1 Estimating Dermal Transfer of Copper Particles from the Surfaces of Pressure-Treated Lumber
2 and Implications for Exposure

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4 William E. Platten, III¹, Nicholas Sylvest¹, Casey Warren¹, Mahendranath Arambewela¹, Steve
5 Harmon², Karen Bradham³, Kim Rogers³, Treye Thomas⁴, and Todd P. Luxton^{2*}

6
7 ¹Pegasus Technical Services, Inc., 46 E. Hollister St., Cincinnati, OH 45219

8 ²National Risk Management Research Laboratory, U.S. Environmental Protection Agency, 26
9 West Martin Luther King Dr., Cincinnati, OH 45268

10 ³National Exposure Research Laboratory, U.S. Environmental Protection Agency 109 TW
11 Alexander Dr., Research Triangle Park, NC 27711

12 ⁴Office of Hazard Identification and Reduction, U.S. Consumer Product Safety Commission,
13 4330 East West Highway Suite 600, Bethesda, MD 20814

14
15 *Corresponding author: Todd Luxton

16 Tel: 513-569-7210

17 E-mail address: Luxton.Todd@epa.gov

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 ($\sim 1.5 \text{ mg m}^{-2}$) 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. The particles were little changed after 1 month, but showed significant deterioration at 2 months. Based on the wipe sample data, a playground visit may result in a potential exposure to 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.

39 **Keywords**

40 Pressure-treated Wood, Nanoparticle, Copper Exposure, Micronized Copper Azole, Ionic

41 Copper, Copper Speciation

1.0 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 human through contact with the wood surface. Previous work by the U.S. Consumer Product Safety Commission (CPSC) suggested 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 ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) 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 μ m) 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 (Kartel 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 percent 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).

2.0 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 meters) 2" x 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 a 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 cm². The weight was attached to a sampling apparatus developed by the CPSC laboratory staff, which was secured to the board section at marks to ensure correct placement over the desired wipe area. The cloth was dragged over a distance of 50 cm for an effective surface area of 450 cm². A total of 10 wipe cycles (dragging back and forth once, representing one cycle) were conducted for each event, where five wipe cycles were performed before rotating the disc 90° and performing another five wipe cycles. After sampling, the cloths were extracted with 15 mL of 10% nitric acid solution to solubilize any copper retained on the cloth. The cloths and nitric acid solution were heated at 60°C in a water bath for between 22 and 24 hours. After cooling, the samples

were mixed and the extract was analyzed by inductively coupled plasma optical emission spectrometry.

The fourth replicate was extracted with 30 mL of Milli-Q water and placed on an end-over-end shaker for 30 minutes. The extract was sequentially filtered through a 0.45- μ m and 10-kDa filters. The resulting filter papers were analyzed via microscopy and/or XAFS.

2.4 Simulated Wear

To simulate wear on the boards, the weathered boards were sanded twice after the final sampling event on day 399. For the first sanding, an attempt was made to produce uniform, reproducible results using the sampling apparatus adapted to use a sanding disk instead of a cloth. An 80-grit sanding disk was secured to the weight on the sampling apparatus and the board was wiped in the same manner described above, repeated twice, for a total of 20 wipes. The boards were then sampled three times to determine if there was a spike in the amount of copper released immediately after sanding. A second, more rigorous sanding was conducted after these sampling events using an 80-grit sanding disk and a power sander. This method was less reproducible for the amount of material removed, but completely removed the weathered surface and restored the board to its original appearance. The boards were then sampled four additional times.

2.5 Analytical Techniques

Samples were prepared for metals analysis (primarily total copper) using standard U.S. EPA methods for microwave-assisted acid digestion, Methods 3051a and 3015a (U.S. EPA, 2007a; U.S. EPA, 2007b). The total metal concentration of copper was measured by inductively coupled plasma-atomic emission spectrometry (Thermo Scientific iCAP 6500), in accordance with EPA Method 6010b after digestion (U.S. EPA, 2007c). The detection limit for Cu was 4 μ g

L⁻¹. Accuracy and precision were assessed through triplicates, matrix spikes, and method blanks. Metal recoveries from matrix spikes were within 80 percent to 120 percent of the expected values.

