous trace metals and organics enter environmental systems from wood treatment sites.



**Figure 1:** Representation of how heavy metals and organics enter the food chain and ultimate exposure to

Herein, we have reviewed the state-of-the-art knowledge on heavy metal pollution, organic pollution, their environmental fate, and human etiology. Therefore, this paper is expected to offer an essential understanding of wood treatment sites and radvanced remediation efforts.

# 2. Chemical Pollutants from Wood Treatment Plants

Industrial sites such as wood treatment plants produce chemicals that adversely affect public and environmental health. Previous studies conducted on environmental modeling and sampling to assess the fate of hazardous waste have presented serious environmental health [21]. On numerous occasions. neighborhoods complained of strong odor from chemicals such creosote. airborne as particulates, and oily ditch water emanating from wood treatment plants [21]. Creosote, for instance, contains aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes generally referred to as BTEX. Other aromatic hydrocarbons in this category include styrene, methyl styrene, and trimethyl benzene. Creosote large percentage contains a polychromatic hydrocarbons (PAHs) such as naphthalene, acenaphthene, pyrene, benzo(ghi), benzo(e)pyrene, anthracene, penanthrene. methyl naphthalene, dimethyl naphthalene. benzo(a)pyrene, benzo(a)fluorene, benzo(k)fluoranthrene, dibenzo(ah)anthracene, and benzo(a)pyrene [21-22]. It also contains other organic compounds, including methyl benzonitrile, benzofurans, benzothiophenes, xylenols, diphenyl, phenol, cresols, isoquinoline, indenes, and methyl indenes. Usually, high pressure and heat are applied during the wood treatment process to ensure that creosote and pentachlorophenol (PCP) penetrate wood [23potentially inducing polychlorinated aromatic hydrocarbons (PCAHs) of dibenzo furan and dioxin types into the environment. Therefore, normal daily operations at wood treatment sites have resulted in transiently elevated levels of organic pollutants in the biosphere.

Although many studies that focus developing wood preservatives for long-term durability and replacement cost reduction have been performed, the use of wood preservative chemicals such as ammoniacal copper arsenate (ACA), ammoniacal copper zinc arsenate methyl (ACZA), creosote, arsenic (MA), chromated copper arsenate (CCA), copper dimethyl dithiocarbonate (CDDC), pentachlorophenol (PCP), and chromated copper borate (CCB) account for the presence of heavy metals - lead (Pb), mercury (Hg), nickel (Ni), arsenic (As), and chromium (Cr) and POPs in water and soils systems around wood treatment sites. These chemicals contaminate soils and water bodies through chemical spillage, poor handling of the raw material deposition of the sludge, and leaching from the woodpiles due to rainwater. Water-soluble chromated copper arsenate (CCA) in wood impregnation accounts for groundwater and soil heavy metal pollution through leaching [25]. As a result, many countries started regulating the use of CCA in wood treatment in the past three decades and subsequently shifted to copperbased wood treatment chemicals [26]. Besides, previous studies also indicate that various wood treatment methods such as impregnation with nano-compounds have been done to minimize unfavorable effects of wood treatment on natural ecosystems and human health [27-28].

# 2.1 Heavy metal pollution in wood treatment sites

The organic components of wood - lignin, cellulose, and hemicellulose are prone to chemical and biological damage by abiotic and organisms. Consequently, living research works have focused on improving wood's life-times by using chemical preservatives [29-31]. Previous researchers have frequently cited biomass impregnation with heavy, alkali, and alkali earth metals-basedpreservatives as a feasible approach to increasing the durability of wood [32-35]. Treated wood finds its application in electric poles, timber, railway ties, and poles for fencing [36]. Accordingly, the service life span of wood is increased. The chemistry behind wood treatment aims at reducing the moisture and sap content of wood hence introducing the preservative chemicals through high pressure. Heavy metals have increased in the human ecosystem, and their drastic effects have been a significant health concern globally; they are phototoxic and can act as micropollutants [37-40]. Lead (Pb), Hg, Ni, Cr, and As present severe challenges to human health and natural ecosystems.

Whereas biochar is essential in improving soil quality and reducing soil toxicity by adsorbing trace elements such as Zn. As. Cd. Hg. Cu. and Ni other organic chemicals such hydrocarbons, antibiotics, and agrochemicals, biochar production can lead to the leaching of heavy metals which are toxic to plant growth and agricultural productivity [10, 41-43]. Heavy metals undergo neither microbial nor chemical degradation, unlike organic contaminants, which are easily degraded by microbial activities. The non-biodegradability of heavy metals leads to bioaccumulation in food chains with catastrophic effects on wildlife and humans at elevated levels. A high concentration of essential elements such as Cu, As, and Cr can morphological, biochemical. cause physiological alterations in plants [44-47]. Despite the several studies that have been conducted over the years to mitigate the effects of heavy metals on natural ecosystems, waste disposal of wood-treatment chemicals remains a scientific challenge to date [48-50].

In wood treatment, soils that get in contact with the chemicals consist of tetra alkyl lead (TAL), tetramethyl lead (TML), trimethyl lead (TMEL), methyltriethyl lead (MTEL), and tetraethyl lead (TEL). Recently, Jones *et al.* [36] performed Matlab simulations to evaluate the amount of waterborne-preservative treated wood by mass and volume of the metal that enters demolition

and construction waste streams in the United States. They also conducted simulation studies to determine the leaching of heavy metals from different wood products after specific service lives. The estimated average service lives of different wood products used for residential and industrial purposes are reported in **Table 1**.

