Copper Chrome Arsenate Water-Borne Solution

Subjects: Chemistry, Applied | Public, Environmental & Occupational Health
Contributor: Maria de Lourdes Pereira, Simone Morais, Sonia Rodrigues Oliveira

Copper chrome arsenate (CCA) water-borne solution used to make timber is highly resistant to pests and fungi, in particular, wood products designed for outdoor use. Nowadays, CCA is a restricted chemical product in most countries, since potential environmental and health risks were reported due to dermal contact with CCA residues from treated structures and the surrounding soils. However, large quantities of CCA-treated timber are still in use in framings, outdoor playground equipment, landscaping, building poles, jetty piles, and fencing structures around the world, thus CCA remains a source of pollutants to the environment and of increasing toxic metal/metalloid exposure (mainly in children). International efforts have been dedicated to the treatment of materials impregnated with CCA, however not only does some reuse of CCA-treated timber still occur, but also existing structures are leaking the toxic compounds into the environment, with impacts on the environment and animal and human health.

Keywords: chromated copper arsenate ; CCA-treated wood ; arsenic ; chromium ; copper ; soils ; enviromental pollution ; public health

1. Introduction

Oxides of hexavalent chromium (47.5%), copper (18.5%), and inorganic arsenic (34%) are mixed in water to prepare a preservative of wood, known as chromated copper arsenate (CCA) [1][2]. CCA is used to protect wood or wood products and timber from insects, pests, and microbes by layering its fine green coating around wood or wood products that are used for indoor or outdoor purposes. In CCA, chromium, a transition metal, has no wood preservative properties. It acts as an agent to fix chemicals or their complexes in the timbers or wood by their binding with polysaccharides, i.e., lignin and cellulose. It is a very slow reaction process as the fixation of CCA with wood takes several weeks. Copper, another transition element, is primarily responsible for protecting the wood against decay by the action of microorganisms, such as bacteria and fungi. Arsenic, a metalloid, exhibits insecticidal properties. Arsenic also provides timber resistance to weather conditions, along with increased adherence of paint over a longer period [3].

Wood products treated with CCA were found to have an adverse impact on the environment and human health, due to leaching and accumulation of these metals/metalloid, especially arsenic, from the wood into the environment (Figure 1). Decaying materials leach them into soils and waters, which may negatively impact food production or farming, and animal and human health. The affected tissues may include the brain, lungs, liver, stomach, spleen, kidneys, and reproductive organs [4][5][6][7][8][9][10]. The US EPA in 2003, therefore, agreed to reduce its use by adding only a minimum amount of arsenic to CCA [11]. In addition, CCA-impregnated wood products have been restricted to use either for burning or as equipment, such as decks, fences, landscaping features, patios, picnic tables, piling retaining structures, poles, on the playground and walkways [12]. However, such limitations for CCA use and application have not yet been set in some other countries, such as China. The toxic properties of many compounds of arsenic and chromium are known and extensively revised, but relatively limited information is available regarding the toxicology of CCA [4].

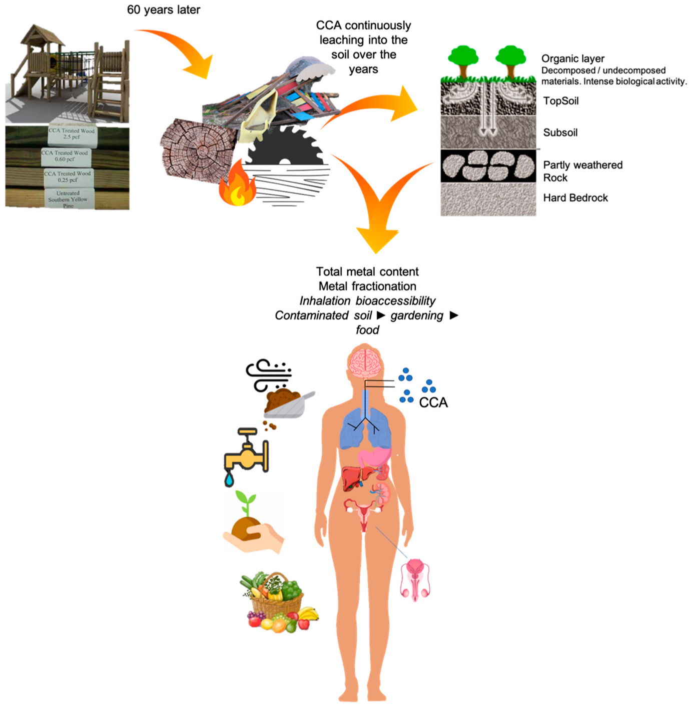

Figure 1. General overview of the potential environmental and human health impacts of chromated copper arsenate (CCA)-treated wood.

