United States
Consumer Product Safety Commission

March 14, 2025

CPSC[1] Staff Statement on: Release of Micronized Copper Particles from Pressure-treated Wood Products

1. Background

The 2014 report titled, "Release of Micronized Copper Particles from Pressure-treated Wood Products" describes studies performed by the United States Environmental Protection Agency (EPA), National Risk Management Research Laboratory in Cincinnati, OH. The study was supported by interagency agreement CPSC-I-12-0013 between the Consumer Product Safety Commission (CPSC) and the EPA.

2. Introduction

Pressure treated lumber (PTL) is used in residential buildings because of its resistance to microbial, fungal, and insect decay using biocidal agents infused into the wood. As a replacement for copper chromated arsenate (CCA), the lumber industry developed copper formulations to remove children's exposure to arsenic from CCA treated wood structures. Ionic copper results in accelerated degradation of metal fasteners and potential for human exposure. The lumber industry then shifted to micronized copper formulations that provide equivalent wood protection and produce less corrosion. However, micronized copper PTL may release nano-sized copper particles into the environment that may adversely affect human health. Nanoparticles are of concern because their nanoscale size enables the particles to penetrate deeply into the lungs when inhaled and the gastrointestinal tract when ingested and to potentially cross membranes and become systemically distributed in the body. Nanomaterials are materials that range in size from 1 to 100 nm in length.[2]

3. Experimental Methods and Results

Studies on material characteristics and leaching and wiping tests were conducted to characterize the release of copper particles from the micronized copper PTL. Four wood types were used: two micronized copper treated woods (MCA-1 and MCA-2), an ionic copper treated wood (ACA), and an untreated wood (UTW).

a. Chemical Characterization

The study used analytical techniques to determine initial total metal concentrations, crystal structure of copper particles, copper speciation, and particle size and shape. Based on

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[1] This statement was prepared by the CPSC staff, and the attached report was prepared by EPA for CPSC staff. The statement and report have not been reviewed or approved by, and may not represent the views of, the Commission.

[2] https://www.cpsc.gov/content/2019-CPSC-Nanomaterial-Statement

product specifications, the copper concentration in the ACA sample was about two times higher than that of the MCA samples. Crystal structure analysis using X-ray diffraction technology identified that copper carbonate is the only crystalline copper component in the micronized wood samples, but copper-organic complexes were also present.

b. Leaching Test

The leaching tests, which quantified total and micronized copper release from the wood samples, were designed to simulate the effect of rainfall. ACA samples released significantly more copper than MCA samples in all tests. The leaching time-course showed that copper release increased over time from all wood samples and indicated that 24 hours leaching was not long enough to reach a steady state. Mass balance and imaging studies showed that individual copper carbonate particles may exist as a free particle, but most of the released copper particles were bound to cellulose. The results also indicated that particulate copper released from micronized PTL constituted a small fraction of the total copper released; ionic copper was the major form of copper dissolved from MCA samples.

c. Wipe Test

The wipe test was designed to simulate transfer of copper from direct human contact with the PTL during foreseeable use. Wipe test results showed higher copper releases initially from MCA-1 samples than MCA-2 and ACA samples, but the copper release from all samples stabilized at a similar concentration after 14 days. Microscopic analysis revealed that copper carbonate was the predominant particle found in MCA samples, present in an aggregated form or with larger pieces of cellulose. Other types of particles, such as calcite and silica, were found in the ACA sample. From the yearlong weathering studies, potential exposure to micronized copper particles by dermal contact with MCA appears to be greatly reduced after three months.

4. Conclusion

The leaching studies indicated that ACA samples released significantly more copper than MCA samples, and that the main form of copper release from MCA samples was ionic copper rather than particulate copper. The wipe tests, a surrogate for hand contact, showed that total copper released from MCA samples was comparable to that from the ACA sample. The EPA noted that data from these tests and previous studies suggest that copper exposure via PTL skin contact, subsequent hand-to-mouth transfer, and ingestion of the transferred copper may pose health risks for younger children, particularly toddlers (1-3 years). The EPA stated that only mild symptoms would be expected, depending on dietary levels of copper, while severe acute or chronic symptoms are unlikely during normal use. Dermal exposure to copper is not known to be hazardous, except for potential allergic reactions. This research was subsequently published in a peer-reviewed journal.[3]

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[3] Platten W.E., Sylvest N., Warren C., Arambewela M., Harmon S., Bradham K., Rogers K., Thomas T., Luxton T.P. (2016). Estimating dermal transfer of copper particles from the surfaces of pressure-treated lumber and implications for exposure. *Sci Total Environ.* 548-549: 441.

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Release of Micronized Copper Particles from Pressure-treated Wood Products

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EPA Report No. EPA/600/R-14/365

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Forward

The US Environmental Protection Agency (US EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, US EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by US EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

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National Risk Management Research Laboratory

Abstract

Micronized copper pressure-treated lumber (PTL) has recently been introduced to the consumer market as a replacement for ionized copper PTL. The presence of particulate rather than aqueous copper raises concerns about the exposure of humans as well as the environment to the particles. Two common pathways of exposure, leaching during contact with water and transfer during physical contact, were investigated to gage potential human and environmental exposure during intended use of the product.

Characterization, leaching tests, and wipe tests were conducted on two representative formulations of micronized copper PTL (micronized copper azole or MCA) to quantify the levels of copper present in the treated material and the amount of copper released during use as well as to determine the form (particle or ion) of the copper after it was released. Additionally, an ionized copper pressure-treated wood (alkaline copper azole or ACA) was tested for comparison. The characterization showed that copper carbonate is the primary particle form in the MCA treated wood, but other forms are also present, particularly in the MCA-1 formulation, which contained a large amount of organically complexed copper. Microscopy showed that MCA-1 contained particles roughly half the size of MCA-2.

The leaching results indicate that mostly (> ~95%) ionic copper is released from the MCA wood and that the particulate copper that was released is attached to cellulose and not free in solution. A small number of particles were captured separate from the cellulose on a 10-kiloDalton (kDa) filter, but the quantity amounts to less than 1% of the total copper leached from the wood during the test. Comparing the MCA wood to the ACA wood, MCA released significantly less copper than the ACA, leading to a lower potential impact on the environment, though ACA has already been shown to have a negligible impact (Forest Products Laboratory, 2000). The wipe tests were a surrogate for hand contact with the treated wood, developed by the Consumer Product Safety Commission for gauging exposure of children using playground equipment constructed with PTL. The results show that the MCA and ACA wood release approximately the same amount of copper with each contact and that the amount of copper released is high initially, but decreases to a constant level after being wiped 2-3 times. The boards which were left outdoors, exposed to the elements, had a higher plateau level than those tested indoors, leading to the conclusion that the exposure, likely to precipitation, causes migration of the copper to the surface. During the initial period of high release, contact with the wood causes far more depletion of the copper than any type of environmental exposure. During testing, MCA-1 released slightly more copper than MCA-2, possibly due to the smaller size of the copper particles in the MCA-1 formulation or the increased concentration of organically complexed copper. Based on previous research on the effect of copper dose and physiological effects, the copper transfer levels observed in this study could impact children under the age of 8 years, particularly those 1-3 years of age, if completely ingested; reaching or exceeding the Tolerable Upper Intake Levels (TUIL) recommended by the Institute of Medicine. Above the TUILs, only mild symptoms could be experienced depending on dietary levels of copper, while severe acute and chronic symptoms are very unlikely during normal use. It should be noted that the copper values found from the newer, micronized formulations are comparable to those found from the older, ionized formulation. In summary, the particulate copper released from micronized copper PTL constituted a small fraction (< ~5%) of the total released. The total copper released was less than or comparable to the current aqueous formulation available to consumers.

Keywords

Pressure-treated Wood, Micronized Copper, Nanoparticle, Nanocopper, Copper Toxicity, Copper Leaching, Copper Exposure, Micronized Copper Azole, Alkaline Copper Azole, Aqueous Copper, Copper Speciation, CCA Alternatives

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Table of Contents

Table of Figures

List of Tables

1 Introduction

Pressure-treating wood is a popular method for preserving lumber from rot caused by exposure to outdoor conditions, particularly insects and microbial agents. Prior to 2003, the majority of the pressure-treated lumber (PTL) in the U.S. was produced using Chromated Copper Arsenate (CCA) aqueous formulations that were forced into the wood under pressure. The copper and arsenic in the solution combined to provide protection from bacterial, fungal, and insect decay while the chromium acted as a fixing, or binding, agent and UV protectant. Concerned about human exposure to the chemical residues, mainly arsenic, the Consumer Product Safety Commission (CPSC) investigated the potential human exposure, focusing mostly on children through hand contact with pressure-treated lumber at playgrounds. After a series of reports from the CPSC detailing the potential exposure level to children, the wood preservation industry voluntarily agreed to remove the CCA formulation from the majority of wood intended for residential use.

Several alternatives to the CCA formulation were developed as a replacement. Based around copper, the formulations used ionic copper as the primary insecticide and fungicide along with a co-biocide to provide additional resistance. Examples of these new formulations include acid copper chromate, alkaline copper quaternary, and aqueous alkaline copper azole (ACA) (Lebow, 2004). These formulations were effective in preserving the wood, but released significantly more ionic copper into the surrounding environment than the CCA formulations (Forest Products Laboratory, 2000). The increased release of ionic copper resulted in the degradation of metal fasteners and other metal in the area of the treated wood. Corrosion of galvanized surfaces from the ionic copper was targeted as the primary mechanism responsible corrosion of metal fastener and subsequent structural failure (Forest Products Laboratory, 2000). A newer formulation using micronized copper particles was developed to reduce the release of ions and, therefore, the corrosive effects, while still maintaining the desired preservation characteristics.

Micronized copper formulations (micronized copper azole (MCA) and micronized copper quaternary) were developed to address the issues of the ionic copper formulations. They offer many advantages over the previous systems including: reduced mass of copper required to produce the same protection as the ACA treatment, reduced corrosion of the treating plant equipment and metal fasteners, reduced mold growth on the treated wood, and less copper leaching from the material. For example, research has shown that the micronized formulas are as effective as the ACA and CCA treated samples for wood preservation while retaining a greater quantity of copper over the field trial time period (Cookson *et al.*, 2010; Yu *et al.*, 2011). The difference between the formulations is the use of “micronized copper” as the active ingredient. The micronized formula is comprised of copper carbonate particles ranging in size from several microns to a few nanometers in size (Evans *et al.*, 2008).

Micronized copper pressure-treated lumber currently accounts for ~80% of the pressure-treated lumber being produced and sold within the United States and Canada (Cushman, 2009). The use of micronized copper particles in residential applications may eventually lead to the release of copper nano sized particles into the environment. The fate and potential impact of these particles is currently unknown. Concerns over the fate of these particles were raised in a petition by the International Center for Technology Assessment to the U.S. EPA, requesting further testing of the material. Thus, in a joint effort between the U.S. EPA and the U.S. CPSC, the release of micronized copper particles and the potential health and environmental effects of their release was examined.

In an investigation parallel to this report, commissioned by the CPSC, the types of PTL that utilized micronized copper were determined. The hierarchy of manufacturers, distributors, and retailers is complex and there are a number of distinct treatment formulations. A single commercial entity can act as a manufacturer, distributor, and/or retailer while also supplying products to other companies, which, in turn, can participate in any of those roles. At each stage in the manufacturing and distribution of the wood product, there is potential for a modification or addition to the treatment formula, resulting in a new variation. Manufacturers vary the concentrations of the solutions and, in addition to the copper and biocide chemicals, add a number of additives, producing a similar but separately distinct product. During the investigation, two primary manufacturers were identified as supplying the entire industry with the pure micronized copper treatment solutions (containing no biocides or additives) [redacted] (formerly [redacted]), and [redacted] (formerly [redacted]). The chemical formulations and treatment technologies are then subsequently licensed by secondary manufacturers who generate the pressure-treated lumber product. Because of the complexity of the industry and the near impossible task of locating and testing all of the various treatment formulations, the current investigation focuses on two readily available micronized copper azole pressure-treated lumber sources from the two different manufacturers of the treatment solution (MCA-1 and MCA-2) and an aqueous alkaline copper azole treated sample (ACA) and an untreated material (UTW) for comparison.

2 Materials and Methods

To investigate the release of micronized copper, as-purchased materials were thoroughly characterized and two experiments were conducted to evaluate the release of copper under different experimental conditions: leaching and wiping. The leaching test simulated the effects of rainfall and water on the release of copper from wood. The wipe test simulated direct human contact with the pressure-treated lumber during intended uses, such as construction using PTL, sitting, walking, or climbing on the PTL wood.

