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Estimating dermal transfer of copper particles from the surfaces of pressure-treated lumber and implications for exposure

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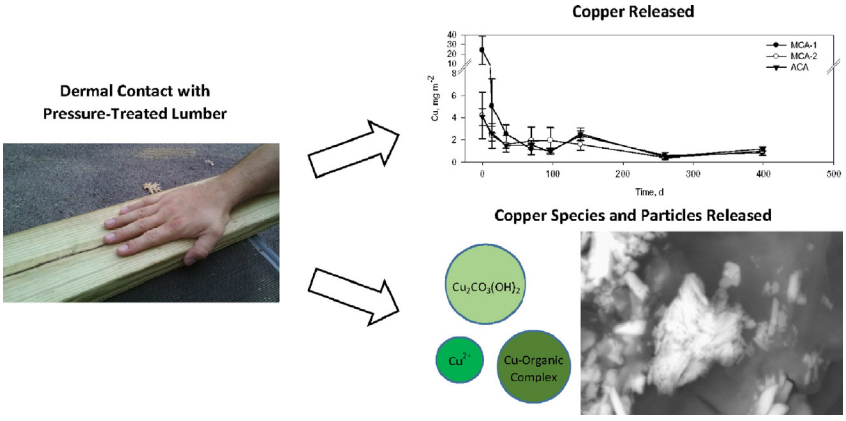
HIGHLIGHTS

- Micronized copper treated lumber was assessed for copper and particulate release.
- ~1.5 mg m^{-2} of Cu was released during dermal contact.
- Release levels similar to ionic treatments on the market for 10+ years.
- Copper particles were released in the micro and nano ranges.
- Particulate copper released was mostly associated with larger cellulose particles.
- At levels found, children under age 8 could be affected by chronic ionic Cu exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

Lumber pressure-treated with micronized copper was examined for the release of copper and copper micro/nanoparticles using a surface wipe method to simulate dermal transfer. In 2003, the wood industry began replacing CCA treated lumber products for residential use with copper based formulations. Micronized copper (nano to micron sized particles) has become the preferred treatment formulation. There is a lack of information on the release of copper, the fate of the particles during dermal contact, and the copper exposure level to children from hand-to-mouth transfer. For the current study, three treated lumber products, two micronized copper and one ionic copper, were purchased from commercial retailers. The boards were left to weather outdoors for approximately 1 year. Over the year time period, hand wipe samples were collected periodically to determine copper transfer from the wood surfaces. The two micronized formulations and the ionic formulation released similar levels of total copper. The amount of copper released was high initially, but decreased to a constant level (~1.5 mg m^{-2}) after the first month of outdoor exposure. Copper particles were identified on the sampling cloths during the first two months of the experiment, after which the levels of copper were insufficient to collect interpretable data. After 1 month, the particles exhibited minimal changes in shape and size. At the end of 2-months, significant deterioration of the particles was evident. Based on the wipe sample data, a playground visit may result in a potential exposure to

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2.58 mg of copper, which is near or exceeds the daily tolerable upper intake limits for children under the age of 8, if completely ingested through hand-to-mouth transfer. While nanoparticles were found, there is not enough information to estimate the exposure from the released particles due to a lack of published literature on copper carbonate.

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1. Introduction

Pressure treated lumber is used extensively in residential construction where contact with water or environmental conditions is possible. Pressure treatment refers to the process by which biocidal agents, using both organic and inorganic components, are infused into the wood structure to protect against microbial, fungal, and insect decay. Therefore, the use of the material in outdoor wooden structures represents a potential biocidal exposure pathway to humans through contact with the wood surface. Previous work by the U.S. Consumer Product Safety Commission (CPSC) suggested that the greatest potential exposure route for children is hand-to-mouth ingestion (Thomas et al., 2004).

In 2003, the wood industry voluntarily stopped producing copper chromated arsenate (CCA) lumber for residential applications in favor of an ionic copper based treatment. The transition resulted from research, by the CPSC, into the potential for children to be exposed to elevated levels of arsenic during play activities on CCA treated equipment (Thomas et al., 2004). More recently, the industry has shifted from the ionic copper treatment formulation to a micronized copper formulation (Leach and Zhang, 2006). The micronized copper formulation provides similar protection from microbial, fungal, and insect attack, while avoiding arsenic and chromium, releasing less copper, and producing less corrosion (Forest Products Laboratory, 2000; Freeman and McIntyre, 2008; Kartal et al., 2009). The primary biocide in the micronized formulations is copper carbonate ($Cu_2CO_3(OH)_2$) particles. The copper carbonate particles are rectangular in shape and range from several microns to a few nanometers in size (Evans et al., 2008; Matsunaga et al., 2009).