2. Removal of CCA

The concern with the disposal of wood residues treated with CCA has grown due to the risk of environmental contamination. Open burning of CCA-treated wood products has shown to emit 11–14% of the total arsenic content into the atmosphere (in contrast with chromium and copper, emissions of which contain less than 1% of the total), with the remaining arsenic in the residual ash. Moreover, the identified oxidation states of the CCA components in the particulate matter were As (III) and As (V), Cr (III), and Cu (I) and Cu (II), suggesting that open burning of CCA-treated wood may be the origin of the more toxic trivalent form of As in inhalable particulates. Acute and chronic arsenicism have been described due to burning of CCA-treated wood [13]). Consequently, the USA Consumer Product Safety Commission has recommended to not burn CCA-treated timber [14]. Thus, the release of CCA-treated wood components is an increasing environmental concern and strategies to remove copper, chromium, and arsenic from treated waste wood are required for economic and environmental purposes. By using effective methodologies to remove components, wood fibers can be recycled into composite products.

CCA-treated wood presents chromium in largest proportion, making it the main challenge in the extraction process, as chromium has the strongest affinity to wood lignin, so it is the most resistant to extraction [15].

Several approaches have been used to remove CCA components from treated wood; acid extraction with citric, acetic, formic, oxalic, nitric, or sulfuric acids are the most common approaches [15]. Acid extractions are usually combined with steam explosions, bacteria or fungi that can tolerate the high levels of metals present in CCA-treated wood. In fact, the most efficient strategies in removing CCA involve combined methods.

Claus and co-workers [16] tested the wash off of CCA from treated wood using oxalic acid extraction, steam explosion and bacterial fermentation with *Bacillus licheniformis* CC01. Steam explosion as a mean of opening the chemical structure of wood for releasing copper, chromium, and arsenic demonstrated low applicability [17]. One of most efficient methods is the chemical fiber modification with oxalic acid, which eliminates 62–89% of copper, chromium, and arsenic from CCA-treated wood scobs. In addition, these authors have also combined some microbial and mechanical methods to remove all components of CCA from treated wood [17]. The combination of steam explosion with further oxalic acid extraction or bacterial fermentation showed a lower release of components from treated wood, with values of 35% depletion in chromium, whilst values were almost null when using the oxalic acid extraction *per se*. In relation to the extraction with oxalic acid as a precursor to *Bacillus licheniformis* CC01 fermentation, high values of removal were obtained (90% copper (CuO), 80% chromium (CrO_3), and 100% arsenic (As_2O_5)), which make it the most efficient treatment combination to clear relevant amounts of metals from CCA-chipped wood. In another study with CCA-treated wood wafers, Clausen and co-workers [18] found that 18 h exposure to oxalic acid provided a most favorable release of copper, chromium and arsenic from CCA-treated wood. The reductions of 78% copper, 97% chromium and 93% arsenic were obtained using 0.80% acid extraction combined with culture of *Bacillus licheniformis* CC01 [18].

The microbial conversion of CCA-treated wood has been also achieved by brown rot fungi of the genera Antrodia and Meruliporia, recognized for their tolerance to copper and generation of high levels of oxalic acid. The great generation of oxalic acid enhances the acidity of the substrate, promoting the solubility of chromium and arsenic; this can be applied as a possible method to commercial oxalic acid.

Other authors demonstrated a high decrease in copper, chromium and arsenic levels by brown rot fungi *Fomitopsis palustris*, *Coniophora puteana* and *Laetiporus sulphureus* [19], *Daedalea dickinsii* and *Polyporales* (unkown sp) [20]. High rates of removal of copper, chromium and arsenic (96%, 92% and 98%, respectively) were reached by *Fomitopsis palustris* [20].