Four wood types were used in the current studies. Two micronized copper treated samples (MCA-1 and MCA-2), an aqueous copper treated sample (ACA), and an untreated wood sample (Untreated/UTW). All three pressure-treated woods types utilized Southern Yellow Pine as the wood type, and a Spruce wood for the untreated sample. Southern Yellow Pine and Spruce woods used for construction do not refer to a specific wood species, but are used as generic terms for different wood types with similar structural properties (U.S. Forest Service, 1936). The four wood samples were obtained from national hardware retailers and wood suppliers within 50 miles of Cincinnati, OH. Market research was used to select two micronized copper formulations from different manufacturers of the active biocidal component, copper carbonate, and an aqueous copper pressure-treated lumber source. Untreated Southern Yellow Pine was not available in the area; therefore an untreated indoor wood source (spruce) was used as the untreated material. 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 wood samples used in the current studies were recommended for above ground use by the manufacturer. Pressure-treated lumber rated for ground contact use has a significantly higher concentration of copper (approximately 5x). This is related to the increased exposure to insects, mold, or fungus with the wood. While the concentration is greater for the ground contact materials, the above ground material represents a more direct route of contact and exposure. Further, the market share of lumber sold is above ground use material. Therefore, based on market share and more importantly direct exposure route, the current study focused on materials rated for above ground use. The biocidal ingredients listed on the manufacture's label included copper carbonate ($Cu_2CO_3(OH)_2$), tebuconazole ($C_{16}H_{22}ClN_3O$), and propiconazole ($C_{15}H_{17}Cl_2N_3O_2$). The release of the two organic azole pesticides listed were not investigated in the current study since the focus was on the potential release of nanomaterials and copper from lumber.

2.1 Leaching Experiment

Leaching experiments were conducted to determine the quantity of total and micronized copper released when in contact with aqueous solutions. Three different solution chemistries were examined: 0.01 M NaCl solution (pH 7), 0.01 M $NaNO_3$ solution (pH 7), and Super Q water adjusted with synthetic precipitation leaching procedure (SPLP) solution (pH 4.2). The three solutions were chosen to address the impact of anions (Cl^- and NO_3^-) and simulated acid rain on the wood. The wood samples were tested as wood blocks and sawdust, to evaluate the role of particle size, at two different mixing durations (24 and 72 h). In total, 48 conditions were tested in triplicate with a fourth replicate set aside for imaging and speciation (see Table 2-1). The sawdust was generated by sanding the cross section of 2×6 boards with a random orbital sander and 80 grit sand paper. The specific surface area of the sawdust was measured by nitrogen gas adsorption. The measured specific surface areas were 1.23, 1.21, 1.18, and 1.2 $m^2\ g^{-1}$ for MCA-1, MCA-2, ACA, and Untreated, respectively.

Table 2-1: Leaching Experiment Testing Conditions. Columns indicate the different wood types, form, chemistry, and duration of the experiments.

Wood Type	Wood Form	Solution Chemistry	Duration
MCA-1	Wood Block	0.01 M NaCl – pH 7	24 h
MCA-2	Sawdust	0.01 M $NaNO_3$ – pH 7	72 h
ACA		Super Q SPLP – pH 4.2	
Untreated Lumber (UTW)			

Wood blocks, approximately 10 g in weight, and sawdust, approximately 1 g, were placed in acid-washed, 250 mL plastic containers and 100 mL of leaching solution was added. The containers were capped and placed on a reciprocating (back and forth motion) shaker for the desired duration. After the elapsed time period, the solution was fractionated to determine the form of copper in solution. A 10 mL subsample of the unfiltered solution was taken for total elemental analysis, and the remainder of the solution was passed through 2.5 µm, 0.45 µm and 10 kDa filters, sequentially. After each filtration step, a 10 mL sample was collected for elemental analysis and the filter membrane was retained for subsequent acid digestion and elemental analysis. The filtrates and the filters were digested with nitric acid or nitric and hydrochloric acid following US EPA Methods 3015a and 3051a, respectively, and analyzed via inductively couple plasma optical emission spectroscopy (ICP-OES) using US EPA Method 6010 (U.S. EPA, 2007).

2.2 Wipe Experiment

The wipe experiment was conducted to determine the release of micronized copper during intended uses. Three different sets of conditions were tested. A set of boards ("Outdoor") were left outdoors exposed to environmental conditions at the U.S. EPA Center Hill research facility in Cincinnati, Ohio and sampled at 0, 14, 34, 70, 97, 140, 260, and 399 days. Another set ("Freeze/Thaw") was put through several cycles of freezing at -80 °C for 24 hours and thawing at room temperature for 48 hours, simulating thermal expansion cycles from being outdoors in cold climates. The boards were moistened once each cycle, just prior to returning to the freezer. Samples were collected at 4, 8, 12, and 24 cycles. Procedural and analytical issues resulted in the loss of reportable data for wipe measurements conducted prior to the first Freeze/Thaw cycle. A third set of boards ("No Weathering") were wiped repeatedly without having undergone any surface modification. The boards were wiped a total of 12 times over two days, 6 per day. This set was used to determine the baseline effect of just wiping the boards. In all instances, eight-foot boards were divided into four sections and each section was wiped using a polyester cloth (details below). Samples from the first three sections were digested and analyzed for copper. Samples from the fourth section were preserved for scanning electron microscopy (SEM) and X-ray adsorption fine structure spectroscopy (XAFS). In the case of the No Weathering and Freeze/Thaw experiment, imaging samples and XAFS samples were not collected. Three boards for each type of wood were tested for the Outdoor conditions, one board was tested for the Freeze/Thaw conditions, and two boards were tested for the No Weathering conditions. The Freeze/Thaw boards were cut into sections and stored in plastic containers so they could be more easily moved in and out of the freezer. The Outdoor and No Weathering boards were left intact.

The samples were collected based on the wipe method developed and defined by the CPSC (Cobb, 2003; Thomas et al., 2004). In brief, a piece of polyester fabric (cloth) (Texwipe TX 1099), approximately a 10 cm square, was placed into a 50 mL conical centrifuge tube followed by 2 mL of 0.9% NaCl solution and left capped overnight to soak. The following day, the cloth was secured to an aluminum disc, 8 cm in diameter with a mass of 1.1 kg (weight). 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 supplied by the CPSC. The apparatus 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 cm^2. A total of 10 wipe cycles (dragging back and forth once equaled one cycle) were conducted where there were five wipe cycles before rotating the disc 90° and performing another five wipe cycles. The cloth was removed from the apparatus and placed back into the 50 mL tube for digestion or microscopy and XAFS analysis.

To simulate wear on the boards, the Outdoor boards were sanded after the day 399 sampling event. To produce uniform, reproducible results, the CPSC wipe method was adapted using a sanding disk instead of the cloth. An 80-grit sanding disk was trimmed to fit onto the weight on the sampling apparatus and secured using double-sided tape. The board was then wiped twice in the same manner described above, for a total of 20 wipes: five wipes, the weight was rotated 90°, another five wipes, the weight was rotated back to its original position, five wipes, the weight was rotated 90°, and another five wipes. A new sanding disc was used for each board. The sawdust produced from the sanding was blown off using compressed air. Three sampling events were then conducted to determine the amount of copper released immediately after sanding and in subsequent wipes.

Cloth samples were extracted with nitric acid to solubilize copper retained on the cloth. The procedure involved adding 15 mL of 10% nitric acid solution to each 50 mL conical centrifuge tube followed by heating in a water bath at 60°C for between 22 and 24 hours. After cooling, the samples were vortexed and 6 mL of each sample was place in an ICP sample tube and diluted with 6 mL of Super Q water. The samples were mixed for 20 minutes on a swirl shaker and then analyzed by ICP-OES. Cloths from the fourth set were placed in 50 mL conical centrifuge tubes and 30 mL of Milli-Q water was added to the tube and placed on an end over end shaker for 30 minutes. The extract was sequentially filtered through a 0.45 μm and 10 kDa filter. The resulting filter papers were analyzed via SEM and/or XAFS.

2.3 Analytical Methods

Analytical Techniques Samples were prepared for metals analysis (mainly total copper) using standard US EPA methods for microwave assisted acid digestion. Method 3051a (Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils) was used for any solids samples using nitric and hydrochloric acids. Method 3015a (Microwave Assisted Acid Digestion of Aqueous Samples and Extracts) was used for all of the liquid samples using nitric acid (U.S. EPA, 1986 and 2007). Briefly for the solids, 0.1 g of sawdust, 0.5 g of the 2.5 μm filter membrane, or all of the 0.45 μm and 10 kDa membranes were weighed out and quantitatively transferred to a Teflon® reaction vessel to which 9 mL of concentrated nitric acid and 3 ml of concentrated hydrochloric acid were added. The vessels were allowed to react with the wood material or filter membrane overnight prior to microwave digestion the following day. After digestion, the samples were quantitatively transferred to 50 mL centrifuge tubes and diluted to 50 mL and stored at 4^O C prior to analysis by ICP-OES. For the solution samples 45 ml of solution and 5 mL of concentrated nitric acid were added to a Teflon® reaction vessel followed by microwave digestion. If 45 mL of filtrate was not available, the sample of interest was diluted to 45 mL followed by the addition of nitric acid. After digestion the samples were quantitatively transferred to 50 mL centrifuge tubes and stored at 4^0 C prior to analysis by ICP-OES.

ICP-OES Analysis. 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. The detection limit for Cu was 4 μg L^{-1}. Accuracy and precision were assessed through triplicates, matrix spikes, and method blanks. Metal recoveries from matrix spikes were within 80-120% of the expected values.

Solid Phase Characterization. The crystal structures of the micronized copper particles were determined by X-ray diffraction (XRD) using a PANalytical Xpert pro MPD (Westborough, MA) with CuKa radiation. Six scans were collected and averaged prior to analysis. Sawdust from the four as-purchased wood types was compressed into a 3 cm disc prior to analysis to ensure the greatest detection of copper in the samples.

The oxidation state and local bonding environment of Cu were examined using X-ray absorption fine structure (XAFS) spectroscopy. The copper K-edge spectra were collected at beam line 10-BM (Materials Research Collaborative Access Team, Advanced Photon Source, Argonne National Laboratory, Argonne IL). For the as-purchased materials, sawdust samples were compressed into 13 mm pellets using a hand press and sealed between two strips of Kapton tape prior to analysis. For the leaching and rubbing experiments, the XAFS spectra were collected directly from material retained on the filter membranes. Adsorption spectra were collected at the K-edge energies of 8979 eV. Scans were collected from 8779–9979 eV. Data collection was done in fluorescence mode using a 4-element solid-state Si-detector. The synchrotron was operated at 7.0 GeV at a nominal 100 mA fill current. The energy of a Si (111) double crystal monochromator was calibrated using an elemental Cu foil. All spectra were collected under ambient conditions. A minimum of three scans (and up to 5) were collected for each sample.

Particle size and shape were determined by field emission scanning electron microscopy (FESEM) and scanning transmission electron microscopy (STEM). FESEM analysis was conducted on a (FESEM) (JEOL JSM-7600F, Tokyo, Japan) in Secondary Electron Imaging (SEI) and Backscatter Electron Imaging. Elemental analysis was conducted by Energy Dispersive X-ray Analysis. Data reduction, qualitative elemental analysis, and x-ray mapping was done with an Oxford 50 mm^2 silicon drift detector running Isis analytical software (Oxford Analytical, Oxfordshire, UK). Prior to analysis of the as-purchased material samples, sawdust, generated using a random orbital sander with 80 grit sand paper, was compressed into 13 mm discs using a hand press and affixed to 12 mm carbon tabs mounted on 12 mm aluminum stubs. For the leaching and rubbing samples, the filters were cut and affixed to 12 mm carbon tabs mounted on 12 mm aluminum stubs. The SEM operated at 15 kV with a 2 nm resolution.

TEM micrographs were collected using a FEI Titan 80-300 probe aberration corrected scanning transmission electron microscope (STEM) with a monochromator operating at 200 kV. Samples were cut into matchstick-sized fragments using a razor blade. The fragments were dehydrated by placing them in an increasing concentration of acetone solution. The dehydration procedure was repeated three times and the wood samples were transferred to a rotator. The Epon-Araldite epoxy used to embed the wood samples consisted of 20.9 g nadic methyl anhydride resin hardener (NMA) and 24.8 g Eponate 12 of which 8 g batches were mixed with 0.3 ml batches of benzyl di-methy amine epoxy cure accelerator (BDMA). One drop of resin was added to 1 ml of dehydrant every 5 minutes until the mixture was approximately 25% resin. After 1 hour, 75% of the dehydrant was removed and resin was added until the solution was 75% resin. The mixture remained in the rotator uncapped for 12 hours. The solutions were replaced with fresh 100% resin every 8 hours for the next 24 hours. Next, the samples were embedded in fresh resin and cured for 18 hours at 60°C. A microtome (Leica UC7 Cryo Ultramicrotome) with a diamond knife at room temperature and a maximum cutting speed of 1 mm/sec was used to slice 100-120 nm thick sections. Sections were imaged at North Carolina State University (Raleigh, NC). .