**Table 1.** The average service lives of wood products treated with different wood preservatives [36]

Timber type	Average service life in years
Lumber and timbers (Highway, commercial, industrial applications)	25
Lumber and timbers (Residential applications	10
Railway Ties (Crossties and Switches)	35
poles	60
piles	40
Agricultural fence posts	30
miscellaneous	10

As can be noted from **Table 1**, timber and lumber used in residential applications are disposed of within 10 years because of aesthetic reasons. Conversely, the timber used for non-residential applications has longer service lives of over 25 years. The various wood types were estimated to have service lives of 10 years – similar to residential timber and lumber because similar preservatives are used in both cases [36]. Service lives of fence posts, poles, railway ties, and poles were estimated based on previous reports [51-53].

Wood preservatives used in different wood products affect public health by leaching into the soil. Under the exposure of rainfall contact with water and soil, wood preservatives continually leach throughout their service lives [34, 54-55]. Computational simulations using Matlab indicated that residential timber and lumber treated with CCA-wood preservatives were estimated to lose 17% of Cu, 9% of Cr, and 20% of As at their time of disposal [36]. Highway and lumber treated with preservatives were also reported to lose 48%. 21%, and 46% of Cu, Cr, and As, respectively, during the same period of disposal [36]. In 2013, the yearly metal mass disposed off was estimated at 24,500 and 18, 400 metric tons of Cr and As, respectively [36]. The results of this computational study indicated that the volumes of water-borne preservative-treated wood products disposed of would potentially exceed

16 million M<sup>3</sup> each year by 2030. Additionally, it is reported that the mass of copper disposed will likely exceed 20,900 tons by 2030 [36].

# 2.1.1 Copper-based wood preservatives

Depending on their chemical solubility properties, wood treatment preservatives can water-borne oil-borne either or preservatives [56-58]. Generally, wood products treated with oil-borne and water-borne preservatives are for industrial used applications. Oil-borne preservatives include copper naphthenate, PCP, and creosote and are predominantly used in treating utility poles, marine construction poles, piling, and railway [59]. Whereas water-borne preservatives are used for industrial purposes, they are also commonly used in commercial and residential fencing and decks. Water-borne preservatives yield wood products that are stainable, paintable, odor-free, and clean, thus accounting for increased applications for outdoor structures. Water-borne wood preservatives were used around the mid-20th century and are widely used preservatives in the U.S [60-61]. Before 2003, water-based wood preservatives were used with As as the active They included zinc arsenate, ingredient. ammonical copper zinc arsenate (ACZA), ammonical copper arsenate, and copper-based water-borne wood preservatives such as ammonical copper quaternary (ACQ) and

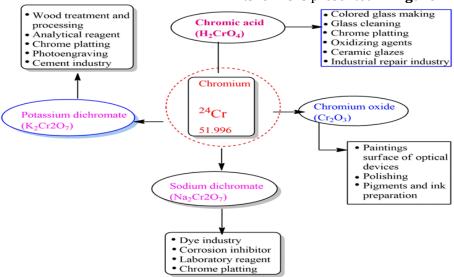
chromated copper boron [62-63]. CCA was commonly used among these preservatives, whereas ACZA was rarely used [64]. These preservatives were associated with potential environmental and human health effects mainly because of the disposal of waste containing As compounds which are well-known priority contaminants. Nonetheless, alternative non-arsenical preservatives, including alkaline copper azole (CA) and ACQ, became common after 2004 [60].

Prior to public health concern in 2003, CCA was a widely used wood preservative for wood exposed to aquatic environments [65-66]. Advancements in nanotechnology, however, have influenced the utilization of metal-based biocides. Copper (Cu) is an essential biocide in wood preservation. Wood treatment industries have started to profit from micronized Cu which can easily penetrate the wood. Moreover, Cubased biocide treated wood has successfully used as long-term building material with minimum leakage problems [67]. However, recent toxicity tests have shown that leakage of wood-treatment chemicals in an aquatic environment is harmful to aquatic life and the general environment [68]. Copper is an essential element that sustains metabolism in living organisms and can cause irreversible damage to metabolic activities. Copper nanoparticles (NPs) used in wood treatment have long retention

but potential exposure environment has been evident [34]. It persists by binding to the organic materials in the biological environment and soil matter. Besides leaching into soil surfaces from wood treatment sites, fungicide and fertilizer applications also account for increased Cu concentrations in soils plant matter [69-70]. Bioavailable quantities of Cu influence the microbial population's activity, diversity, and total biomass. Therefore, its continuous application has increased environmental and human health concerns around wood treatment plants which are well-documented in literature [71-72].

# 2.1.2 Chromium-based wood preservatives

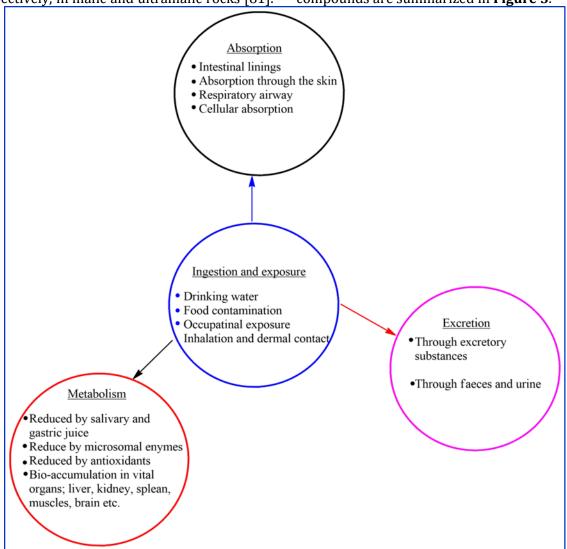
Chromium (Cr) is the 21st most abundant element in the earth's crust [73]. It exists mainly in two different oxidation states - Cr (VI) and Cr (III). Anthropogenic activities such as wood treatment, anti-corrosion of industrial cooling waters, and leather tanning account for the increased concentrations of Cr in the ecosystem [19, 74-75]. Chromium (VI) exists as chromate oxyanion,  $H_x CrO_4^{x-2}$  and is highly mobile in the environment [76]. Chromium (Cr), on the other hand, exists in other forms such as chromium oxide  $(Cr_2O_3)$ , sodium dichromate  $(Na_2Cr_2O_7)$ , acid  $(H_2CrO_4)$ , and potassium dichromate (K<sub>2</sub>Cr2O<sub>7</sub>). The use of chromium and its forms is presented in **Figure 2**.