Dos Santos and co-workers showed that the acid extraction of CCA components from *Eucalyptus sp*. and *Pinus resinosa* processed wood using hot sulfuric acid provided over 79% CCA removal [21]. Furthermore, effluents generated in acid decontamination were treated by precipitation with $FeCl_3$ and NaOH or $Ca(OH)_2$, as coagulant and alkalizing agents, respectively, displaying rates of removal over 98.5% [21].

Other techniques, such as electrodialysis and dialysis methods, were also applied to CCA-treated *Pinus pinaster* poles for removal of Cu, Cr and As from the maximum removal values (Cu, 84%; Cr, 87%; and As, 95%) were achieved under electrodialytic conditions generated for 14 days [22]. More recently, Jones et al. [23] recommended the separation and removal of metals in recycled construction and demolition wood, such as CCA, aiming to reduce adverse effects on the environment.

3. Conclusions

We emphasize that, although the use of CCA has been banned for many years in several countries, and despite significant efforts being made to reduce its impact on the environment, its components still persist as documented in the literature. Previous studies have described that the bioavailability and bioaccessibility, and distribution of Cr, Cu and As in soils and aquatic ecosystems from CCA-treated wood and contaminated sites are element- and site-specific. Aged CCA-treated facilities (e.g., playgrounds, agricultural structures, zoological gardens) still pose risks for environmental, animal and human health due to leaching and accumulation of toxic elements. They should be specifically targeted in terms of maintenance or even removal. Individual components of CCA, namely As and Cr, pose severe human health problems, therefore, their removal from the environment should be promoted. In addition, the risk for both the environment and human health induced by Cu must be addressed through appropriate measures for its removal. Evidence suggests that arsenic, chromium and copper levels in surface soils, close to CCA-treated wood constructions, may surpass permitted levels, inducing concerns about both human and environmental health. The data discussed in this review show that it is of urgent need to act more efficiently in terms of the remediation of soils contaminated with CCA, and in terms of appropriate measures, such as hand washing after contact with CCA-wood and avoiding the contact of pets in these settings.

References

1. Chen, A.Y.-Y.; Olsen, T. Chromated Copper Arsenate–Treated Wood: A Potential Source of Arsenic Exposure and Toxicity in Dermatology. Int. J. Womens Dermatol. 2016, 2, 28–30.
2. Coles, C.A.; Arisi, J.A.; Organ, M.; Veinott, G.I. Leaching of Chromium, Copper, and Arsenic from CCA-Treated Utility Poles. Appl. Environ. Soil Sci. 2014, 2014, 1–11.
3. Gosselin, M.; Zagury, G.J. Metal(Loid)s Inhalation Bioaccessibility and Oxidative Potential of Particulate Matter from Chromated Copper Arsenate (CCA)-Contaminated Soils. Chemosphere 2020, 238, 124557.
4. Katz, S.A.; Salem, H. Chemistry and Toxicology of Building Timbers Pressure-Treated with Chromated Copper Arsenate: A Review. J. Appl. Toxicol. 2005, 25, 1–7.
5. Matos, R.C.; Vieira, C.; Morais, S.; de Lourdes Pereira, M.; Pedrosa, J. Nephrotoxicity Effects of the Wood Preservative Chromium Copper Arsenate on Mice: Histopathological and Quantitative Approaches. J. Trace Elem. Med. Biol. 2009, 23, 224–230.
6. Matos, R.C.; Vieira, C.; Morais, S.; de Lourdes Pereira, M.; de Jesus, J.P. Nephrotoxicity of CCA-Treated Wood: A Comparative Study with As2O5 and CrO3 on Mice. Environ. Toxicol. Pharmacol. 2009, 27, 259–263.
7. Matos, R.C.; Vieira, C.; Morais, S.; Pereira, M.L.; Pedrosa, J. Toxicity of Chromated Copper Arsenate: A Study in Mice. Environ. Res. 2010, 110, 424–427.