3 Characterization

The wood samples were thoroughly characterized to determine the chemical composition and particle size distribution within the lumber. Total elemental composition of the lumber was determined from microwave assisted acid digestion of sawdust samples generated using the method outlined in Section 2.1 (Table 3-1). The presence of Si and/or Cr in the sample was used as an indicator of contamination of the sample from materials dislodged from the sanding disc. The non-detect for Si and Cr indicated that there was a minimal amount of material transferred from the sanding disc during sanding dust collection. Excluding copper, the chemical compositions of the different wood types were similar (Table 3-1). Differences between samples were noted (concentration of Ca and Mg in MCA-1 compared to MCA-2 and ACA), however they were not substantial. The copper concentration in the ACA sample was twice that of the micronized samples, which was expected based on the reported manufacturers values listed on the product. One of the advantages of the micronized copper formulation, as described above, is the ability to exhibit similar biocidal effectiveness with less copper present. There was a statistically significant difference (p-value =0.013) in the total copper between the two micronized formulas. The total copper in the lumber was converted to a volume concentration and compared with manufacturers reported concentration (Table 3-2). The measured values for the total copper were 10 to 20% less than the manufacturer reported values.

As previously mentioned, the primary copper biocidal ingredient in micronized copper pressure-treated lumber is copper carbonate ($Cu_2CO_3(OH)_2$). The presence of copper carbonate was confirmed by X-ray diffraction (XRD) patterns for MCA-1 and MCA-2 (Figure 3-1). XRD patterns were further analyzed to determine if additional copper phases were present (copper(II) hydroxide, copper(II) oxide, copper(I) oxide, Azurite ($Cu_3(CO_3)_2(OH)_2$), and copper phosphate). Based on diagnostic peak locations, copper carbonate was identified as the only crystalline copper component in the wood. In Figure 3-1, the dashed lines numbered 1 and 2 mark the location of diagnostic diffraction peaks for copper carbonate and the dashed line labeled 3 indicates the location of a diffraction peak associated with the cellulosic wood structure. All four lumber types exhibit two broad diffraction peaks between 10^{O} and 30^{O} 2Θ and a smaller more well defined peak near 34^{O} 2Θ (Figure 3-1). Figure 3-1B and C provide an enlarged view of the area near the location of the copper carbonate diffraction peaks. Interestingly, diffraction peaks for copper carbonate were present in the ACA sample (Figure 3-1C) along with several other peaks. Extensive review of the International Center for Diffraction Data database did not identify another specific copper compound with similar diffraction peaks. However, calcium carbonate does have diagnostic diffraction peaks near the peak locations in the ACA sample.

The intensity and width of XRD peaks can be used to indicate the relative abundance and size, respectively, of the crystalline structures present. The peak intensity (width at half the maximum peak height) for MCA-1 is significantly less than MCA-2. The 12% increase in the total copper content of MCA-2 compared with MCA-1 does not fully account for the difference in peak intensity, suggesting that other non-crystalline copper phases are present. Crystallites with nano-sized dimensions exhibit broader diffraction peaks compared to larger particles as a result of the increased influence of the relaxation of surface atoms. The broad diffraction peaks for copper carbonate for MCA-1, MCA-2, and ACA, indicate the crystallites present are likely in the sub-micron range.

Table 3-1: Chemical composition of the four wood types as determined by microwave assisted acid digestion and ICP-OES analysis. Averages are based on seven replicate samples. Additional

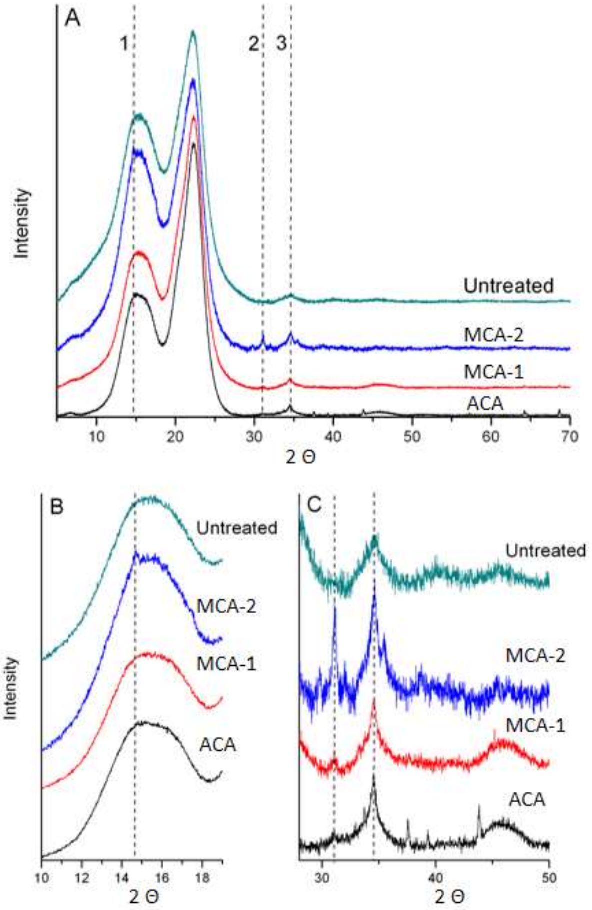
elements analyzed included Al, Ag, As, Ce, Co, Cr, Fe, K, Mo, Ni, P, Pt, Sb, Se, Si, and V, however there were no detectable quantities in the samples.

Elements	*Cu*	B	Ba	Ca	Mg	Mn	Pb	S	Sr	Ti	Zn
					mg kg^{-1}						
					MCA-1						
Average	*1327*	ND	4.8	595.8	122.2	48.2	ND	79.7	2.2	2.5	8.1
St Dev	*26.6*	ND	0.1	8.9	2.4	0.6	ND	2.3	0	0.5	0.2
Rel St Dev	*2*	ND	2.1	1.5	2	1.2	ND	2.9	1.6	18.1	3
					MCA-2						
Average	*1574*	ND	6	892.8	259.9	33	ND	113.8	3.8	1.3	14
St Dev	*158.6*	ND	0.5	65.8	21.4	2.8	ND	8.1	0.3	0.3	5.4
Rel St Dev	*10.1*	ND	8.2	7.4	8.2	8.5	ND	7.1	8.5	21.3	38.4
					ACA						
Average	*3833*	65.8	2.4	908.4	253.2	20.4	2	63.7	2.1	1.3	11.2
St Dev	*133.6*	1.6	0.1	10.8	3.9	0.6	0.3	7.3	0	0.3	0.3
Rel St Dev	*3.5*	2.4	2.3	1.2	1.5	2.7	13.1	11.4	0.7	20	2.8
					UTW						
Average	*3.9*	ND	18.3	907.8	76.2	16.8	ND	29.2	5.5	2.3	6.7
St Dev	*0.4*	ND	0.3	14.7	0.6	0.2	ND	1.6	0.1	0.5	0.7
Rel St Dev	*11.5*	ND	1.4	1.6	0.8	1.4	ND	5.4	1.3	23.2	10.6

Table 3-2: Volumetric concentration of copper in the 4 selected wood products. Calculated using the elemental concentrations from Table 1 and mass measurement of known volumes of lumber.

Wood Type	**Measured Copper**		**RSD**	**Reported Copper**	
	kg m^{-3}	**lb ft^{-3}**	**%**	**kg m^{-3}**	**lb ft^{-3}**
MCA-1	0.61	0.04	2	0.8	0.05
MCA-2	0.73	0.045	10	0.8	0.05
ACA	1.77	0.11	3.5		
UTW	$1.8*10^{-3}$	$1.1*10^{-4}$	11.5	N/A	N/A

Figure 3-1: X-Ray diffraction patterns for the as-purchased lumber. The dashed lines labeled 1 and 2 mark the location of diagnostic diffraction peaks for copper carbonate. The dash line labeled 3 indicates the location of a diffraction peak associated with the cellulosic wood structure.



The speciation of copper in the pressure-treated samples was further investigated by Cu K-edge XAFS spectroscopy and linear combination fitting (LCF) of the normalized first derivative of the XANES spectra. The XANES spectra of the three samples were compared with a variety of reference copper spectra to identify copper species with similar spectral features (Figure 3-2). Reference spectra evaluated included: Copper oxide (Cu_2O and CuO), copper carbonate ($Cu_2CO_3(OH)_2$), copper phosphate ($Cu_5(PO4)_2(OH)_4$), and Cu complexed with acetate, oxalate, cysteine, histidine, or ferrihydrite. Copper complexed with acetate, oxalate, cysteine and histidine were used as analogues for copper organic complexes that might be present. Copper carbonate and copper complexed with acetate (AcO) and oxalate were identified as the three compounds with the greatest similarities to the samples. Results from the LCF analysis indicate there is a large variation in the relative abundance of copper species present. For the micronized copper samples, the relative abundance of copper carbonate in MCA-2 is twice that of the MCA-1. The importance of this finding becomes apparent when considering the total abundance and speciation of copper that is released from the wood samples. If copper ions are more readily released in comparison to the crystalline material then the interpretation of an increase in the copper released from MCA-1, compared to MCA-2, must take into consideration the relative abundance of the copper species present initially. The average sensitivity of XANES LCF analysis is approximately 5% (Kelly *et al.*, 2008; Bunker, 2010). Therefore, any species with a relative abundance of less than 5% is speculative. The presence of 10% of copper carbonate in the ACA sample and the diffraction data provide ample evidence that copper carbonate is present in the sample.

Figure 3-2:First derivative XANES spectra for the three wood samples (MCA-1, MCA-2, and ACA) and reference compounds. The highlighted blue area shows the location of the first derivative peaks that correspond to copper carboxylate complexes.

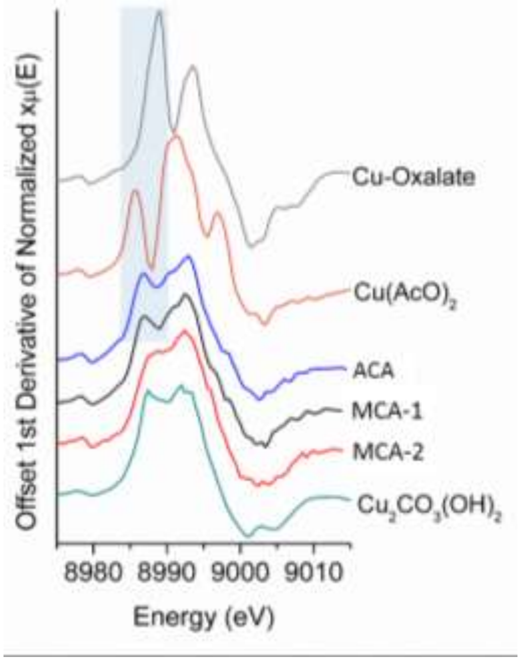


Table 3-3: Results from the linear combination fitting of the first derivative XANES spectra. Values are presented as average/standard deviation.

Wood Type	Copper Species	
	Copper Carbonate	Cu-organic*
	Percent/Standard Deviation	
MCA-1	42/3	58/2
MCA-2	88/1	12/1
ACA	10/2	90/4

*The summation of Cu-Acetate and Cu-Oxalate

The flow paths used to transport fluids in trees are the same paths that facilitate the distribution of preservatives within the wood. Previous research has identified that micronized copper is deposited along the fiber cell walls responsible for longitudinal and radial distribution of fluids and on the pits (valves) that connect void spaces together (Evans *et al.*, 2008; Stirling *et al.*, 2008; Matsunaga *et al.*, 2009; Evans *et al.*, 2012). More detailed analysis of the distribution of copper carbonate has revealed that the copper carbonate deposited in the wood structure does not readily penetrate the cell wall (Stirling *et al.*, 2008; Matsunaga *et al.*, 2009; Matsunaga *et al.*, 2010; Evans *et al.*, 2012). Understanding the distribution of copper carbonate within the wood microstructure is important for considering potential release of nanoparticles from the wood.

TEM and SEM electron images of the three pressure-treated wood types were collected. SEM images and EDS spectra revealed a broad range of particles present in the wood samples in addition to copper carbonate. Other phases present included iron oxides, calcite, and silicates (data not shown). The presence of non-copper materials is not unusual. The SEM and TEM micrographs in Figure 3-4 provide examples of the size and shape of the copper carbonate particles present. The SEM and TEM images of MCA-1 and 2, respectively, clearly show the rectangular shape of the copper carbonate present in the wood. The rectangular shape is consistent with the long prismatic or acicular shape of malachite (copper carbonate: $Cu_2CO_3(OH)_2$). Also evident in both images is the wide particle size distribution present. Based on the particle shape, it is difficult to calculate an average particle size value of any significant meaning. Therefore, the average particle length (longest dimension) and width (shorter dimension) of individual particles were measured to determine an average length, width, and aspect ratio (length:width). The measured length and width for copper carbonate in both micronized copper samples varied greatly. The standard deviation for the average values was at least half the mean value, indicating a high degree of variability. There were also notable differences between the copper carbonate present in both samples. The copper carbonate materials present in MCA-1 were half the size of those in MCA-2 (Table 3-4). Histograms and total frequency and box plots for MCA-1 and 2 are presented in Figure 3-5.

Figure 3-3: Micrographs of (A) BSE SEM MCA-1 and (B) Bright Field TEM MCA-2.