**Figure 2.** Different forms of Cr oxides in the environment and their applications

The toxicity of Cr (VI) is widely reported in the literature - it is a known precursor for carcinogenicity when exposure occurs via ingestion or inhalation [77-79]. It also compromises water quality. By contrast, Cr (III) is an essential component in human nutrition at low concentrations [80]. Chromium (VI) contamination also stems from natural sources and potentially affects flora, fauna, and aquatic life. Weathering of metamorphic derivatives or ultramafic bedrock produces soils with approximately over 10 000 mg kg-1 Cr contamination [81]. It also occurs naturally on the earth's surface (100 mg kg-1) and at higher concentrations of 200 mg kg<sup>-1</sup> and 400 mg kg<sup>-1</sup>, respectively, in mafic and ultramafic rocks [81].

Remarkably, there is an ever-growing database of Cr contamination in the environment due to anthropogenic activities. The advancement of chemical fixatives like "Cr" in wood preservation industries is notable. These pollutants have been found to leach out from timber and wood after prolonged use - they ooze out under low atmospheric conditions and high pressure, thus contaminating flora, fauna, water, and soil [29]. Accordingly, these chemical pollutants have severe toxic impacts on biodiversity and ecosystem status. Due to the different chemical properties of Cr, it is essential to assess its potential risks to humans and environmental health. The pharmacokinetics of Cr (VI) compounds are summarized in Figure 3.



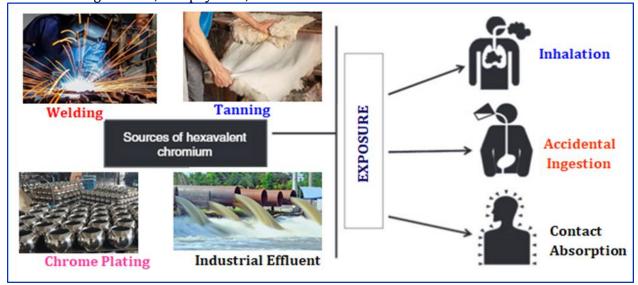
**Figure 3.** Pharmacokinetics of Cr (VI) compounds – modified from [82]

Chromium (VI) is a corrosive irritant that easily gets absorbed in the digestive tract, lungs, and

potentially through thermal contact. Moreover, it is well described in the literature as the second

allergen after nickel-induced eczematous lesions [83]. It also causes more chromosomal aberrations [83]. Workers at wood-treatment plants risk contracting occupational ailments such as lung cancer, emphysema, chronic

bronchitis, and bronchial asthma [82, 84]. The mechanistic processes by which humans get exposed to hexavalent Cr compounds are summarized in **Figure 4**.



**Figure 4.** Human exposure to Cr (VI) compounds – modified from [82]

## 2.1.3 Arsenic-based wood preservatives

Arsenic is one of the most abundant elements in the earth's crust, occurring in approximately 300 minerals in nature [85-86]. It forms compounds with sulfur, chlorine, and oxygen thus making it one of the most widely distributed elements in ores and minerals that contain Pb or Cu [85]. Arsenic distribution in environmental compartments is anthropogenic and geological sources. Some anthropogenic include sources wood preservation, refining and smelting of metals, and combustion of fossil fuels [10, 85, 87-88]. Organic and inorganic forms of arsenic can be found in soil, groundwater, food, and beverages. Inorganic arsenic combines with oxygen, sulfur, and iron and forms a substantial level of toxicity whereas organic arsenic combines with hydrogen and carbon and has no considerable toxicity levels [85]. Arsenic concentration in the environmental compartment has a critical risk implication on human and ecological health [85]. Studies have shown high concentrations of arsenic in timber treated with CCA [89], which is potentially hazardous to neighborhoods in wood treatment sites [4]. As a result, researchers have conducted studies how arsenic

concentrations in wood ash and CCA-treated timbers influence arsenic concentration in the soil, groundwater, and air [89-91].

Chromated copper arsenate is a pesticide and wood preservative which is a potential source of arsenic exposure and toxicity [89]. It degrades into arsenic and chromium leading to contamination of drinking water and soils [89 – 91]. Chromated copper arsenate (CCA) wood treatment chemicals have already been banned in the United Kingdom (UK), Italy, France, Ireland, Spain, and Germany [92]. However, New Zealand and Australia are the most significant consumers of wood treated with CCA globally [89]. Currently, in New Zealand, there are no restrictions on CCA-treated timber among particular consumers [93].

Nevertheless, there are restrictions on using CCA-treated wood in food containers, smoking of meat or fish, barbecues, domestic fires, and toys [89]. Safa *et al.* [89] conducted a case study in Christchurch, New Zealand, on how ash, treated timbers, and other contaminants influence As concentration in compost production [89]. Their results demonstrated that most treated timber and all ash of untreated and treated timbers contained significant As

concentration. Accordingly, the concentration in untreated wood ash was 96 ppm, whereas the ash of treated timber wasbetween 133,000 and 179 000 ppm [89]. Besides, the researchers

noted that one kilogram (kg) of treated timber ash increases the As concentration by 10 ppm in 13-18 tons of dry compost [89]. The results of their studies are summarized in **Tables 2** and **3**.