The presence of micro/nanoparticle copper, rather than ionic, has raised concerns over the potential for human exposure to nanoparticles as well as their release into the environment (Hansen and Kimbrell, 2010). Previous research, has established limits for exposure and daily ingestion for ionic copper, as well as studies about its impact in the environment, but particulate copper adds a new dimension that is not as well understood (Institute of Medicine, 2001; Osterhout, 2004; Evans et al., 2008). Metallic and metal oxide nanomaterials are known to possess properties that differ from the bulk version of the same material, opening the possibility that exposure to copper nanoparticles may result in differing toxicological responses (Roco, 2006). For instance, a study involving copper oxide nanoparticles (23.5 nm) found acute toxicity in mice similar to that of ionic copper, while the micron-sized particles (17 μm) produced an order of magnitude less toxicity (Chen et al., 2006). Additionally, in a follow-up study, the same researchers found that the nanoparticles caused accumulation of copper in internal organs over time, while the ionic and micron species did not (Meng et al., 2007). A recent review evaluated the available information on copper nanoparticle treatment formulations and concluded that they are poorly characterized and understood and that their safety is unknown (Ding et al., 2013; Civardi et al., 2015). Much of the research on nanocopper in treated lumber has focused on copper oxide, while very little is known about the release of copper carbonate nanoparticles (Kartal et al., 2009; Civardi et al., 2015). Furthermore, even less of the research has examined materials available to consumers, focusing primarily on laboratory-based formulations and specimens.

Due to the prevalence of the micronized formulation in the marketplace, approximately 80% of the pressure-treated lumber produced and sold within the United States and Canada in 2009, and treated lumber's broad application, there is a need to better understand the levels of release and exposure to humans from these copper nanoparticles (Cushman, 2009; Civardi et al., 2015). Therefore, an investigation was conducted to characterize and evaluate the amount of copper and copper micro/nanoparticles, primarily copper carbonate, transferred during physical contact with the wood surface. This research focuses on the copper released and available for potential ingestion through hand-to-mouth contact using surrogate dermal transfer methods developed previously for evaluating CCA lumber for arsenic (Cobb, 2003; Thomas et al., 2004).

2. Materials and methods

2.1. Wood specimens

Three commercial formulations were used in the current study: two micronized copper azole-treated samples (MCA-1 and MCA-2) and an aqueous (ionic) copper azole-treated sample (ACA). Market research was used to select two micronized copper formulations, one from each of the two primary manufacturers of the copper carbonate component, as well as an aqueous copper pressure-treated lumber source. The wood samples were obtained from national hardware retailers and wood suppliers within 50 miles of Cincinnati, OH. Samples were purchased in bulk to help minimize variation between individual boards and prevent variations that might result from a change in product formulation or manufacturer. All of the treated wood specimens were recommended for above-ground use by the manufacturer.

2.2. Experimental setup

Three 8 ft. (approximately 2.4 m) 2″ × 6″ nominal boards treated with each formulation were left outdoors exposed to environmental conditions for approximately 1 year at the U.S. Environmental Protection Agency (EPA) Center Hill research facility in Cincinnati, OH (climate conditions for Cincinnati, OH are presented in the Supplementary Information, Supplementary Figure (SF) 1). Each board was divided into four sections: three for total copper analysis (9 replicates per formulation) and one for particulate analysis (3 replicates per formulation). Each section was sampled periodically at 0, 14, 34, 70, 97, 140, 260, and 399 days using a polyester cloth, as defined by the wipe sampling method developed by the CPSC (Cobb, 2003; Thomas et al., 2004). The samples collected from the first three sections of each board were processed and analyzed for total copper, while the samples from the fourth section were preserved for microscopy and X-ray adsorption fine structure spectroscopy (XAFS).

Two additional boards of each wood type were wiped repeatedly without having undergone any weathering treatment or surface modification. The boards were wiped a total of 12 times over 2 days, 6 times per day. This set was used to determine the baseline effect of wiping the boards.

2.3. CPSC wipe sampling method

The method was developed by the CPSC and is described in detail elsewhere (Cobb, 2003; Thomas et al., 2004). In brief, a piece of polyester fabric (cloth) (Texwipe TX 1099), approximately 10 cm square, was soaked with 2 mL of 0.9% NaCl solution and left overnight. The following day, the cloth was secured to a weight, 8 cm in diameter, with a mass of 1.1 kg. The effective surface area of the cloth after it was secured to the weight was 50 cm^2. The weight was attached to a sampling apparatus developed by the CPSC laboratory staff, which was secured to the board