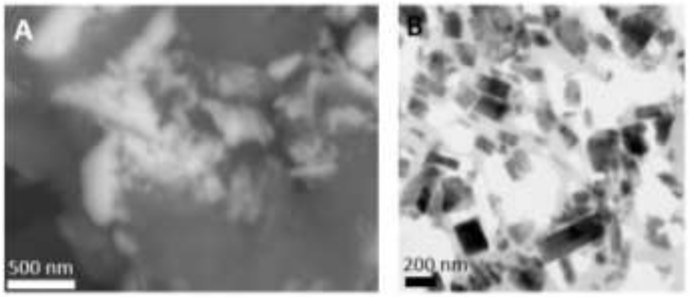


Table 3-4: Average particle size for MCA-1 and MCA-2. Values are presented as average/standard deviation.

Wood Type	Average			Percent of particles less than 100 nm		Number of Particles Counted
	Length	Width	Aspect Ratio	Percentage (L, W)		
	nm	nm	L/W			
MCA-1	121/65	56/42	2.5/1.2	59	94	314
MCA-2	244/125	105/58	2.7/1.6	14	68	370

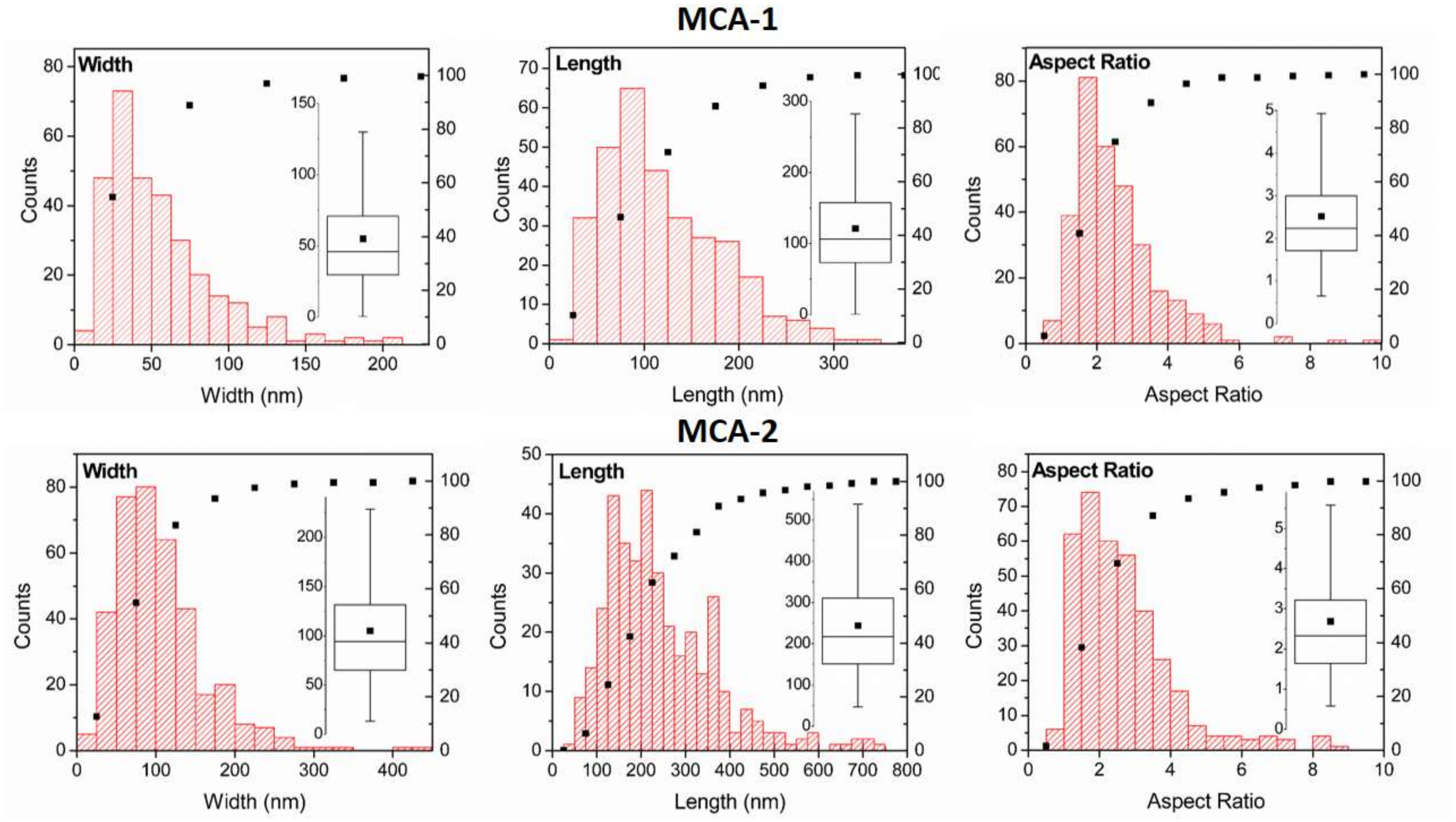
The histograms for both micronized copper samples are skewed towards lower values, indicating a much higher concentration of smaller particles. The total frequency plots for both samples show that greater than 50% of the measurements for length and width are less than the mean value calculated. SEM images for

MCA-1 and MCA-2 (data not shown) indicate that the copper carbonate in the samples was present in aggregated forms. There were few copper carbonate particles that were identified as isolated particles.

A question that has arisen is whether the materials used in pressure-treated lumber are truly nano in size. The current general definition for a nanoparticle is a material with at least one dimension less than 100 nm. As previously mentioned, the particle size distribution is very large. Based on the cumulative count and histograms it is possible to determine the relative percentages of particles with either 1 or 2 dimensions less than 100 nm. Table 3-4 provides a summary of the relative abundance of particles with a width of length less than 100 nm. Based on the general definition of nanoparticles, 94% and 68% of the material have widths less than 100 nm, for MCA-1 and 2, respectively. In the current study, length was always the longest of the two dimensions, therefore 59 and 14% of the materials were less than 100 nm in 2 dimensions, for MCA-1 and 2, respectively. Classifying a material as a nanoparticle becomes difficult with a broad size distribution, especially when only a percentage of the material is less than 100 nm.

The variation in total elemental composition, crystalline abundance, copper speciation, and particle size distribution are all factors that must be considered when interpreting the leaching and wipe data. Interpreting the results based only on the concentration of copper released may easily lead to false conclusions about the stability, fate, and/or the release mechanism of micronized copper in pressure-treated lumber. The differences in the chemical and physical properties of the three pressure-treated wood samples (especially the MCA samples) also offer an opportunity to see how copper speciation and copper carbonate particle size impact the release of copper.

Figure 3-4: Histogram, cumulative abundance, and box plots for particle length, width and aspect ratio (length/width) for Cu particulates identified in the SEM and TEM images for MCA-1 and MCA-2, respectively.



4 Leaching Experiment

4.1 Copper Release

The results for the leaching experiments were grouped into four figures, Figures 4-1 – 4-4, for comparing the variation between treatment type (MCA v. ACA v. UTW), the wood form (block v. sawdust), the duration (24 v. 72 hours), and the water chemistry (NaCl v. NaNO3 v. SPLP). The figures display the total amount of copper leached and the copper leached normalized to the surface area of the wood. In the case of the wood blocks, each block was measured prior to the experiment to determine the surface area, while 1 m^2 of surface area, the approximate area measured for each wood type, was used for each gram of sawdust. For easier comparison, the average and standard deviation of the SPLP leachate results are summarized in Table 4-1. This example was typical of all the results.

Figure 4-1: Leaching Experiment: 24-Hour Wood Block Leachate Fractionation.

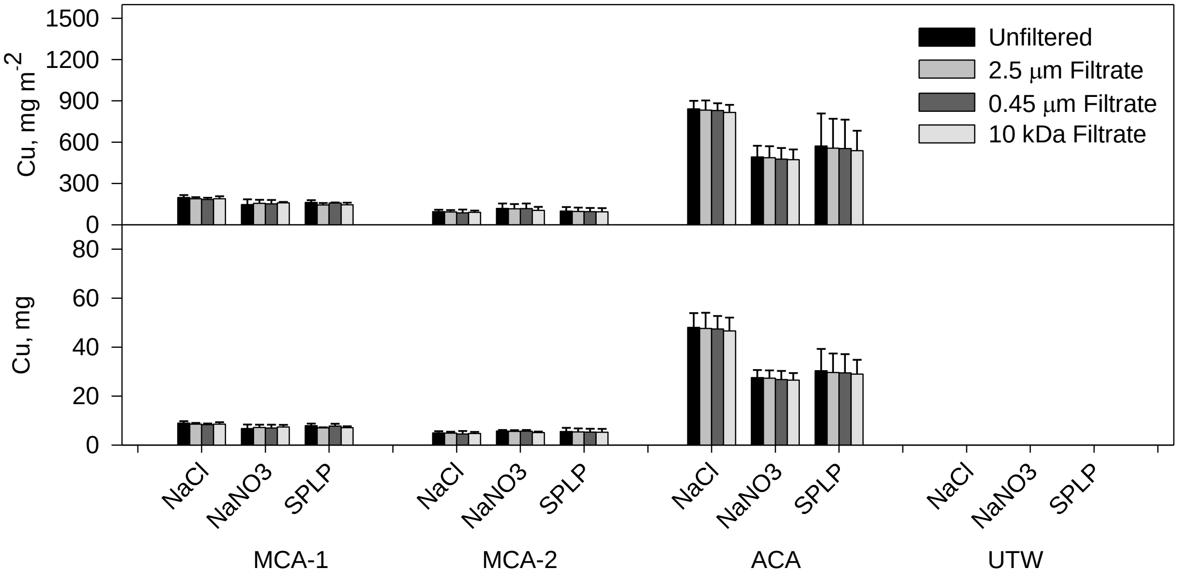


Figure 4-2: Leaching Experiment: 72-Hour Wood Block Leachate Fractionation.

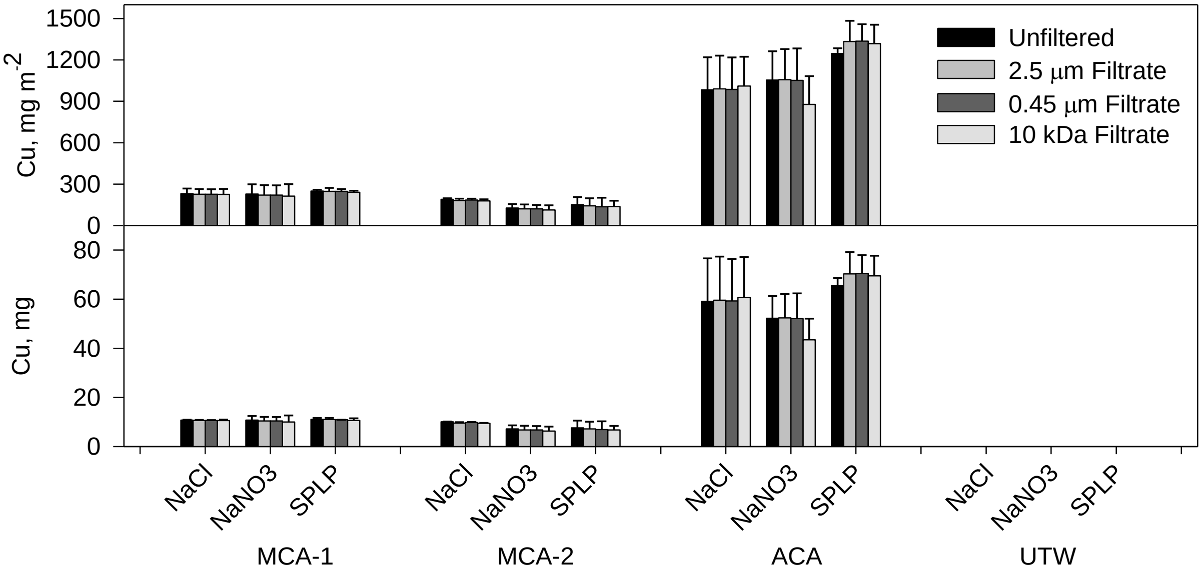


Figure 4-3: Leaching Experiment: 24-Hour Sawdust Leachate Fractionation.