**Table 2.** Average arsenic, copper and chromium contents in samples ppm [89]

Sample name	Number of samples	Arsenic (ppm)
Untreated	4	2
H1,2	3	2
H3 & H3,2	7	1410
H4	7	2098
H5	3	8435
Untreated Timber Ash	4	96
Ash H1,2	3	160
Ash H3 & H3,2	7	133,175
Ash H4	7	155,456
Ash H5	3	179,496

**Table 2** shows that ash and treated timber are among the most important As contaminants, especially during winter seasons. This implies that compost production using these materials poses a series of environmental and public health concerns because of possible high levels

of arsenic contamination. Therefore, the general public must be well informed on the use of any treated or untreated timber ash in organic waste bins [90, 94-95]. Additionally, the human population should avoid burning any treated lumber or timber to manage waste of any nature.

Table 3. Effect of treated timbers and ashes on compost arsenic concentrations (10 ppm) [89]

Sample name	Volume of compost (kg) contaminated in 10 ppm per 1 kg of sample	Volume of the sample (kg) to contaminating average monthly during winter of 2017 compost production
Н3	141	10,707
H4	210	7, 298
Н5	844	1,816
Untreated timber ash	10	158,888
Ash H1,2	16	95, 615
Ash H3	13,317	115
Ash H4	15, 546	99
Ash H5	17, 950	85

It can be inferred from **Table 3** that although untreated wood were the main sources of fuel in open chimneys and log burners, the researchers reported that untreated timber ash had higher concentration of As as compared to the

permissible limits. Residents in the region believed untreated timber ash was safe for use and could be put in organic waste bins, but As concentration was still high at between 32 and 200 ppm [89]. These reports revealed that composing production poses critical concerns as treated wood, ash of untreated and treated wood contained significant levels of As concentration [89].

#### 2.1.4 Other Metal-based Wood Preservatives

Inorganic pollutants have minor and major constituents [96] of approximately 28 minor elements, 12 major elements, and 13 less minor elements [96]. contaminants depict different physiochemical properties and varying health concerns. Among all inorganic pollutants, heavy metals, in particular, have attracted intense attention due to their high toxicities [2, 97-100]. Although nanotechnologies have been performed to eliminate heavy metals such as Hg from polluted water, its continued use as an ingredient in wood preservatives has increased bioaccumulation in the ecosystem [101]. For instance, in Sweden, CCA and Arsenic-based chemicals for wood treatmen tresulted in metal contamination in soils near wood treatment plants [102]. Under low pH conditions, the chemicals from freshly impregnated wood leached due to rainwater run-offs. Moreover, deposition of sludge, spills and raw material handling also resulted in high quantities of pollutants in soils and water systems around Sweden wood treatment sites [102]. Notably, wood preservation has contributed to Zn, Pb, Hg, and Ni environmental contamination [18]. Lead, for instance, can quickly accumulate through ingestion and inhalation [103-104]. These heavy metals are very toxic, even at deficient concentrations. Their quantities environment exponentially increasebecause of continuous discharge of metal-containing industrial waste into water systems and soil. These heavy metals cause eye and skin irritation, hematemesis, blood pressure, gastrointestinal distress, liver cirrhosis, and hypertension [96, 105]. They get absorbed into the body through bones and blood tissues. They are also wellestablished precursors for behavioural disorders and mental retardation. They also induce teratogenesis, heart diseases and blood pressure. Zinc (Zn), for example, impairs the body temperature control system, affects the lungs, and causes nausea and stomach cramps

[106]. The introduction of human activities and naturally occurring heavy metals into water systems has shown potential impacts on the atmosphere and human health, including disastrous impacts on marine life. Dissolved metals are widely distributed in the ecosystem [107-108], and their human exposure increases due to an increase in the application of metal-based wood preservatives [34].

# 3. Heavy Metal Toxic Load

The heavy metal toxic load (HMTL) measures the heavy metal concentration present in the organism that may potentially affect human and environmental health and illustrates the degree of treatment [109]. It provides valuable insights to the regulatory authorities and medical health practitioners on how to carry out the treatment in order to improve water and air quality for human exposure. It also defines the level at which the organism's system breaks down due to heavy metal toxicity. Additionally, this definition is fundamental in documenting effective management and a treatment plan. HMTL is the product of a particular heavy metal's hazard intensity and concentration in the biological system. It is expressed by equation 1 [110].

$$HMTL = \sum_{i=1}^{n} C \times HIS$$
 (1)

where HIS, C, n are the hazard intensity score, the concentration of heavy metal, and the number of heavy metals in the environment of interest.

# 3.1 The Health Impacts of Heavy Metals Associated with Wood Treatment Sites

Industrial discharge from wood treatment sites has adverse health effects on humans, wildlife, and marine life [111-112]. Therefore, the exponential increase in the amount of heavy metal in soils and natural waters are among the dangerous contaminants which have drawn enormous attention among researchers in the scientific community. Heavy metals are highly toxic when they are not metabolized in the body and can accumulate in soft tissues, ultimately health aberrations. causing severe Anthropogenic sources, including woodtreatment sites, metallurgical, mining, runoffs, and agricultural activities release heavy metals to different environmental compartments resulting in numerous severe etiological impacts [113-114]. These toxicants affect the atmosphere, biosphere, lithosphere, and hydrosphere. Of all the potential targets, air, soil, and water are significantly impacted by heavy metal contamination and poisoning [115]. Persistent organic pollutants have unique chemical properties, widespread production, environmental distribution, long-term persistence, bioaccumulative potential, and associated risks for human health [114-114].

Typically, soils are the major sinks of heavy The non-biodegradable metals [116].characteristics of these pollutants make their total concentrations last longer after being released from natural and anthropogenic sources into the water, air or the soil environments. Heavy metals have long residence times in food chains and can potentially destroy the entire ecosystem [117]. Plants, animals and humans take heavy metals through absorption, direct ingestion, consumption of contaminated water and food. The US Environmental Protection Agency (US EPA) has observed that wood treated with CCA was a potential source of arsenic exposure and toxicity, especially to soils, plants, and people working around wood treatment plants [118]. The carcinogenic effect of As, for instance, is commonly exhibited through contaminated soils, plants, and water. The contamination experienced is a result of As (III), As (V), H<sub>2</sub>AsO<sup>4</sup>-, and HAsO<sub>4</sub><sup>2</sup>- present in soil flocculants that originate from the CCA used in wood treatment [119].