2.6 Particle Characterization Techniques

To characterize the copper particles present initially in the wood and in any samples collected, a variety of techniques were used. The crystal structures of the micronized copper particles were determined by X-ray diffraction (XRD) using a PANalytical Xpert pro MPD (Westborough, MA) with CuK α radiation. The oxidation state, local bonding environment, and speciation of copper were examined using XAFS by collecting the copper K-edge spectra at beam line 10-BM (Materials Research Collaborative Access Team, Advanced Photon Source, Argonne National Laboratory, Argonne IL). Speciation was determined through linear combination fitting of the first derivative of the X-ray absorption near edge structure (XANES) spectra. A suite of copper reference materials was used as standards for LCF analysis and is presented in SF 2, located in the Supplementary Information. Particle size and shape were determined by field emission scanning electron microscopy (SEM) (JEOL JSM-7600F, Tokyo, Japan) and scanning transmission electron microscopy (STEM) (FEI Titan 80-300, Hillsboro, Oregon). Additional details on the instrumentation, sample preparation, and characterization analyses can be found in the Supplementary Information.

3.0 Results and Discussion

3.1 Characterization of the As-Purchased Material

The as-purchased materials were thoroughly characterized to determine the chemical composition and particle-size distribution of the copper within lumber, summarized in Table 1.

The micronized formulation samples were found to contain slightly less copper than advertised on their labeling, while the ACA formulation contained twice the amount of copper, as compared to the micronized copper formulation. XRD and XANES results indicated that copper carbonate was the only crystalline copper component in the wood samples of MCA-1 and MCA-2 and that there was also copper-organic complexes within the wood (SF-3 and SF-4). MCA-2 contained mostly copper carbonate, while MCA-1 contained roughly half copper carbonate and half copper-organic complexes. For the ACA, surprisingly, a small amount of copper carbonate crystallites were present, although the majority of the copper was organically complexed. Microscopy (SEM and STEM) was used to confirm the particle shape (long prismatic, rectangular) and to determine the particle size distributions. Because of their shape, the particles were described by two dimensions (length and width) as well as an aspect ratio (L/W). Both micronized formulations had particles ranging from only a few nanometers up to more than 400 nanometers, but the distributions were skewed to the smaller sizes, centered around 100-200 nm (SF-5 and SF-6). MCA-1 (105 x 56 nm) contained particles approximately half the size of MCA-2 (244 x 121 nm), while both had an aspect ratio of approximately 2.5 nanometers.

3.2 Simulated Dermal Transfer

The weathered boards released a high quantity of copper during the first few sampling events, which decreased and stabilized over time, as shown in Figure 1. The initial copper release was highly variable between replicates of the same formulation, particularly for MCA-1, likely due to manufacturing techniques as well as natural variations in the wood material. MCA-2 and ACA showed very little difference despite their differing copper content (ACA contained twice the quantity of copper per cubic foot). MCA-1 was significantly higher than the others during the first month of sampling before eventually converging, a surprise, given the similarities to MCA-

2 in copper content. All three formulations, independent of primary copper species, released similar quantities after this initial period (Day 28+), approximately 1.5 mg m^{-2} (Figure 1). The difference in the total quantity of copper released between the MCA-1 and the others is not immediately apparent. Attributing the increased initial release of copper to the presence of copper carbonate nanoparticles or copper organic complexes is difficult, because MCA-2 is enriched in the former, and ACA is enriched in the latter. Copper form and formulation could play a role in the amount of copper released because MCA-1 has a smaller particle size than MCA-2, while the fixation mechanism for micronized copper (particle deposition) differs from that of ionic copper (chemical reaction) (Freeman and McIntyre, 2008; Kartal et al., 2014). Additional differences in the formulations, such as co-biocides or stabilization chemicals, could also affect how the copper migrates through the wood influencing release. Finally, the initial release may result from excess or residual pressure-treatment solution remaining on the wood surface, visible on the surface of the as-purchased material.

3.3 Impact of Weathering

The weathering that the boards received during the yearlong test was significant. Visually, the weathered boards were heavily cracked and faded, and the initial green hue associated with the as-purchased material was absent. To gauge the role of the weathering conditions on the copper transfer, particularly the significant decline during the first 3-4 wipe events, a pair of fresh boards of each formulation was wiped repeatedly without undergoing any weathering. Figure 2 compares the copper release from these “un-weathered” boards with that of the weathered boards from Figure 1 on a sampling event basis. The copper release is consistent between the two experiments: decreasing copper concentration with successive sampling over the initial period, reaching a stable concentration after 3-4 sampling events.