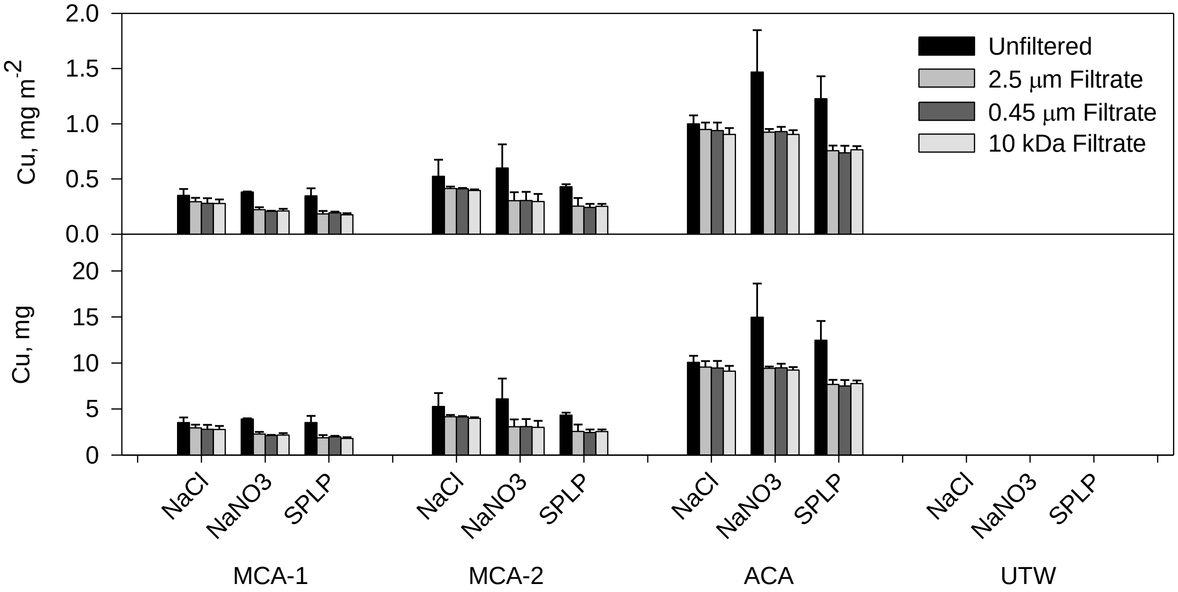
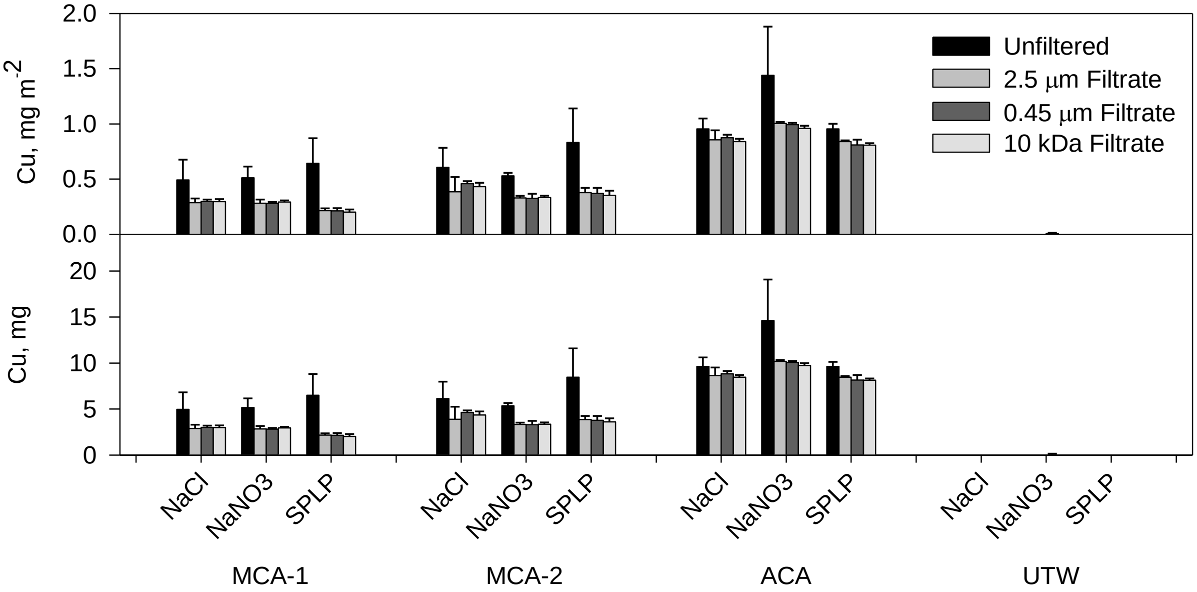


Figure 4-4: Leaching Experiment: 72-Hour Sawdust Leachate Fractionation.



The figures show that the ACA released significantly more copper than the MCAs over all the conditions tested while MCA-1 released slightly more copper than MCA-2 and the UTW released no copper. These results are expected, since the ionized copper formulation (ACA) has a higher copper concentration than the micronized formulations and is known to leach copper significantly. The increase in the quantity of copper released from MCA-1 compared with MCA-2 is likely related to the copper speciation initially present in the wood. Based on the LCF of the XANES data, 58% of the copper present in MCA-1 is organically complexed compared to only 12% in MCA-2. The increased quantity of organically complexed copper would likely result in increased leaching of copper from the wood. The observed differences are consistent with results published in the literature as well. Using lab treated specimens, Kartal et al. (2009) tested specimens that had been treated with both copper sulfate (ionized) as well as a nanocopper formulation. They found a negligible amount of copper was released from the nanocopper treated wood while seeing over 20% released from the copper sulfate treated wood.

Table 4-1: Summary of Leaching Results with SPLP Water Chemistry.

PTL Type	Copper Measured in the Unfiltered Fraction After Leaching (mg (mg m^{-2}))			
	Wood Block		Sawdust	
	24 Hour	72 Hour	24 Hour	72 Hour
MCA-1	7.9 ± 0.8 (162 ± 16)	11.1 ± 0.5 (251 ± 8)	3.5 ± 0.7 (0.35 ± 0.07)	6.5 ± 2.3 (0.64 ± 0.22)
MCA-2	5.5 ± 1.5 (99 ± 30)	7.6 ± 3.0 (151 ± 55)	4.3 ± 0.3 (0.43 ± 0.02)	8.5 + 3.1 (0.83 ± 0.31)
ACA	30.3 ± 9.0 (571 ± 237)	65.6 ± 3.0 (1246 ± 39)	12.5 ± 2.1 (1.23 ± 0.20)	9.6 + 0.5 (0.96 ± 0.05)

The wood blocks leached more copper into solution than the sawdust, a result that is somewhat counterintuitive. A possible explanation involves the re-adsorption of copper by the wood particulates. The surface area of the sawdust was roughly 1 m^2 g^{-1}; equaling 1 m^2 in each sample (1 g of sawdust per sample) the average surface area for the 10 g wood blocks was 4.28*10^{-3} m^2, three orders of magnitude less. The high affinity of copper for organic material combined with the large surface area of the sawdust results increase adsorption of copper and a subsequent decrease in the solution concentration of copper.

Solution chemistries had little effect on the quantity of copper released. There was no noticeable difference between the three solution chemistries tested for the MCAs. While there was a difference in the ACA results for the 24-hour duration, the differences were not observed in the 72-hour test and the variability of the ACA results in general make it difficult to draw any definitive conclusions. The duration of the experiment affected the amount of copper released from the wood blocks, but not the sawdust. For example, the ACA wood block increased from 500-800 mg m^{-2} at 24 hours up to 1000-1300 mg m^{-2} at 72 hours, while the sawdust stayed constant between 1 and 1.5 mg m^{-2}. The increase indicates that 24 hours is not long enough for the leaching to reach steady-state for the wood blocks, but it is sufficient for the sawdust. The leaching from the wood blocks would likely be controlled by the migration of the copper to the surface, where it then would be released into the liquid phase. The significantly larger surface area and smaller particle size of the sawdust would remove any need for migration through the wood, allowing for the direct transition of the copper into the liquid phase.

Each of the leachates was filtered to fractionate the solution, as described in Section 2.1. By separating the different size ranges (above 2.5 μm, between 2.5 μm and 0.45 μm, between 0.45 μm and 10 kDa, and below 10 kDa), some conclusions can be drawn about the type of copper released and whether it is free in solution or attached to cellulose. There was very little difference in the solution copper concentrations between the 4 fractionated solutions (No filtration, 2.5 μm, 0.45 μm, and 10 kDa), indicating the majority of the leached copper passed through all three filters. In order to pass the 10 kDa filter, the copper would have to be in an ionic form because any micronized or nanoparticle copper above ~3 nm would have been retained. The lack of particulate copper likely means that when the copper is released or very soon after it is released, it dissolves and does not persist as a particle. This conclusion is important since the environmental fate of copper micro/nanoparticles is currently not well understood and could be potentially harmful. The fate, exposure routes, and toxicity of ionic copper is better understood (Forest Products Laboratory, 2000). The environmental impact is discussed in more detail in Section 4.4 of this report.

4.2 Mass Balance

The release of copper through leaching discussed above pertained to the amount of copper measured in the liquid filtrates. As can been seen in the figures, the deviation in the results make it difficult to see small differences between the different fractions. Micro/nano-copper may be present, but in amounts too small to be distinguished from the solutions. During the filtration process, the filter membranes were collected and analyzed, allowing for the amount of copper in the particulates to be determined and a mass balance to be performed. The mass balance was only performed on the wood block conditions. It was not practical for the sawdust conditions because of the large amount of sawdust collected during filtration on the 2.5 μm filter papers.

Table 4-2 shows the results of the mass balance. The table displays the total amount of copper released and the ionic fraction, both taken from the solution concentrations; the particulate copper released, determined from the amount of copper retained on all three filter papers; and the filtration recovery, determined from the ionic fraction and the particulate copper compared to the total released. The copper in the particulates could be in a number of forms: ionic copper attached to cellulose fibers, micro/nanoparticle copper attached to cellulose fibers, or free micro/nanoparticle particles. For the MCA samples, roughly 2-6% of the copper released is attached in some way to a particle and was retained during filtration.

Table 4-2: Mass Balance of Copper Released from Wood Blocks during Leaching.

Duration (hr)	Solution Chemistry	Total Released (mg)	Ionic Released		Particulate Released		Filtration Recovery (%)
			mg	%	mg	%	
			MCA-1				
24	NaCl	0.90	0.86	95	0.04	4.8	100
	NaNO3	0.67	0.74	110	0.02	3.6	113
	SPLP	0.79	0.71	89	0.05	6.3	96
72	NaCl	1.08	1.06	98	0.02	1.6	100
	NaNO3	1.08	0.99	92	0.04	4.1	96
	SPLP	1.11	1.06	96	0.07	6.3	102
			MCA-2				
24	NaCl	0.49	0.47	95	0.02	4.9	100
	NaNO3	0.57	0.51	89	0.02	3.6	93
	SPLP	0.55	0.52	95	0.03	5.2	100
72	NaCl	1.00	0.95	94	0.03	2.9	97
	NaNO3	0.71	0.63	89	0.03	4.5	93
	SPLP	0.76	0.67	89	0.05	6.0	95
			ACA				
24	NaCl	4.81	4.66	97	0.06	1.2	98
	NaNO3	2.76	2.66	96	0.03	1.2	98
	SPLP	3.03	2.90	96	0.07	2.4	98
72	NaCl	5.92	6.07	103	0.08	1.3	104
	NaNO3	5.22	4.34	83	0.09	1.7	85
	SPLP	6.56	6.95	106	0.12	1.8	108

Table 4-3 provides a breakdown of the released copper contained within each size range. The majority of the copper was found in the material retained on the 2.5 μm filter, between ~1-5% of the total copper released from the MCA and ACA samples. Between 0.5% and 1% was retained on the 0.45 μm filter while 0.1%-0.3% was retained on the 10 kDa filter. The majority of the copper carbonate present in the MCA-1 and 2 samples was significantly smaller than 2.5 μm and, since most of the copper was retained on the 2.5 μm filter, it is likely associated with cellulose particulates and not as free particles. The quantities of copper found in the smaller two fractions do indicate that a small amount of micro/nanocopper could be released. The results of the speciation analysis, Section 4.3, expand upon these results and identify the form of copper present.

Table 4-3: Particulate Copper Released and Copper Associated with Each Filtration Fraction.