Moreover, chromium (VI), which has high membrane permeability and oxidative properties, is leached in soils around wood treatment sites [120]. Exposure to soils contaminated with Cr (VI) may cause skin ulcers in animals, liver cirrhosis, and kidney damage [121]. Based on the US EPA, hexavalent and Arsenic compounds from CCA also have neurotoxicity, ecological, and carcinogenic effects [120].

Heavy metals including Pb, Hg, Ni, Cr, and As and their organic derivatives cause skin and lung cancer, hyperkeratosis, damage of organs such as kidneys, lungs, coronary diseases, genetic defects, and constant itching [122]. These effects may also affect metabolic processes in humans by altering and inhibiting the action of bioenzymes [123]. Under chronic conditions, high exposure to heavy metals may ultimately cause death [124]. The environmental hazards of heavy metals (HMs) mainly occur when the soil, water, and vegetation are contaminated.

# 4. Hazardous Organics in Wood Preservatives

Creosote is a mixture of coal and tar and is conventionally applied in wood treatment and preservation. In the process of wood treatment using creosote, the chemical gets in contact with the soil surface through wrong methods of disposal and spillage. The contaminated soil poses an environmental concern due to potential organic toxicants considered harmful to humans, animals, and plants [125]. Therefore, the detrimental effects of creosote are mainly attributed to the presence of phenol-based compounds and PAHs, which are possible pollutants to man and the natural environment. Benzo(a)pyrene is the most toxic PAH with a high persistence order in the environment. Accordingly, the ability of creosote compounds to leach into the soil and water makes it a pollutant with high toxicity index, carcinogenic, immunotoxic, teratogenic, and genotoxic [126].

Pentachlorophenol (PCP) is another organic wood preservative [127-128]. The presence of an aromatic ring provides PCP with extra stability due to the presence of  $\pi-\pi$  bonds. It is highly soluble in an organic solvent but sparingly soluble in water. Besides being the most preferred impregnation product, PCP is also used as an antimicrobial agent in industrial cooling systems – an active ingredient in exterior paints and stains and used in food packaging [6]. It is a priority environmental pollutant with high toxicities on animals and humans. It makes the cell membranes permeable to harmful protons by decoupling oxidative phosphorylation [6].

Pentachlorophenol accounts for the alteration in the functionality of the cell membranes and is considered a serious environmental pollutant alongside its degradation products. For instance, PCP degrades into more than 30 different products depending on the various ecological conditions [129]. The degradation products include dichloro-, trichloro-, & tetrachlorohydroquinones (DCHQ, TCHQ,

TeCHQ), tetrachlorocatechols (TeCC), and dichloro-, trichloro-, & tetrachlorophenols (DCP, TCP, TeCP), hexachlorobenzene (HCB), and pentachloroanisole, polychlorinated dibenzo-p-dioxins and polychlorinated dibenofurans. Mammals absorb PCP through skin contact and inhalation [6, 130]. The thermal degradation of pentachlorophenol into toxic by-products of grave concern is presented in **Scheme 1**.

tetrachlorophenol

Scheme 1. Proposed degradation products of pentachlorophenol during wood treatment

Vapour-phase PCP with a half-life of 29 days is degraded via a photochemical reactions into hydroxyl and benzvl radicals. Pentachlorophenol has dissociation a constant ( $P_{ka}$ ) of 4.7, showing that it exists predominantly in the anionic form in the environment and does not adsorb strongly into Instead. when released soils. to environment, PCP adsorbs to sediments and suspended soils. Furthermore, this compound does not hydrolyze because it lacks functional groups that undergo hydrolysis under environmental conditions. Exposure to PCP may be through dermal contact, inhalation, or ingestion at work place – wood treatment sites [131]. Fatty tissues, spleen, kidney, liver, and brain are the major PCP deposition sites in humans with fatal health effects such as

carcinogenicity, genotoxicity, and possible nervous breakdown [132]. It also induces

ecotoxicology by bio-accumulating in aquatic organisms, as summarized in **Table 4**.

**Table 4.** Effect of pentachlorophenol on aquatic organisms [132]

Organism	Effect of pentachlorophenol
Rainbow trout	LC <sub>50</sub> 0.12-0.26 mg l <sup>-1</sup> (96 h)
Golden orfe	LC <sub>50</sub> 0.60 mg l <sup>-1</sup> (96 h)
Water flea	LC <sub>50</sub> 0.33-0.41 mg l <sup>-1</sup> (96 h)
Bacteria (div.)	NOEC 12.3 mg l <sup>-1</sup> (30 min), growth
Algae	EC <sub>50</sub> 10-7000 μg l <sup>-1</sup> (96 h), growth

Legend: NOEC - no observed effect concentration;  $LC_{50}$  - lethal concentration at 50%;  $EC_{50}$  - half maximal effective dose

