



Assessment of the bioaccessibility of micronized copper wood in synthetic stomach fluid



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ABSTRACT

The widespread use of copper in treated lumber may result in a potential for human exposure. Due to a lack of information concerning the release of copper from treated wood particles following oral ingestion, the *in vitro* bioaccessibility of copper from copper-treated wood dust in synthetic stomach fluid (SSF) and DI water was investigated. Copper-containing particles ranging in size from nano-scale to micron-scale were observed by transmission electron microscopy (TEM) in thin sections of these micronized copper-treated wood products. Three copper-treated wood products (liquid alkali copper quarternary and two micronized copper quarternary products) from different manufacturers were incubated in the extraction media. The released copper was then fractionated by centrifugation and filtration through 0.45 μm and 10 kDa filters, respectively. Soluble copper released into isolated fractions was measured using Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES). Total copper from each wood product was also determined using microwave-assisted acid digestion of dried wood samples and ICP–OES. The bioaccessible copper released into SSF was between 83 and 90% for all wood types. However, the percent of copper released in DI water was between 14 and 25% for all wood products. These data suggest that copper is highly bioaccessible at the low pH values present in the stomach and may pose a potential exposure risk upon ingestion.

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1. Introduction

Copper is an essential element that is naturally found in organisms and the environment; however, excessive copper is known to be biocidal. Since the 18th century, copper-based preservatives were often used to protect against fungi, bacteria, insects, algae, and mold. Copper has also been widely used as a wood preservative for a variety of products including utility poles, fence posts, buildings, decks, and furniture (Janin et al., 2011). Chromated copper arsenate (CCA), which is formulated from copper oxide, chromium and arsenate, was the predominant wood preservative used in the USA for over 30 years (Clausen, 2003). The toxicological concerns over chromium and arsenate use in residential wood products led to the restricted use of CCA in 2003 and the development and widespread

use of ammoniacal and amine copper-based formulations (USEPA, 2003) such as liquid alkali copper quarternary (LACQ) and aqueous copper alkaline (ACA) referred to as an alkali copper (AC) class of compounds. The new formulations; however, showed disadvantages in that the LACQ preservatives had high corrosion potential and high leachability rates due to the use of water-soluble Cu compounds (Freeman and McIntyre, 2008). As an alternative, micronized copper quarternary (MCQ) formulations were introduced to the wood market.

MCQ preservatives consist of water-insoluble Cu particles ground to a range of 0.001–25 μm prior to being injected into wood under pressure (Dhyani and Kamdem, 2012; Freeman and McIntyre, 2008). These formulations commonly use copper carbonate due to its low solubility in water ($K_{sp} = 10^{-33}$ for malachite); and, copper carbonate-treated wood has also been shown to be less corrosive and more leach-resistant than its soluble copper-based counterpart (Xue et al., 2013). Despite MCQ's advantages, there is a lack of conclusive evidence as to whether MCQ preservatives are more or less efficacious compared to alkali copper (AC)

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preservatives (Barnes et al., 2008; Freeman and McIntyre, 2008; Preston et al., 2008). In addition, there is public concern about the possible human health and environmental effects originating from the use of particles with a size less than 100 nm, also known as nanoparticles (Hansen, 2010). This concern stems from evidence that suggests that nanoparticles have a higher surface area and thus higher surface reactivity than micro-particles. Another concern for exposure to copper-containing nano-scale particles is their increased rate of dissolution due to their increased surface area particularly in low pH environments such as the stomach. The United States Environmental Protection Agency (USEPA) has established that the acceptable drinking water standard for Cu is 1.3 ppm (mg/L) (ATSDR, 2013). The Food and Nutrition Board of the Institute of Medicine has developed recommended dietary allowances (RDAs) by individual age of: 340 μg Cu/day (1–3 years), 440 μg Cu/day (4–8 years), 700 μg Cu/day (9–13 years), 890 μg Cu/day (14–18 years), and 900 μg Cu/day (adults) (ATSDR, 2013). The potential release of copper carbonate-containing wood particles from MCQ-treated wood during sawing, sanding, machining, cleaning, and normal wear and tear could make the particles available for human inhalation and oral ingestion. Gastrointestinal exposure to Cu at sufficient concentrations can result in nausea, vomiting, and/or abdominal pain at a threshold concentration of 4–6 ppm (ATSDR, 2013). Pizarro et al. (1999) report acute gastrointestinal effects at 3–5 ppm. In addition, copper carbonate, if ingested, can cause such symptoms as metallic taste, nausea, vomiting, diarrhea, headache, sweating and shock (Bremner, 1998; Laporte-Saumure et al., 2011). Mild gastrointestinal effects have also been observed in workers who swallowed airborne Cu dust (ATSDR, 2013).

The determination of exposure through the GI route requires an estimate or measurement of the bioavailability, defined as “the fraction of an ingested dose that crosses the gastrointestinal epithelium and becomes available for distribution to internal target tissues and organs” (USEPA, 2007). For particulate materials such as micronized copper carbonate, the concept of bioaccessibility or the “physiological solubility” of a toxic metal at the portal of entry into the body (NRC, 2003) becomes an important factor. In the case of the wood dust used for this study, the greatest uncertainty for bioaccessibility of the copper carbonate particles is whether they are dissolved, dislodged or remain bound to wood fragments. The bioaccessibility would be determined by the leaching of Cu-containing nano-scale particles, the released Cu ion or both. Consequently, the greatest issues of uncertainty for the determination of potential exposure to Cu from treated lumber would include the size and number of particles and amount of Cu ion released from ingestible wood fragments in the low pH stomach environment.