Duration (hr)	Solution Chemistry	Particulate Released		>2.5 µm	>0.45 µm	>10 kDa
		mg	%	%	%	%
			MCA-1			
24	NaCl	0.04	4.8	3.9	0.8	0.1
	NaNO3	0.02	3.6	2.9	0.5	0.2
	SPLP	0.05	6.3	5.2	1.0	0.1
72	NaCl	0.02	1.6	0.9	0.6	0.1
	NaNO3	0.04	4.1	3.4	0.6	0.2
	SPLP	0.07	6.3	5.4	0.7	0.1
			MCA-2			
24	NaCl	0.02	4.9	4.1	0.7	0.1
	NaNO3	0.02	3.6	2.7	0.8	0.1
	SPLP	0.03	5.2	4.1	1.0	0.1
72	NaCl	0.03	2.9	2.1	0.7	0.1
	NaNO3	0.03	4.5	3.7	0.6	0.2
	SPLP	0.05	6.0	5.1	0.8	0.1
			ACA			
24	NaCl	0.06	1.2	0.8	0.3	0.1
	NaNO3	0.03	1.2	0.8	0.3	0.1
	SPLP	0.07	2.4	1.9	0.4	0.1
72	NaCl	0.08	1.3	0.9	0.3	0.1
	NaNO3	0.09	1.7	1.3	0.3	0.1
	SPLP	0.12	1.8	1.4	0.4	0.1

4.3 Copper Speciation

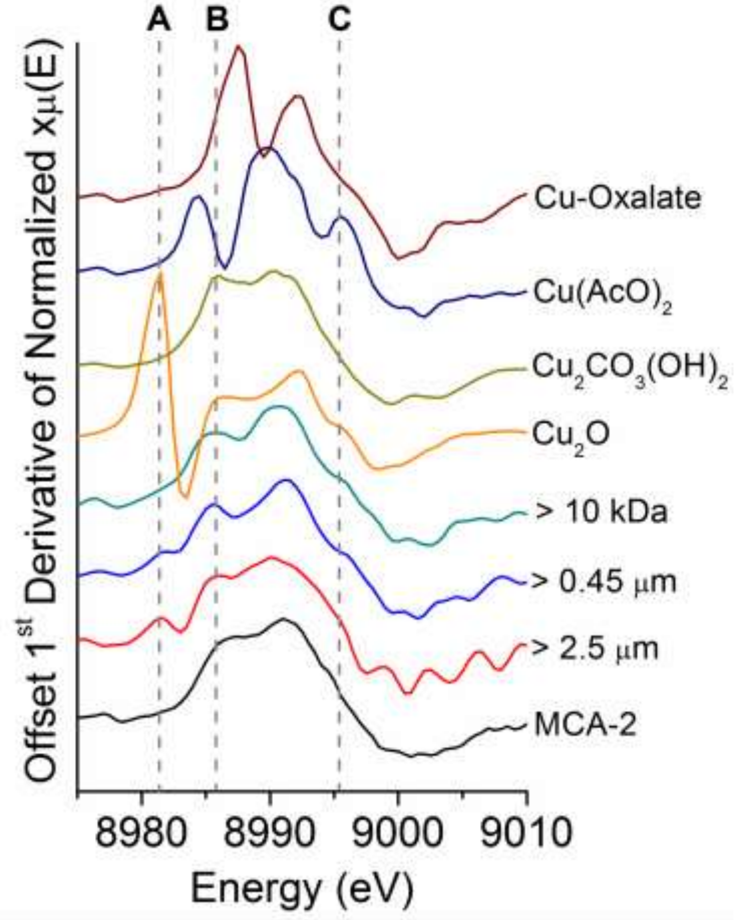
4.3.1 X-ray Absorption Fine Structure Spectroscopy

The mass balance data indicates that only a small fraction of the total copper released was associated with the solid phase. The speciation of the copper retained by the filters was determined using Cu K-edge XAFS spectroscopy. XAFS data was collected from the materials that were retained on the three different filters (2.5 µm, 0.45 µm, and 10 kDa). For the current discussion, >2500 nm refers to the solid phases that were retained on the 2.5 µm filter after filtration. Subsequently, >450 nm refers to the solids that passed through the 2.5 µm filter but were retained on the 0.45 µm filter, and finally >~3 nm refers to materials that that passed through the 0.45 µm filter but were retained by the 10 kDa filter, which is approximately a 3 nm membrane. The previous Copper Release and Mass Balance sections, 4.1 and 4.2, respectively, indicated that there was little difference in the total quantity of Cu released as a function of the leaching solution chemistry. Due to the similarity in the total ion and particulate Cu released from the lumber, the speciation analysis focuses on changes in Cu speciation for wood blocks that were leached with the SPLP solution for 72 h. The SPLP solution was chosen because of its use as an analogue for precipitation, and almost all pressure-treated wood surfaces are exposed to precipitation. The wood blocks were chosen over the sawdust samples for speciation analysis for two reasons. First, solid wood surfaces are the only pressure-treated surface found in the built environment aside from the sawdust generated during construction. Second, in order to fully understand the potential materials that could be leached from a pressure-treated wood surface it was important to capture the fraction that would be retained by the 2.5 μm filter. With the sawdust, as discussed previously, it is impossible to differentiate between materials released from the sawdust and the sawdust itself with respect to materials retained by the 2.5 μm filter.

The MCA-2 first derivative XANES spectra for the original material and the solid phases retained by the filters is presented in Figure 4-5 along with four reference compounds as an example for all three wood types. The reference compounds chosen were based on known copper phases that would be present (copper carbonate and copper complexed with organic materials) and the similarity in spectral shape with the samples (Cu_2O). Other copper organic complexes were investigated as potential analogues for copper complexed with organics including sulfur and amine enriched compounds. However, the Cu carboxylate complexes exhibited the most similarity to the solid phases retained on the filters. In additional to additional organic phases, other potential inorganic copper phases were compared to the sample spectra, but there were either no or limited similarities.

Visual inspection of the XANES spectra reveals substantial changes in the Cu speciation for each size fraction compared with the original material (Figure 4-5). The presence of a Cu^{1+} species is immediately evident in the > 2500 and > 450 nm fractions as evidenced by the derivative peak present and its coincidence with the first derivative peak of Cu_2O (Line A). The presence and relative abundance of copper carbonate in the samples is evidenced by the presence and shape of the derivative peak shoulder near 8986 eV (Line B). A well-defined derivative peak shoulder present near Line B indicates minimal presence of Cu complexed with organic carboxylate functional groups. The shoulder would be absent or broad if Cu complexed organic carboxylate groups were present due to the presence of strong derivative peaks present in the Cu-Oxalate and Cu-Acetate complexes. The presence of organically complexed copper is evident by derivative peak near 8983 or 8987 eV (derivative peak locations for Cu-Acetate and Cu-Oxalate complexes) and the presence of a well-defined peak or shoulder in the derivative spectra near the area highlighted by Line C. All four of the MCA-2 sample spectra presented exhibit features associated with the reference compounds. The same trends (presence of Cu^{1+} (Line A), well defined copper carbonate shoulder (Line B), and strong shoulder/peak near 8995 eV (Line C)) were present in the other two wood samples—MCA-1 and ACA (data not shown).

Figure 4-5: First derivative Cu Kα XANES spectra for the materials retained on the filter papers after sequential filtration of the supernatant from a sample of MCA-2 lumber leached with SPLP solution for 72 h. A) Indicates the position of the Cu^{1+} first derivative peak, B) indicates the low energy shoulder of copper carbonate ($Cu_2CO_3(OH)_2$) first derivative peak, and C) indicates a first derivative shoulder and peak position for copper complexed with organic acids.



In order to determine the relative abundance of each phase present in the samples, LCF analysis of the first derivative of the XANES spectra was conducted for each wood type and sample fraction (Table 4-2 and Figure 4-6). In addition to the copper speciation, the surface normalized concentration of copper particulates is presented in Table 4-2. Copper(I) oxide was identified in all three of the pressure-treated samples for the >2500 and >450 nm fractions. The mechanism responsible for the copper reduction is unclear, but previous research has demonstrated that organic matter can reduce copper (II) to (I) under oxidizing conditions (Leal and Van Den Berg, 1998; Fulda *et al.*, 2013). In previous research, 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 malachite. The total mass of copper retained by the three membranes for the different wood types did not exceed 30 mg m^{-2}, of which Cu(I) made up no more than 20% of the total copper present.

There were notable changes in the speciation of copper retained by the membranes and the as-purchased materials. For the ACA wood there was a decrease in the total organically complexed copper and an increase in the aqueous copper from the >2500 to >~3 nm. The aqueous copper species is most likely related to copper that is loosely bound to the organic fraction. Changes in the speciation of copper retained on the membranes for the two micronized treated samples differed. For MCA-1 there was an increase in the abundance of copper carbonate with smaller size fractions, while the reverse was true for MCA-2. The LCF results for MCA-1 would seem to indicate that copper carbonate may exist in solution as free particles since there is an increase in the abundance of material with smaller size fractions. However, a similar argument may be made for the opposite based on the MCA-2 results. If there was a strong association of copper carbonate with wood fibers then there would a decrease in the relative abundance copper carbonate in the smaller size fraction.

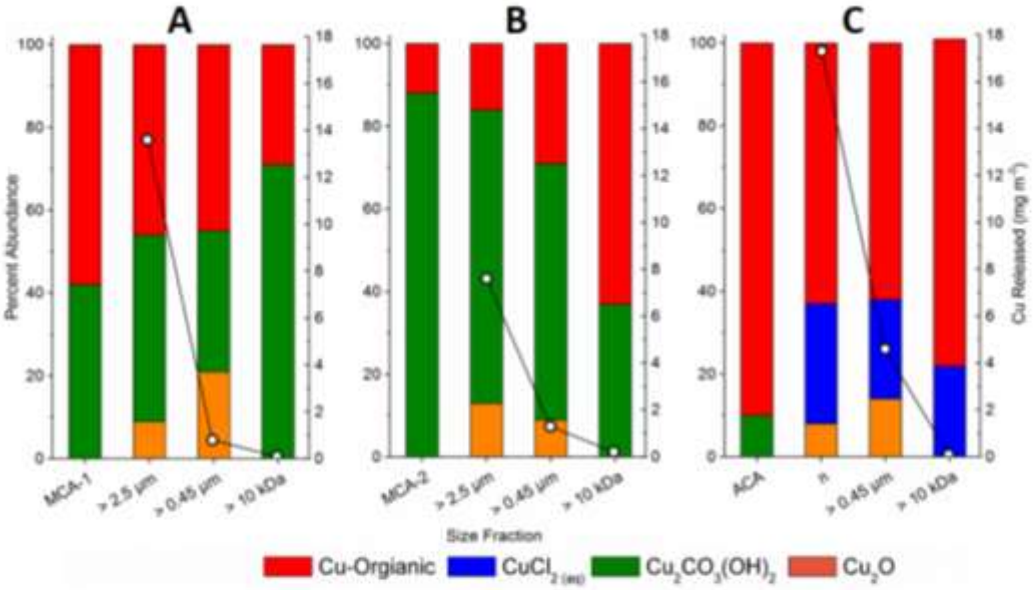
Table 4-4: Copper speciation (percent abundance) and mass of cooper leached from wood blocks leached with the SPLP solution for 72 h as a function of filter particle cutoff. Data presented is the relative abundance of each copper phase that was retained on the filter paper after sequential filtration of the supernatant. Unleached refers to the as-purchased materials.

Copper Species	**Wood Type**			
	Unleached	**> 2.5 μm**	**> 0.45 μm**	**> 10 kDa**
	MCA-1			
Cu Released (mg (mg m^{-2}))		*5.4 (13.6)*	*0.8 (1.9)*	*0.1 (0.3)*
Cu_2O		9%	23%	
$Cu_2CO_3(OH)_2$	42%	45%	34%	71%
$CuCl_{2\ (aq)}$				
Cu-Organic*	58%	46%	45%	29%
	MCA-2			
Cu Released (mg (mg m^{-2}))		*5.0 (7.6)*	*0.8 (1.3)*	*0.1 (0.2)*
Cu_2O		13%	9%	
$Cu_2CO_3(OH)_2$	88%	71%	62%	37%
$CuCl_{2\ (aq)}$				
Cu-Organic*	12%	16%	29%	63%
	ACA			
Cu Released (mg (mg m^{-2}))		*1.4 (17.3)*	*0.4 (4.6)*	*0.1 (0.9)*
Cu_2O		8%	14%	
$Cu_2CO_3(OH)_2$	10%			
$CuCl_{2\ (aq)}$		29%	24%	22%
Cu-Organic*	90%	63%	62%	78%

*The summation of Cu-Acetate and Cu-Oxalate

Figure 4-6: Copper speciation and mass of cooper leached from wood blocks leached with the SPLP solution for 72 h as a function of filter particle cutoff. Data presented is the relative abundance of each copper phase that was retained on the filter paper after sequential filtration of the supernatant

and the mass per unit area of copper that was leached from the lumber. The first column in each graph refers to the original copper species distribution in the as-purchased materials.



4.3.2 Microscopy

SEM images for the materials that were retained on the 2.5 µm, 0.45 µm and 10 kDa filter membranes for wood blocks leached for 72 h in the SPLP solution are presented in Figures 4-7, 8, and 9. In the BSE SEM images, the brighter objects are the copper particles present in the samples. The 2.5 and 0.45 µm membranes were Whatman® Nuclepore® Polycarbonate Track Etched membranes. These membranes have a smooth surface and are designed for environmental sample collection and subsequent microscopy analysis. The larger particle present in the images do not resemble the SEM micrographs provided by the manufacturer, indicating the particles must be bound/associated with cellulose that was dislodged from the wood surface during leaching. Based on the small number of particles identified, it was not possible to determine an average particle size for the copper carbonate. The difference in the scale bars between Figures 4-7 and 8 indicate that smaller copper carbonate particles were present on the 0.45 µm membrane compared with the 2.5 µm. While all of the particles imaged are associated with cellulose, the enrichment of smaller particles retained on the 0.45 µm filter would suggest that copper carbonate may exist as free particle/aggregate in solution. Analysis of the 10 kDa filters resulted in finding a single aggregate of copper particles for the MCA-2 sample (Figure 4-9). The very low concentration of copper present made it extremely difficult to isolate particles. Unlike the images for the 2.5 and 0.45 mm fraction, the particles are not well defined making it difficult to visually distinguish individual particles. The overall aggregate is several microns in size indicating that the aggregation of the materials likely occurred after filtration.