# 4.1 Polycyclic Aromatic Hydrocarbons and Persistent Organic Pollutants

Polycyclic aromatic hydrocarbons (PAHs) refer to a group of environmentally persistent organic compounds with various toxicity indices depending on their structures [133]. These compounds are chemically related and consist of two or more fused aromatic rings [134-135]. The incomplete combustion of organic materials such as coal, petroleum products, conventional fossil fuels, and wood accounts for the many PAHs observed in the environment. Typically, PAHs are ubiquitous contaminants found in various PAH matrices in marine sediments. freshwater, ice, and the atmosphere [133]. Selective weathering effects and anthropogenic activities account for the increased environmental and human health problems associated with PAHs [136]. These compounds enter the environment and manifest various properties such as heat resistance, light sensitivity, imitability, resistance to corrosion, and conductivity. They also feature low vapor pressure, high boiling and melting points, high lipophilicity, and low aqueous solubility. According to the International Union of Pure and Applied Chemistry (IUPAC), anthracene and phenanthrene are the simplest PAHs which consist of three fused rings [133]. Additionally, naphthalene also forms another class of PAHs include substituted naphthalene. Nevertheless, the PAHs have different toxicity levels on humans – 17 PAHs are a risk to human health [137-138]. They induce toxicity by

interfering with the normal functioning of enzyme systems associated with cellular membranes. Numerous studies have been performed to identify their potential sources and toxicity mechanisms on humans, wildlife, and aquatic life. The widely reported sources of PAHs into the environment include industrial emissions (wood preservation, manufacture of bitumen, waste incineration, power generation, of primary aluminum), and production agricultural activities (burning of brushwood), environmental tobacco smoke, accidental oil spills, and other sources such as plastics, dyes, pharmaceuticals, pesticides, and leaching from treated timber and wood [139-143]. PAHs are persistent in the environment and classified as persistent organic pollutants (POS).

In general, persistent organic pollutants (POPs) are a class of compounds with specific physiochemical properties, including long-range atmospheric mobility, long environmental halflives, potentially toxic, and recalcitrant in the environment [144]. Stockholm The Conventional on persistent organic pollutants restricts production and use of POPs owing to their adverse health effects on environmental and public health systems. Nonetheless, industrial activities such as producing and using pesticides, fungicides, and termiticides in wood preservatives emit significant proportions of POPs [145-146]. Chromated copper arsenate (CCA), dieldrin. DDT. PCP. polychloronaphthalenes (PCNs), and chlordane are POPs-based wood preservatives [146,147].

Therefore, treated timber waste, wood, electricity, and fence poles emit high POPs into the environment when subjected to various conditions.

On the other hand, emerging organic pollutants (EOPs) refer to artificial organic substances that do not naturally exist in the environment [148]. They inflict maximum damage to the ecosystem after being introduced by artificial activity and industrialization procedures. Many emerging organic contaminants (EOCs) are widely used in domestic, agricultural, and industrial practices [149]. Wood preservatives such as PCP and creosote constitute an example of EOPs of the heterocycles. phenolic compounds. polycyclic aromatic hydrocarbon (PAHs) derivatives [149,150]. Creosote enters the soil from treated wood such as utility poles, telecoms, and wooden railway sleepers. Furthermore, it also gets to the soil due to the leakage and spillage of creosote as it is being pumped into wood [150]. Waste sludge in landfills and creosote-polluted soil can result in secondary pollution of groundwater. Of the EOPs, PAHs have high potency for inducing carcinogenicity in humans and the environment in general. Creosote contains 5% heterocycles, 10% phenolic compounds, and 85% PAHs [151-153]. These compounds are degraded via chemical and biological processes. Nitration, oxidation, and volatilization are some of PAHs' abiotic chemical degradation reactions. Multiple studies have reported the adverse carcinogenic teratogenic effects propagated PAH and exposure [154-156]. Typically, PAHs with low molecular weights are relatively mobile and bioaccumulated soil microorganisms. Conversely, PAHs with high molecular weights are very stable less soluble in water but feature characteristic hydrophobicity [157-158].

# 4.2 Health Implications of Organics from Wood Treatment Sites

PAHs are released as a by-product from the incomplete combustion or pyrolysis of organic matter and fossil fuel and constitute a significant fraction of carbonaceous aerosols [133]. Exposure of PAH metabolites such as PHA-based

expositions to humans and microorganisms potentially results in health hazards such as mutagenicity and carcinogenicity - this is an emerging global health concern [159]. Their health hazards depend on routes and lengths of innate exposure, toxicity, and concentration [133]. Moreover, an organism's age and health status are essential factors determining the extent of PAH toxicity. Workers at treatment sites are exposed to elevated concentrations of PAH compounds, which may cause severe eye irritation, mental confusion, diarrhea, vomiting, nausea, skin inflammation, irritation [160]. Naphthalene anthracene are known skin irritants in humans and animals [161].

Generally, exposure to PAHs from wood treatment sites may also precipitate cataracts, breathing problems. lung function abnormalities. asthma-like conditions. decreased immune function, liver cirrhosis, and damage [161]. Naphthalene, in particular, damages red blood cells when ingested in elevated concentrations [137]. Benzo[a]anthracene has shown embryotoxic effects on pregnant mice and potentially results in premature delivery, lower IQ, and heart malformations in humans. Studies have also indicated that PAHs induce immunotoxicity by suppressing the immune reactions in rodents [133,137]. In vitro tests using mammalian cells indicate that PAHs are first metabolized to their corresponding diol epoxides, which precursors for genotoxic effects upon reaction with DNA [133]. Epoxides and dihydrodiols bind to DNA and cellular proteins, resulting in tumors, cancer, developmental malformations, and biological disruption of organ functions in humans [162]. There is enough evidence to show that PAHs are potential precursors for gastrointestinal and bladder cancer among workers employed in wood treatment plants [163]. Additionally, occupational hazards such as skin and lung damage are occasioned by PAH contamination. Indeno(1,2,3-cd)pyrene, benzo(k)fluoranthene, benzo(a)anthracene, chrysene, and benzo(a)pyrene are PAHs with striking carcinogenicity according to US EPA [133].