There is a dearth of evidence on the dissolution and bioaccessibility of Cu from micronized copper carbonate-treated wood and only a few studies that report the Cu ion released from CuO nanoparticles in GI systems. In a study conducted by Cho et al. (2012), copper oxide nanoparticles were found to quickly dissolve in artificial lysosomal fluid (pH 5.5); however, the Cu particles remained insoluble in artificial interstitial fluid (pH 7.4). Midander et al. (2007) reported similar findings in a study in which Cu nanoparticles, copper (II) oxide nanoparticles, and artificial Cu patina were exposed to artificial lysosomal fluid (pH 4.5), artificial sweat (pH 6.5), and Gamble’s solution (i.e. by artificial sweat and Gamble’s solution). The authors concluded that Cu solubility increased as the solution-dependent pH decreased. Lei et al. (2008) found that Cu nanoparticles suspended in artificial gastric fluid (pH 2) began to dissolve within 5 mins of exposure and dissolution continued to increase over the next 2 h. In all of these studies, Cu particle dissolution was enhanced in solutions with pH below 7.0. In this study, we report the relative amounts and forms (ionic

or particulate) of Cu released from wood dust from various treated lumber sources into a simulated gastric environment.

2. Materials and methods

2.1. Exposure setup

Prior to the study, all vessels and glassware were acid washed in 20% nitric acid for a minimum of 24 h and rinsed three times with deionized water (DI, 18 M Ω \times cm, ASTM Type I trace element quality, Millipore, Bedford, MA). All solutions were prepared using DI water. Synthetic stomach fluid (SSF) was prepared as previously described (Bradham et al., 2011) using 0.42 M HCl (32–35% analytical grade) and 0.40 M glycine (certified ACS grade) obtained from Fisher Scientific, Inc. (Pittsburgh, PA) and DI water with a pH of 1.5 to mimic the high acidity environment in the stomach. Wood dust samples were prepared from four different commercially-produced lumber materials (two micronized copper-treated [MCQ], one liquid copper-treated [LACQ], and one untreated). A rotary disk sander with 220 grit quartz-based sand paper (average 53 μm) was used to sand the face surface of 2 \times 6 \times 8 ft. boards generating saw dust ranging in size from 1 to 183 μm with an average particle size of 55 \pm 12 μm and a specific surface area between 1.03 and 1.15 m² g⁻¹. Due to the circular motion of the sandpaper, both with-grain and cross-grain, particles representative of both sanding types were released. Approximately, 0.3 g of MCQ-1, MCQ-2, LACQ, or untreated wood dust was weighed into a 50 ml glass beaker followed by the addition of 30 ml of SSF or DI water. The solution was stirred constantly with a magnetic stir bar for 1 h at room temperature. After 1 h, the solution was centrifuged in 50 ml Nalgene polypropylene co-polymer centrifuge tubes (Nalge Nunc International, Rochester, NY) at 7500 \times g for 5 min. The supernatant was decanted and the remaining pellets were dried in glass beakers at 70 $^{\circ}\text{C}$ for 48 h prior to microwave extraction. A 5 ml aliquot was collected from the supernatant and designated as the released fraction (soluble, colloidal and particulate). A separate 10 ml aliquot of the supernatant was filtered through a Whatman cellulose acetate syringe filter with a pore size of 0.45 μm (GE Healthcare Biosciences, Piscataway, NJ) and 5 ml of the filtrate was collected and designated as the 0.45 μm filtrate. The remaining supernatant was transferred to a 10 kDa centrifuge filter unit (Amicon Ultra-15, 10 K, Millipore, Bedford, MA) and centrifuged at 5000 \times g for 10 min. An aliquot of 5 ml of the filtrate was collected and designated as the 10 kDa filtrate. The three collected fractions were acidified in 2% nitric acid (67–70% OptimaTM, Fisher Scientific, Inc., Pittsburgh, PA) and stored at 4 $^{\circ}\text{C}$ until further ICP-OES analysis (Fig. 1). Matrix and matrix spiked with 50 ppm (parts per million) of Cu standard (1000 ppm) were included in this assay. To achieve 50 ppm matrix spiked samples, 1.5 ml of 1000 ppm Cu standard solution was added to 28.5 ml of SSF or DI water. Prior to ICP-OES analysis, all samples (excluding untreated wood and matrix-only samples) were diluted 10 fold using DI water. Untreated wood and matrix only samples were excluded from dilution due to projected low or non-quantifiable levels of Cu in in these samples. All extractions were performed in triplicate.

2.2. Microwave assisted extraction

The digestion of all pellets collected after exposure to SSF and whole (i.e. non-size fractionated) wood dust samples were carried out using MARS-5 microwave system (CEM Corporation, Matthews, NC). The samples were transferred to Teflon digestion vessels containing 10 ml of concentrated nitric acid (67–70% OptimaTM, Fisher Scientific, Inc., Pittsburgh, PA) and allowed to pre-digest for 15 min under a fume hood. Next, the vessels were properly

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