Figure 4-7: BSE SEM Micrographs of particulates retained on a 2.5 μm membrane (A) MCA-1 and (B) MCA-2. The white square outline indicates the location of where EDX spectra were collected to determine elemental composition of the particles.

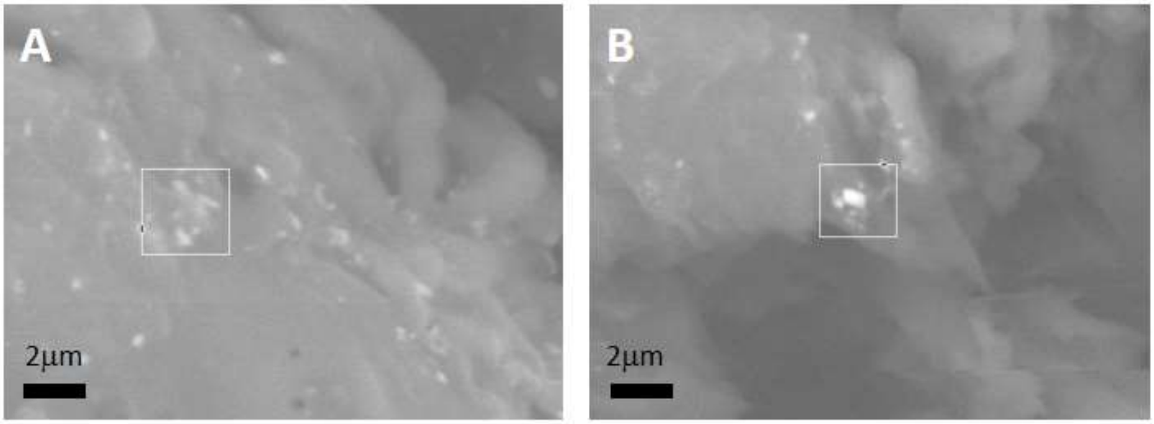


Figure 4-8 BSE SEM Micrographs and EDX chemical maps of particulates retained on a 0.45 mm membrane (A) MCA-1, (B) EDX copper map, (C) MCA-2, (D) EDX copper map.

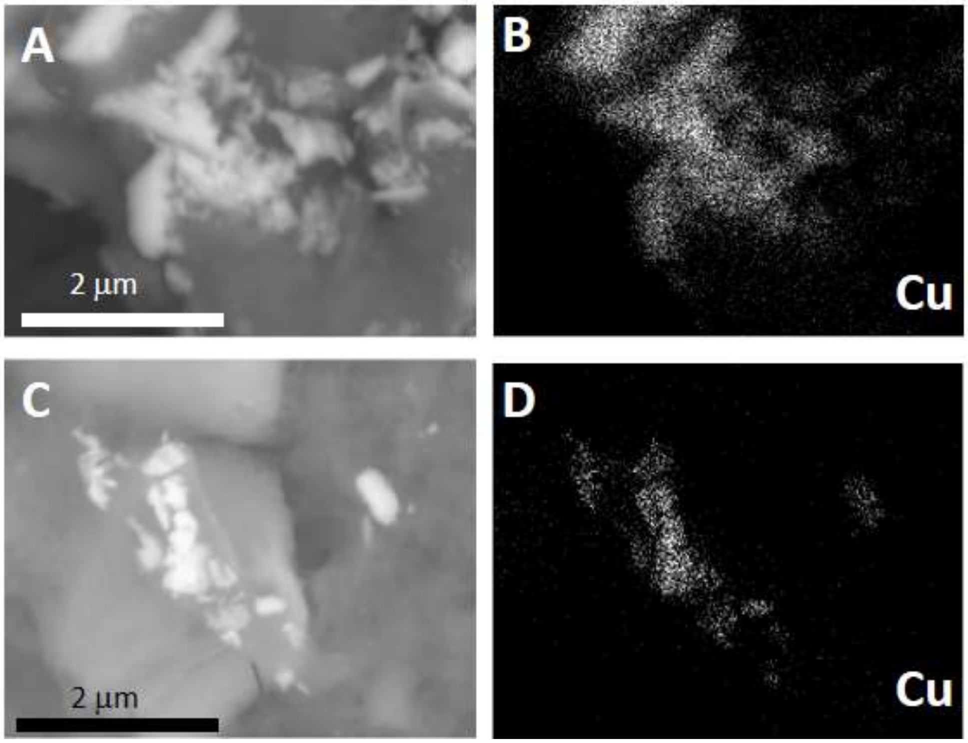
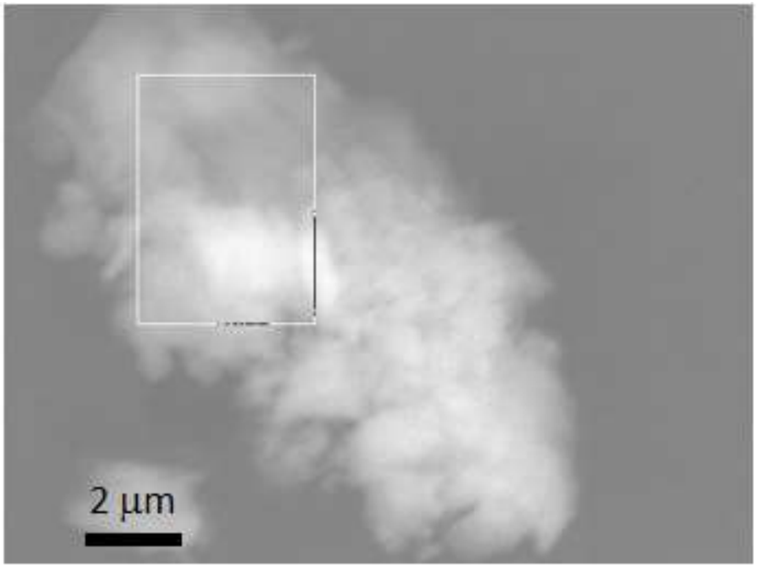


Figure 4-9 BSE SEM Micrographs of particulates retained on a 10 kDa membrane from the MCA-2 sample.



4.4 Environmental Impact

The leaching results show that there is no significant release of copper micro/nanoparticles into the environment, but that copper is released by contact with water. However, the results cannot be used directly for predicting the MCA's environmental impact. The size of the specimens, mainly the wood blocks, leads to accelerated leaching and does not adequately reflect an in-situ release of copper (Forest Products Laboratory, 2000).

MCA is relatively new and studies of copper release into the environment near structures built with it are not available. Studies on ACA have been performed, allowing for the ACA results in this study to provide a point of comparison. Since the MCA wood has significantly less copper and released much less copper during testing than ACA, the release of copper into the environment can be assumed to show a similar trend.

A study by the Forest Service of a boardwalk created with ACA assessed the impact of the release of copper on the flora in the localized area around the boardwalk. The ACA used was rated for ground contact and had a very high concentration of copper (7.0-8.2 kg m^{-3} (0.44-0.51 lb ft^{-3})), significantly higher than the ACA (1.77 kg m^{-3} (0.11 lb ft^{-3})) and MCA (0.8 kg m^{-3} (0.05 lb ft^{-3})) used in the current study. Despite the high concentration, the study found no significant impact on the local environment. High concentrations of copper (373 ppm compared to a baseline of 30 ppm) were found immediately next to the wood and it was shown to be migrating into the soil after 6-12 months, but no drop in the soil microbial flora was seen (Forest Products Laboratory, 2000). This suggests that the MCA, when factoring in the leaching results and comparing to the ACA, would release less copper.

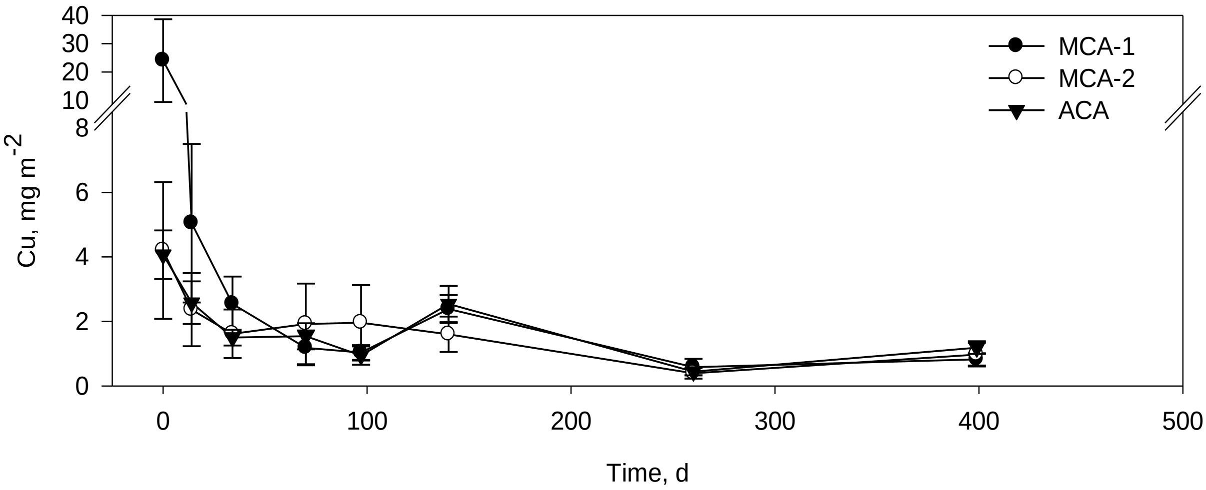
The above discussion focuses on the total ionic copper released and does not consider the impact of the micronized copper on the environment. Currently, data is not available in the literature on the impact of micronized copper on the environment. The results indicate the potential for a small fraction of particulate copper to be released, though the significance of the amount is unknown. Given the current data set, it is not possible to determine that exact form of copper carbonate leached from the wood: bound to cellulose, isolated particles/aggregates in solution, or a combination of the two. The importance of the question is related to the potential transport of the materials and exposure dose. If the copper carbonate is bound to the cellulose, than any potential transport will be limited by the size of the cellulose fragment. However, if copper carbonate exists as a free particle/aggregate in solution then transport and exposure will be governed by the size of the particle.

5 Wipe Experiment

5.1 Copper Release

The wipe experiment was conducted in three parts. First, a set of boards that did not undergo any surface alteration or exposure were samples to establish a baseline for comparisons with the two treatments to determine the net effect of weathering on the release of copper. Second, a set of boards was left outdoors to undergo natural weathering and finally, a third set of boards was artificially weathered through freeze and thaw cycles. Results from the ICP analysis were determined as a concentration, which was then converted to total mass of copper released, and then normalized to the copper released per square meter. The results from the Outdoor and Freeze/Thaw tests are shown in Figures 5-1 and 5-2.

Figure 5-1: Copper Released by Wiping - Outdoor Weathering.

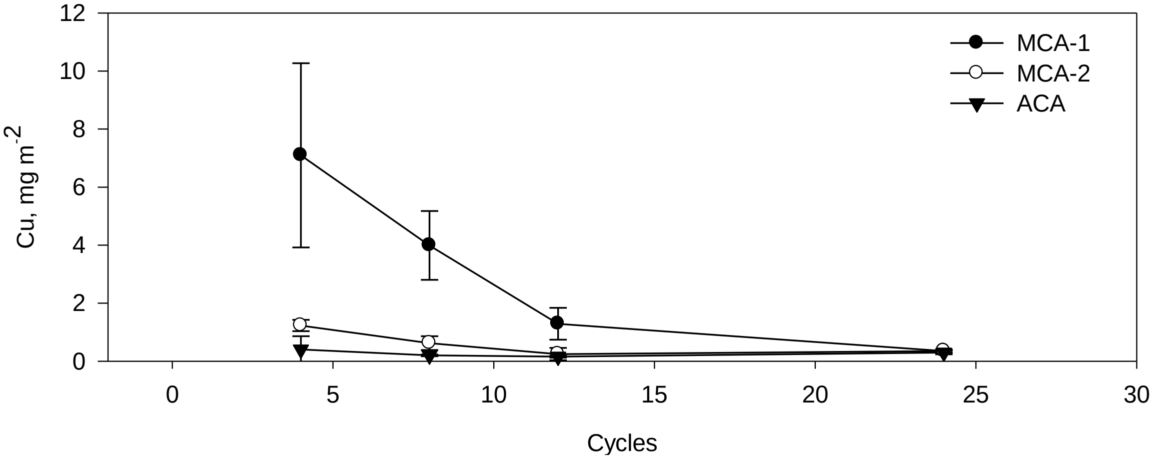


The Outdoor experiment results indicate a large initial release of copper that stabilizes over time. The initial quantity of copper released was variable within each type of wood, particularly for MCA-1, and is likely due to manufacturing techniques and pressure-treating formulations as well as natural variations in the wood material. There was very little difference between the release of copper from the MCA-2 and ACA. MCA-1 was significantly higher than the others initially, but stabilized at a similar concentration after the Day 14 sampling event. After the day 34 sampling event (the 3rd sampling), the average copper released for each wipe event (Table 5-1) was ~1.5 mg m^{-2}.