7,12-dimethylbenzo anthracene-3,4-diol-1,2-epoxide

7,12-dimethylbenzo anthracene-3-4 diol

**Scheme 2.** Metabolic activation of 7,12-dimethylbenzo anthracene to carcinogenic forms –Adapted from [133]

CYP1A1

The widely studied PAHs are benzo(a)pyrene and 7.12-dimethylbenzoanthracene which are well-known causes of carcinogenic effects via various mechanistic processes. In particular, 7,12-dimethylbenzoanthracene can induce breast cancer. commonly isolated from barbequed meat, overheated cooking oil, tobacco smoke, and diesel exhaust. 7,12dimethylbenzoanthracene is fat-soluble and thus quickly bio-accumulates in adipose tissues, which triggers metabolic activation mechanisms resulting in carcinogenicity [164]. Phase I enzymes such as CYP metabolizes 7,12dimethylbenzoanthracene 7,12dimethylbenzoanthracene-3-4-oxide [165]. It is then converted 7,12dimethylbenzoanthracene-3-4 diol by epoxide hydrolase, which is then further oxidized by CYP to its carcinogenic and teratogenic forms of 7,12dimethylbenzoanthracene-3,4-diol-1,2-epoxide [165] as depicted in **scheme 2**.

The epoxide (7,12-dimethylbenzoanthracene-3,4-diol-1,2-epoxide) reacts with DNA to give

adducts that induce carcinogenicity and mutagenicity in humans [133]. Despite the increasing awareness of the toxicity of 7,12dimethylbenzoanthracene, there are enormous financial, technical, and management difficulties in reducing the net effect of PAH emissions. Moreover, as widely documented in literature, benzo(a)pyrene has shown sufficient evidence of its toxicity to humans and animals. Benzo(a)pyrene forms carcinogenetic products via three metabolically activated processes: (i) formation of (7R,8S)-epoxy-7,8dihydrobenzo(a)pyrene catalyzed by P450 enzymes, (ii) formation of (7R,8R)-dihydroxy-7,8-dihydrobenzo(a)pyrene catalvzed epoxide hydrolase, and (iii) cytochrome P450 enzyme catalyzes the reaction to yield four isomers of 7,8-diol-9-10-epoxide [166]. Out of these possible isomers, (7R,8S)-dihydroxy-(9S,10R)-epoxy-7,8,9,10-

tetrahydrobenzo(a)pyrene is an important carcinogenic isomer that binds to DNA at the guanine residues to produce carcinogenic adducts as detailed in **Scheme 3**.

**Scheme 3.** Metabolic activation of benzo(*a*)pyrene – adapted from [133]

Wood is an environmentally benign building material compared to other materials. It has good electrical and thermal insulation characteristics. Moreover, it requires a minimum amount of handling during its process and, thus, potentially mitigates global warming

and climate change by reducing the net greenhouse gas emissions.

**Table 5.** Benefits and drawbacks of using different types of wood preservatives [6]

Wood preservative	Benefits	Drawbacks
Boron compounds	✓ Soluble in water ✓ Effective ✓ Cheap	✓ Highly leachable
CCA	<ul> <li>✓ Resistant to leaching</li> <li>✓ Soluble in water</li> <li>✓ Cheap</li> <li>✓ Highly effective</li> </ul>	✓ Environmentally restricted ✓ Highly toxic due to the presence of chromium and arsenic
Creosote	✓ Not leachable- Insoluble in water ✓ Low cost	✓ It cannot be used in applications requiring finishing ✓ Exudation problem
Azoles and quaternary ammonium	✓ Resistant to leaching ✓ Low toxicity	<ul><li>✓ Greater susceptibility to moldy fungi</li><li>✓ High cost</li></ul>
ССВ	<ul> <li>✓ Effective</li> <li>✓ Soluble in water</li> <li>✓ Cheap</li> <li>✓ Less environmental degradation compared to CCA</li> </ul>	✓ Toxicity due to the presence of chromium ✓ Greater leaching
PCP	✓ Efficient	✓ Its degradation products are highly toxic

Table 5 reports some of the critical environmental challenges in wood caused by wood treatment. The soils around wood treatment sites have become sinks for toxic chemical waste. This has affected plants, the nature of the soil, and the health of the residents around wood treatment plants. Accordingly, the to develop sustainable wood preservatives is gathering momentum towards minimum health concerns. Therefore there is a good reason to believe that heavy metals, organo-heavy metals, and hazardous organics are incredibly toxic to the natural ecosystem and higher-order mammals such as man. These chemicals' carcinogenic and mutagenic properties and their derivatives. Ultimately, wood treatment sites constitute an environmental grave concern of our time. Owing to the potential benefits of wood preservation, it is more likely that wood preservation techniques will involve several passages regardless environmental health concerns of the chemicals and metals present in wood preservatives [68].

#### 5. Remediation strategies in wood treatment sites

Etiological pollution by hazardous organics and heavy metals is an ineluctable anthropogenic that has presented humanity with numerous environmental health difficulties. The continued economic development activities such as wood preservation and the continued industrial revolution will continue to aggravate the supply of safe drinking water [167-168]. As the harmful effects of these contaminants become apparent, particularly on human and ecological health, various government authorities and regulators have taken necessary action to mitigate their effects [169-171]. Governments globally have become stricter on the concentration levels of harmful chemicals in environmental systems such as soil, air and water. For instance, Kingdom (UK) banned the use of CCA wood preservatives to control As and Cr pollution in September 2006 [172]. Besides, CCA-treated wood imported outside the European Union (EU) is only used for industrial and professional purposes to minimize dermal contact among users [172]. Wood products treated using creosote or creosote-related preservatives were only used for industrial and professional purposes such as telegraph posts, railway sleepers, waterways, harbors, and agricultural

purposes [172]. However, contamination of natural media such as water, air, and soil are beyond the threshold limits set by the World Health Organization (WHO) [173]. To comply with these low concentration requirements, the adoption of advanced remediation strategies and technologies are indispensable. In this pursuit, remediation strategies and methods using biological agents such as micro-organisms and plants have been proposed as better ecofriendly methods of removing heavy metals [107,174]. Also, sophisticated nanomaterials (NMs) - organic molecular and inorganic NMs have been widely applied to remediatiate organic pollutants such as dyes, endocrinedisrupting products. detergents. pharmaceuticals, pesticides, and personal care products via degradation, oxidation, and adsorption [175].