Although the trend is the same, the amount of copper released is slightly different between the two experiments, weathered versus unweathered. Figure 2 shows that the MCA-1 plateaued at approximately the same quantity in both tests (1.4 ± 0.8 versus 1.6 ± 0.5 mg m⁻² for the weathered and un-weathered, respectively); while the MCA-2 is slightly higher (1.4 ± 0.6 versus 0.8 ± 0.1 mg m⁻² for the weathered and un-weathered, respectively); and the ACA is clearly higher in the weathering experiment (1.4 ± 0.7 versus 0.3 ± 0.1 mg m⁻² for the weathered and un-weathered, respectively). In the unweathered experiment, the initial quantities of copper released are lower for all three formulations, attributed to differences between individual boards and the time the unweathered material spent in storage and subject to more handling, allowing for potential depletion of the copper treatment solution due to incidental contact. Based on the results, the ACA samples were the most affected by the outdoor exposure as demonstrated by the difference in the average long term release, likely due to precipitation producing increased copper migration to the wood surface. In contrast to the ACA, both MCA samples showed little difference in the average long term release between the weathered and unweathered materials indicating that environment had little influence on the amount of copper released.

3.4 Surface Wear

After the completion of the final sampling event, the weathered boards were sanded to simulate surface wear and to determine if there would be a spike in the copper released. Figure 3 displays the quantity of copper released after two different sanding regimens. The initial light sanding resulted in almost no change in concentration, despite a visible change in the board where material had been removed. Additional sanding of the wood surfaces removed all of the weathered material restoring the faded board surface to the yellow/green coloring of the original material. There was no difference between the amounts of copper released for all three

formulations compared to the long term average. The lack of a spike in copper concentration after surface wear is believed to be related to residual/excess treatment solution that was initially present on the surface of the as-purchased materials and subsequently wiped off after the initial sampling events. This result highlights that disturbance to the wood surface through wear/use does not result in increased release and exposure to copper.

3.5 Released Particle Characterization

The specific form and speciation of copper can play a significant role in biological response upon exposure (Chen et al., 2006 and Meng et al., 2007). The wipe procedure was designed to evaluate the potential material release during dermal contact with the wood surface (Thomas et al., 2004). In the case of MCA pressure-treated lumber, this dislodged material collected on the cloth is representative of the copper concentration and speciation to which consumers may be exposed. Therefore, in addition to the total concentration of copper, detailed characterization (i.e., particle size, chemical speciation) of the dislodged material is necessary for understanding the potential copper exposure from MCA treated lumber.

The copper particles present on the cloths were separated onto 0.45 μm (micron and nano-sized particles) and 10 kDa (nanoparticles) filters, as discussed in the Materials and Methods. No particles or materials associated with the lumber were identified on the 10-kDa filters for any of the sampling events, and, as such, the following discussion focuses solely on the material captured on the 0.45- μm filter papers.

In the wipe samples collected after 1-month of weathering, copper carbonate particles were found on the filters of both MCA formulation samples, as seen in Figure 4a and 4b. The rectangular shapes in the micrographs were the predominant particle present in the samples and were identified as copper carbonate based on their crystal shape and the EDS spectra. Copper

carbonate crystals were not identified in the ACA samples, despite a small presence in the as-purchased material based on XANES analysis; although crystals of calcite and silica can be seen in the figure (Figure 4c).

For both MCA-1 and MCA-2, the copper carbonate crystallites present were aggregated in isolated locations and were always associated with larger cellulose or lignin particles. This is especially evident for the MCA-1 micrograph (Figure 4a). The micrographs are very similar in appearance to those published by Matsunaga et al. (2009), who evaluated the distribution of copper carbonate with the wood structure. The similarity in the images suggests that the malachite dislodged from the wood surface remains associated with the dislodged cellulose and not as a separate entity or free particle. The average particle length, width, and aspect ratio were determined for copper carbonate present in both MCA samples (Table 2, SF-7, SF-8). The similarity in the shape and size indicates that after 1-month of exposure outdoors very little transformation of the copper carbonate occurred.

A second set of filters was analyzed after 2 months of exposure (Figure 5). The copper particulates collected were weathered/degraded (Figure 5), and it was no longer possible to identify or distinguish individual crystallites in the BSE images and collect reliable particle-size information. Additionally, a portion of the copper carbonate was transformed to either cuprite or tenorite (Cu_2O and CuO , respectively) based EDS which indicated only copper and oxygen were present in the particles. As with the 1 month samples, all of the copper particulates identified on the filters were associated with larger pieces of cellulose (5 to 70 microns in size), indicating that the copper particles were not present as individual particles. Copper concentrations from 0.45 μm samples collected after three months did not contain a sufficient quantity of solid materials

for SEM and XANES analysis (See Figure 1). Therefore, subsequent analysis of retained solid phases was not possible.