8. Matos, R.C.; Oliveira, H.; Fonseca, H.M.A.C.; Morais, S.; Sharma, B.; Santos, C.; de Lourdes Pereira, M. Comparative Cr, As and CCA Induced Cytostaticity in Mice Kidney: A Contribution to Assess CCA Toxicity. Environ. Toxicol. Pharmacol. 2020, 73, 103297.
9. Ohgami, N.; Yamanoshita, O.; Thang, N.D.; Yajima, I.; Nakano, C.; Wenting, W.; Ohnuma, S.; Kato, M. Carcinogenic Risk of Chromium, Copper and Arsenic in CCA-Treated Wood. Environ. Pollut. 2015, 206, 456–460.
10. Takahashi, N.; Yoshida, T.; Kojima, S.; Yamaguchi, S.; Ohtsuka, R.; Takeda, M.; Kosaka, T.; Harada, T. Pathological and Clinical Pathological Changes Induced by Four-Week, Repeated-Dose, Oral Administration of the Wood Preservative Chromated Copper Arsenate in Wistar Rats. Toxicol. Pathol. 2018, 46, 312–323.
11. US Environmental Protection Agency (US EPA). Notice of receipt of requests to cancel certainchromated copper arsenate (CCA) wood preservative products and amend to terminate certain uses of CCA products (22 February 2002). In Federal Register; U.S. Environ-mental Protection Agency, Office of Pesticide Programs: Washington, DC, USA, 2002; Volume 6, pp. 8244–8246. Available online: (accessed on 10 January 2021).
12. Lansbury Hall, N.; Beder, S. Treated Timber, Toxic Time-Bomb: The Need for a Precautionary Approach to the Use of Copper Chrome Arsenate (CCA) as a Timber Preservative. Fac. Arts Pap. 2005, 1–49. Available online: (accessed on 10 January 2021).
13. Peters, H.A.; Croft, W.A.; Woolson, E.A.; Darcey, B.; Olson, M. Hematological, dermal and neuropsychological disease from burning and power sawing chromium-copperarsenic (CCA)-treated wood. Acta Pharmacol. Toxicol. 1986, 59 (Suppl. 7), 39–43.
14. U.S. Consumer Product Safety Commission. CCA-Pressure Treated Wood: Chromated Copper Arsenate: Guidance for Outdoor Wooden Structures. Available online: (accessed on 13 May 2021).
15. Warner, J.E.; Solomon, K.R. Acidity as a factor in leaching of copper, chromium and arsenic from CCA-treated dimension lumber. Environ. Toxicol. Chem. 1990, 9, 1331–1337.
16. Leduc, F.; Whalen, J.K.; Sunahara, G.I. Growth and Reproduction of the Earthworm Eisenia Fetida after Exposure to Leachate from Wood Preservatives. Ecotoxicol. Environ. Saf. 2008, 69, 219–226.
17. Clausen, C.A.; Smith, R.L. Removal of CCA from Treated Wood by Oxalic Acid Extraction, Steam Explosion, and Bacterial Fermentation. J. Ind. Microbiol. Biotechnol. 1998, 20, 251–257.
18. Clausen, C.A. CCA Removal from Treated Wood Using a Dual Remediation Process. Waste Manag. Res. 2000, 18, 485–488.
19. Kartal, S.N.; Munir, E.; Kakitani, T.; Imamura, Y. Bioremediation of CCA-Treated Wood by Brown-Rot Fungi Fomitopsis Palustris, Coniophora Puteana, and Laetiporus Sulphureus. J. Wood Sci. 2004, 50, 182–188.
20. Kim, G.H.; Choi, Y.S.; Kim, J.J. Improving the Efficiency of Metal Removal from CCA-Treated Wood Using Brown Rot Fungi. Environ. Technol. 2009, 30, 673–679.
21. Dos Santos, H.S.; Ferrarini, S.F.; Flores, F.Q.; Pires, M.J.R.; Azevedo, C.M.N.; Coudert, L.; Blais, J.F. Removal of Toxic Elements from Wastewater Generated in the Decontamination of CCA-Treated Eucalyptus Sp. and Pinus Canadense Wood. J. Mater. Cycles Waste Manag. 2018, 20, 1299–1309.
22. Velizarova, E.; Ribeiro, A.B.; Ottosen, L.M. A Comparative Study on Cu, Cr and As Removal from CCA-Treated Wood Waste by Dialytic and Electrodialytic Processes. J. Hazard. Mater. 2002, 94, 147–160.
23. Jones, A.S.; Marini, J.; Solo-Gabriele, H.M.; Robey, N.M.; Townsend, T.G. Arsenic, Copper, and Chromium from Treated Wood Products in the U.S. Disposal Sector. Waste Manag. 2019, 87, 731–740.