Bioremediation of wood treatment sites that employ unambitiously microorganisms such as Alcaligenes, Rhodococcus, Mycobacterium, Sphingomonas, and Pseudomonas to minimize mobilization and leaching of heavy heavy metals metals in the environment has been considered one of the best remediation approaches [176]. It is a method aimed at removing harmful substances, degrading organic contaminants, and mineralization of organic substances into nitrogen (N<sub>2</sub>) gas, water, and carbon (IV) oxide (CO<sub>2</sub>) by employing living or dead biomass. Considerable evidence supports fungi in soil remediation near wood treatment plants. Fungus produces high concentrations of oxalic acid in decaying CCA treated-wood products, thus increasing solubility and subsequent removal of the notoriously toxic As and Cr heavy metals [177-179]. This technique has been applied in water and soil treatment through exsitu and in situ procedures. In in situ techniques, there is minimum disruption of soil structure since it involves the introduction of engineered microorganisms or the stimulation indigenous microbial flora [180]. Generally, this process involves pumping nutrients and oxygen into the soil in a process referred to as biostimulation [181].

On the other hand, *ex-situ* techniques involve transporting contaminated water or soil to another area for treatment. They can either be

slurry-phase and pile (mixed media of liquid and soil in bioreactors) or solid-phase (land treatment) techniques [182]. Heavy metals such as Hg, As, Cr, and Fe undergo reduction and oxidation cycles, and through bioremediation techniques, these pollutants are converted into their soluble and mobile forms. bioremediation action reduces As (V) to As (III), Fe (III) to Fe (II), and Hg (II) to Hg (0), which are less harmful [180]. Other methods that have predominantly used physicochemical methods such as reverse osmosis, landfilling, ion exchange, chemical leaching, and electrokinetics [176]. Undeniably, the methylation of heavy metals is a fundamental process in modifying their mobility, volatility, and toxicity in water and soil sediments.

Considerable research has also supported bioremediation techniques in removing organic pollutants in water and soils [183-184]. However, the efficiency of microbial degradation of organic contaminants using anaerobic conditions is relatively low and low and is at its infancy stage. Therefore, the choice of technique remediation requires careful consideration. Moreover, there is also the advent of new technologies based on growing particular tree species to provide stabilization of contaminants at root zones. enhance evapotranspiration to limit leaching, and provide the vegetative cap in polluted sites [185-187].

Common organic chemicals waste from wood treatment sites such as phenols, endocrine disruptors, such as bisphenol A (BPA), fused aromatics, heterocycles, and PAHs, have increased mounting concerns to the risks associated with water quality and damage to endocrine systems. On the other hand, significant efforts have been pursued, such as the use of carbon nanotubes and other sophisticated nano materials (NMs) to remove these hazardous chemicals in water [175]. Other promising materials. including nanoparticles in the form of Fe (0) have been applied in adsorbing and the degradation of heavy metals and organic contaminants, particularly chlorinated organic solvents and polychlorinated biphenvls (PCBs)

groundwater and soil systems. Research is in progress on new bimetallic NPs for efficient adsorption and degradation of organic contaminants. New bimetallic NPs utilizing metals such as gold (Au), palladium (Pd), Ni, and Cu are cost-effective and have high potential activity compared to the conventional Fe NPs [188-189]. More recently, studies show that biologically produced Pd NPs, silver NPs, and cobalt have been successfully used to degrade recalcitrant and highly toxic organic pollutants such as  $\gamma$ -hexachlorocyclohexane, a lindane-based insecticide [175].

Heavy metal removal using living or dead microorganisms is cost-effective, largely available, simple to use, and has high adsorption capacity. The widely used microorganisms include algae, fungi, and bacteria [190-192]. These microorganisms target Hg(II), Cr (VI), Pb (II), Zn (ii), Cd (II), and Cu (II) pollutants [193]. Due to the complexity of environmental conditions, better remediation of heavy metals has been enhanced by combining chemical and physical treatment with microorganisms [194-195]. Generally, biological remediation exhibits numerous advantageous degradation characteristics. Phytoremediation strategies herein proposed, can be applied as a set of site risk management solutions to return low-level risk sites to production practices that can provide a range of economic and environmental benefits.

#### 6. Conclusions

In summary, wood preservatives are a set of methods, techniques, and products designed to enhance the durability of wood. Wood species considered resistant to biological and chemical degradation are scarce. For this reason, further research on chemical, biological, and indirect wood preservative approaches has been advanced. Based on this review, some wood preservatives are leachable and may undergo mechanistic degradation to form highly toxic environmental hazards of public health concern. Presently, research is in progress to develop environmentally benign products such as CCB (a mixture of potassium dichromate, boric acid, and copper sulphate) to replace CCA as a favored

wood preservative but with serious environmental and public health risks.

Moreover, the introduction of POPs to the environment from organic wood preservatives such as PCP, polychloronaphthalenes, dieldrin, DDT. lindane, and chlordanes has precipitated a global public health concern. The continued economic development activities such as wood treatment and the industrial revolution will aggravate the supply of safe drinking water and damage soil quality. As a result, research must explore adaptive technologies and methods in line with heavy metal and organic pollution remediation of wood treatment sites. Fe (0) nano-particles (NPs) have been successfully applied in adsorbing and degrading heavy metals and organic contaminants, particularly organic chlorinated solvents and polychlorinated biphenvls (PCBs) in groundwater and soils. To mitigate the environmental pollutants to limits prescribed by the World Health Organization (WHO), various governmental authorities and regulators are tasked to monitor and assess better remediation procedures in wood treatment environments. Thus, some challenges and recommendations for further research and applications are finally presented.

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## **Conflict of interest**

The authors declare that they have no conflict of interest

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