Copper speciation of the materials retained by the 0.45- μ m filters, for the 1- and 2-month wipe samples, was assessed by XANES (Figure 6). Similar to the microscopy samples, after 2 months the total quantity of Cu retained on the 0.45- μ m filters was not large enough to collect useful XANES data. Immediately evident in all three wood types for both wipe events is the presence of Cu(I) (Figure 6). The species is not associated with the original material indicating *in situ* formation. Previous research has demonstrated that in an organic rich matrix, Cu(II) will reduce to Cu(I) (Leal and Van Den Berg, 1998; Kogut and Voelker, 2001; Pham et al., 2012; Yuan et al., 2012). The mechanism occurred through the reduction of the Cu(II) ion, suggesting that the formation of the Cu(I) is controlled by the ionic Cu present and not copper carbonate.

A variety of copper minerals, adsorption complexes, and aqueous species were used for the LCF. Based on the fitting results, all of the spectra could be adequately represented using copper carbonate, aqueous Cu^{2+} , Cuprite (Cu_2O), copper complexed with acetate, and copper complexed with oxalate. Results from the LCF analysis of the as-purchased and wipe samples are presented in Table 2 and SF 5.

Over the 2-month period, the relative abundance of the copper-organic complexes decreased, with a subsequent increase in copper carbonate for the two micronized copper formulations. The biocidal mechanism for micronized pressure-treated lumber is based on the slow dissolution and subsequent release of ionic copper. Therefore, with time, the ratio of copper carbonate to ionic copper should increase as ionic copper is released from the wood surface. The reason for the increase in copper-organic fraction and decrease in copper carbonate fraction after 1 month for MCA-2 is unclear. The initial distribution of copper species at the wood surface may be different

than the bulk composition (enriched in copper-organic complexes), or it could be attributed to rapid dissolution of nano-sized copper carbonate crystals. The enrichment of copper carbonate at the wood surface over time demonstrates how exposure changes under environmental conditions, for the two MCA formulations.

Unlike MCA samples, there was a marked decrease in the copper-organic phase coupled with an increase in ionic Cu(II) in ACA treated lumber. The increase in ionic copper is likely explained by the initial ionic treatment formulation.

3.6 Copper Exposure Assessment

A 2003 CPSC report pertaining to CCA wood provides a detailed review of the potential toxicity of copper to humans (Osterhout, 2004). Dermal exposure to copper is not known to be dangerous outside of potential allergic reactions, but ingestion of copper has been shown to carry risk (Osterhout, 2004). The report summarizes several case studies, and reproduced in Table 3, lists the known acute and chronic levels of copper that could produce adverse effects in humans, if ingested. Also shown in Table 3 are results and tolerable upper intake levels (TUIL) from other published sources (Institute of Medicine, 2001; Stern, 2010). Above these tolerable levels, mild symptoms, such as nausea, vomiting, and abdominal pain, may be observed. Based on the reported levels presented in Table 3, children between the ages of 1 and 13 are likely to be the most at-risk of excessive copper intake from repeated contact with pressure treated lumber.

To equate the gathered data to exposure levels (Table 3), Thomas et al. (2004) determined that the surface area a child would come into contact with during a typical visit to a playground, which is the most likely place for a child to encounter pressure-treated lumber, would be 1.29 m². Using this area, an estimate can be made as to how much copper could be wiped off and potentially ingested during a playground visit. Rounding up to 2 mg m⁻², the approximate

quantity released from the weathered boards (Figure 2), the amount of copper transferred onto the hand would be 2.58 mg. The larger quantities of copper found when sampling the fresh material would not play a role in a chronic exposure because these quantities would be exhausted quickly, but they could induce acute systems. However, it is difficult to assess what copper levels would be encountered in practice, after a structure has been constructed and is ready for general use. Other factors may increase or decrease the impact. For instance, the method developed by Thomas et al. (2004) assumes only three visits per week though the exposure and TUIL levels in Table 3 are daily limits. Averaged over a week, three visits to the playground would amount to 1.11 mg d⁻¹, much closer to the TUIL for the youngest age group. To arrive at a single value for the wiped area, Thomas et al. (2004) make several assumptions about the average area of a child's hand and how much of the child's hand contacts the wood as well as the number of contacts and duration of the playground trip, parameters that could increase or decrease the exposure significantly on an individual basis, particularly with age. The calculations also assume complete ingestion of the transferred copper, and the TUIL values used for comparison are general recommendations and not known limits that guarantee symptoms will occur. Finally, as a practical point of comparison, the micronized copper formulations release similar amounts of copper to the ionic formulation that has been on the market and in use since 2003.

The above comparison focuses solely on the ingestion of total copper, regardless of form, (ionic versus particulate), as there is limited knowledge on the toxicity of micro/nanoparticle copper. Metallic copper, CuCl₂, and CuO nanoparticles have been shown to have toxic effects, but none of the studies involved human subjects (Chen et al., 2006; Meng et al., 2007; Midander, 2009). Additionally, no studies have been performed featuring copper carbonate particles or micronized

pressure-treatment formulations (Civardi et al, 2015). The relative abundance for copper carbonate for the two MCA samples after 2 months was approximately 70 percent copper carbonate. Converting the total copper released to particulate copper released onto the hand (70% of 2.56 mg) would equal to 1.8 mg of copper carbonate, a portion of which is nano-scale. However, without a reference for toxicity, the impact of this quantity is unknown. A study by Santiago-Rodríguez et al., conducted in parallel to this work, examined the fate of copper carbonate particles after ingestion. The study determined that the particles dissolved completely upon coming into contact with stomach fluids, and the copper was approximately 90 percent bioavailable (Santiago-Rodríguez et al., 2015). This indicates that the toxicity of the particles could be similar to that of ionic copper. However, their study is only an assessment of bioavailability and not a comprehensive investigation on the toxicity of micronized or nanoparticle copper.

4.0 Conclusion

The dermal release of copper and copper particles was examined from the surfaces of lumber pressure-treated with micronized copper. Initial characterization of the as-purchased MCA lumber confirmed the presence of rectangular-shaped copper carbonate particles ranging in size from nanometers to microns and established a baseline for the comparison of material released during sampling. Sampling the surface via the CPSC wipe method found that both MCA lumbers tested released $\sim 1.5 \text{ mg/m}^2$ of copper per contact event. This release rate was approximately equivalent to the previous generation treatment formulation (ACA). Weathering outdoors had little impact on the release of copper from the surface of the MCA treated lumber. In contrast, there was an increase in copper release from the weathered compared to the unweathered ACA treated lumber. Solid phase characterization of the material collected on the

sampling cloths contained several forms of copper: copper complexed with cellulose and micro-/nano-copper carbonate particles. The weathered samples showed an enrichment in copper carbonate particles over time that were always associated with larger cellulose particles and not found individually. As previously stated, the MCA and ACA formulations release similar quantities of total copper resulting in similar exposure levels (~2.5 mg of copper per exposure event). While the total quantity of copper released during a contact event is below values that would result in acute or chronic toxicity in adults and children, the values are near or exceed the tolerable upper intake limit for children under the age of 8, based on the total dietary copper intake. Overall, these results highlight the need for a detailed understanding of potential material release from micro/nano-enabled consumer products during realistic exposure scenarios.

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485

Figure 1: Copper release from weathered boards by wiping with time.

Figure 2: Copper release from weathered and as-purchased boards by wiping. Average copper released per sampling event for events 3+ are presented (excludes events 1 and 2).

Figure 3: Copper release from weathered boards after sanding the weathered surface.

500

501 Figure 4: SEM micrographs of materials collected on 0.45-μm filter papers. MCA-1 (A), MCA-2
502 (B), and ACA (C)

503

Figure 5: BSE SEM Micrographs and EDX chemical maps of particulates wiped from the surface of three different pressure-treated lumber samples and deposited onto a 0.45- μ m filter paper. MCA-1 (A), MCA-2 BSE micrograph and EDX maps (B, C, and D), respectively, and ACA BSE micrograph and EDX maps (E, F and G), respectively.

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511

512 Figure 6: Cu K α XANES spectra for the as-purchased pressure-treated lumber and the material
 513 dislodged from the wood surface and retained on a 0.45- μ m filter after 1 month (Wipe 1) and
 514 two months (Wipe 2). MCA-1 (A), MCA-2 (B), ACA (C). Dashed lines indicate the energy
 515 positions associated with Cu¹⁺ and malachite.

516

Figure 7: Comparison of the percent distribution of particle size between the as-purchased MCA-2 and the MCA-2 Wipe 1 samples. Length (A) Width (B).

Dermal Contact with

Copper Species and Particles Released

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Dermal Contact with

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Copper Released

Copper Species and Particles Released

534 Table 1: As-purchased lumber characterization: Copper concentration, speciation, and particle size distribution.

535

Formulation	Measured Copper (Reported)		Copper Speciation		CuCO ₃ Particle Size				
			CuCO ₃	Cu-organic*	Length	Width	Aspect Ratio	Particles < 100 nm (%)	
	kg m ⁻³	lb ft ⁻³	Percent/Standard Deviation		nm	nm	L/W	Length	Width
MCA-1	0.61 (0.8)	0.04 (0.05)	42/3	58/2	121/65	56/42	2.5/1.2	59	94
MCA-2	0.73 (0.8)	0.045 (0.05)	88/1	12/1	244/125	105/58	2.7/1.6	14	68
ACA	1.77	0.11	10/2	90/4	-	-	-	-	-

*The summation of Cu-Acetate and Cu-Oxalate

536

537

538 Table 2: Characterization of copper particles dislodged from the wood surface after wiping: speciation and particle size distribution.

539 Previous data for the as-purchased pressure-treated lumber is presented for comparison.

540

Formulation	Copper Speciation				Cu ₂ CO ₃ (OH) ₂ Particle Size			
	Cu ₂ CO ₃ (OH) ₂	Cu-organic*	Cu ₂ O	CuCl ₂	Length	Width	Aspect Ratio	Particles Counted
	Percent/Standard Deviation				nm	nm	L/W	
MCA-1	42/3	58/2	-	-	121/65	56/42	2.5/1.2	314
1-Month	41/4	49/4	10/1	-	168/132	65/52	3.0/2.1	537
2-Month	76/8	20/5	5/2	-	-	-	-	-
MCA-2	88/1	12/1	-	-	244/125	105/58	2.7/1.6	370
1-Month	34/5	52/5	14/2	-	291/175	136/83	2.4/1.3	378
2-Month	70/5	16/5	14/3	-	-	-	-	-
ACA	10/2	90/4	-	-	-	-	-	-
1-Month	-	73/3	10/1	18/2	-	-	-	-
2-Month	-	67/5	5/2	28/4	-	-	-	-

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542

543 Table 3: Summary of Copper Toxicity Levels.

544

Copper Dose	Effect	Age / Age Group	Dose Type	Study
5.3 mg	LOAEL ^a	Adult	Acute	Wyllie 1957*
0.6 mg	NOAEL ^b	Infant	Acute	Olivares et al. 1998*
1.2 mg	NOAEL ^b	Adult	Acute	Araya et al. 2001*
0.8 mg	LOAEL ^a	Adult	Acute	Olivares et al. 2001*
1.2 g	Hemolytic Anemia & Renal Damage	1 – 2 y	Acute	Osterhout 2003
0.2 mg d ⁻¹	No effect	Infant	Chronic	Dessel de Vergara et al. 1999*
0.4 - 0.6 mg d ⁻¹	No effect	Infant	Chronic	Olivares et al. 1998*
0.4 - 1.0 mg d ⁻¹	Cirrhosis	Infant	Chronic	Mueller-Hoecker et al. 1988*
5.0 mg d ⁻¹	Cirrhosis	3 – 4 y	Chronic	Trollman et al. 1999*
5.13 mg d ⁻¹	Abdominal Pain and Vomiting	5 – 7 y	Chronic	Spitalny 1984*
10.73 mg d ⁻¹	Abdominal Pain and Vomiting	Adult	Chronic	Spitalny 1984*
20 – 30 mg d ⁻¹	Liver Failure & Transplant	Adult	Chronic	Stern 2010
30 – 60 mg d ⁻¹	Cirrhosis/Liver Transplant	Adult	Chronic	O'Donohue et al. 1999*
1 mg d ⁻¹	TUIL ^c	1 – 3 y	Chronic	IOM 2001
3 mg d ⁻¹	TUIL ^c	4 - 8 y	Chronic	IOM 2001
5 mg d ⁻¹	TUIL ^c	9 – 13 y	Chronic	IOM 2001
8 mg d ⁻¹	TUIL ^c	14 – 18 y	Chronic	IOM 2001
10 mg d ⁻¹	TUIL ^c	19+ y	Chronic	IOM 2001

^a Lowest-observable-adverse-effect level for gastrointestinal symptoms

^b No-observable-adverse-effect level for gastrointestinal symptoms

^c Tolerable Upper Intake Level

* As reported in Osterhout, 2003

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