The Freeze/Thaw experiment results show a similar trend. As stated above, the boards were not sampled at 0 cycles. The amount of copper released decreased after the first two sampling events and stabilized below 1 mg m^{-2} (Table 5-1). Again, the MCA-1 wood had a much higher initial concentration, which eventually fell to a concentration similar to the other two wood types. The MCA-2 and ACA woods showed very little difference in copper release.

The cycles of freezing and thawing were anticipated to have a destructive effect on the wood due to expansion and contraction. However, no visible effect could be seen on the wood and the copper release results suggest very little deterioration occurred. By comparison, the Outdoor boards were expected to have very little copper on the surface, most having been washed away by the weathering. Visually, the boards were heavily cracked and faded and the initial green hue associated with the material was absent. Despite the visual and weathering differences, the release of copper was very similar between the two. To investigate, the third test was conducted on fresh boards with no weathering. The goal was to determine if the copper transfer was related to the number of times the boards were wiped or weathering conditions. The results, Figure 5-3, are consistent with the Outdoor and Freeze/Thaw experiments, decreasing copper concentration with successive sampling events and the concentration of copper released from the wood stabilized after 3-4 sampling events for all three tests.

Figure 5-2: Copper Released by Wiping - Freeze/Thaw Weathering.



While the trend is the same, the amount of copper released is slightly different between the wood types. Figure 5-3 and Table 5-1 shows that the MCA-1 wood released approximately the same amount in all three tests. The MCA-2 and ACA released more copper in the Outdoor experiment than the other two, possibly indicating the additional weathering destabilizes copper in the wood products.

Thomas et al. (2004) found a similar result when performing wipe tests for arsenic on CCA wood. They examined the amount of arsenic transferred with each wipe cycle (one back and forth motion) and found it to decrease with each additional cycle, approaching a plateau after 3-4 cycles. They concluded that a hand would become saturated, preventing further transfer, or the amount of available arsenic was depleted from the surface. They concluded that 10 cycles was optimum to reach equilibrium between the surface and the wipe, which is the basis for the method used in this study. Our results support the depletion of the available material on a larger scale, over multiple, successive wipe events.

Figure 5-3: Copper Released by Wiping - Weathering Comparison.

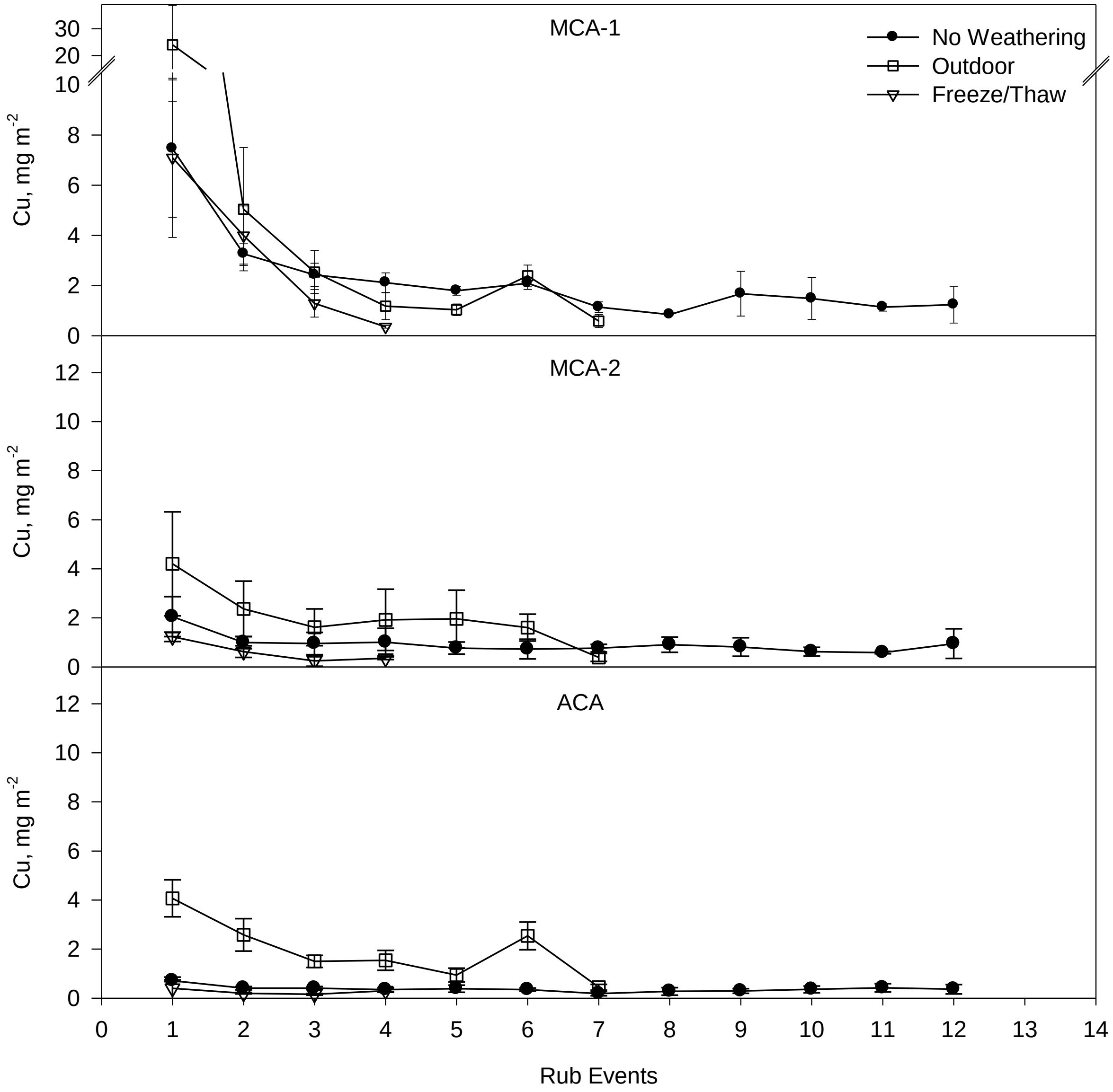


Table 5-1: Average Release of Copper During Wiping Experiments.

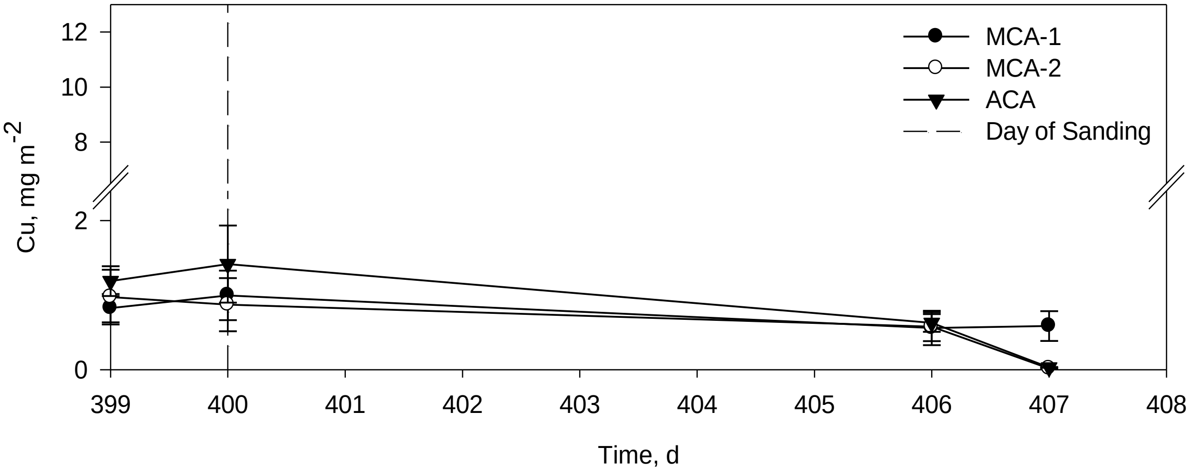
Weathering Experiment	Copper Released by PTL Type (mg m^{-2})			Period*
	MCA-1	MCA-2	ACA	
Outdoor	1.4 ± 0.8	1.4 ± 0.6	1.4 ± 0.7	Days 34 - 399
Freeze/Thaw	0.8 ± 0.6	0.3 ± 0.1	0.2 ± 0.1	Cycles 12 - 24
No Weathering	1.6 ± 0.5	0.8 ± 0.1	0.3 ± 0.1	Samplings 3 - 12

*Excludes the first two sampling events from each experiment (Day 0 and 14, 4 and 8 cycles, and samples 1 and 2 for the Outdoor, Freeze/Thaw, and No Weathering experiments, respectively).

The difference in the total quantity of copper released between the MCA-1, and MCA-2 and ACA is not immediately apparent. The speciation data of the as-purchased materials does not provide any specific insight into the differences in copper released, as the species of copper in the ACA and MCA-2 materials share similarities with MCA-1. It is difficult to attribute the increased initial released of copper to the presence of copper carbonate nanoparticles or copper organic complexes since MCA-2 is enriched in malachite and ACA is enriched in copper organic complexes. Copper form and formulation could play a role in the amount of copper released. Additional differences in the formulations, such as co-biocides or stabilization chemicals, could also affect how the copper migrates through the wood. Finally, the initial release may be a result of excess or residual pressure treatment solution remaining on the wood surface. Often residual materials are visible on the surface of the pressure-treated wood products in the market place.

After the day 399 sampling event for the Outdoor experiment, the boards were sanded to simulate surface wear and to determine if there would be a spike in the copper released. Figure 5-4 shows the day 399 sampling event followed by three other sampling events on day 400, 406, and 407. The sanding occurred on day 400, just before the samples were collected. Sanding resulted in almost no change in concentration, despite a visible change in the board where material had been removed. With the second and third sampling events there is a visual decrease in the total quantity of copper released in Figure 5-4. Two possible conclusions may be drawn from this exercise: 1) the copper is uniform enough in the depth of the board that sanding/surface wear does not impact copper release or 2) the sanding method was not sufficient to remove the top layer of weathered wood material. Further work is required to determine and clarify this result, most likely involving complete sanding of the board surface to restore it to an original, pristine appearance.

Figure 5-4: Copper Released by Wiping - Outdoor Weathering - After Sanding.

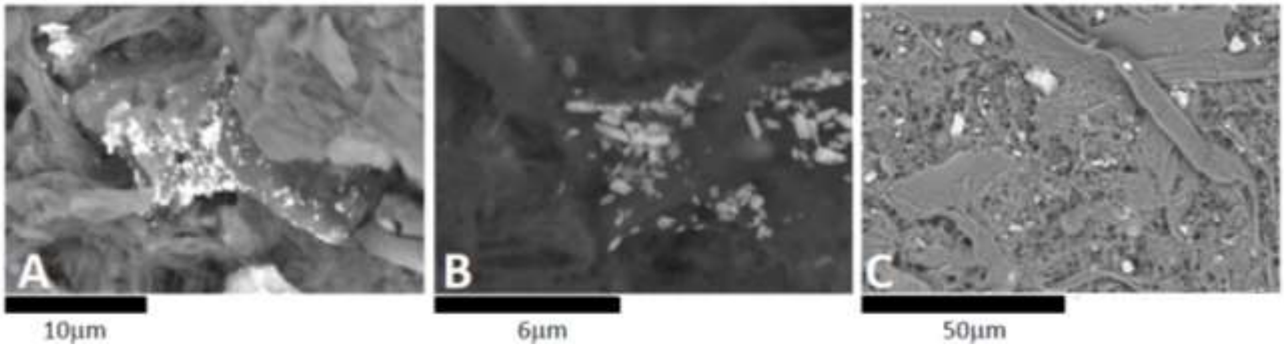


5.2 Copper Speciation

5.2.1 Microscopy

No particulates or materials associated with the lumber were identified on the 10 kDa filter papers. Particulates were identified during analysis, however the particle size was >5 µm indicating the materials were a result of contamination of the filter papers prior to analysis. SEM images of the 0.45 µm filter membranes from the one month wipe sample showed a wide variety of materials present for all three pressure-treated wood types (MCA-1, MCA-2, and ACA) (Figure 5-5).

Figure 5-5: SEM micrographs of materials collected on 0.45 μm filter papers. MCA-1 (A), MCA-2 (B), and ACA (C).



Particles enriched in silica aluminum, iron, and calcium were identified from EDS spectra. In Figure 5-5A and B the rhombohedral shapes were identified as copper carbonate, the active chemical compound in micronized copper pressure-treated lumber, based on crystallite shape and the EDS spectra (Figures 5-6 and 5-7). In the two micronized copper samples, copper carbonate was the predominant particle identified. Copper carbonate crystallites were not identified in the ACA sample. The cubic and non-spherical/irregular particles present in the ACA sample (Figure 5C) were identified as calcite and silica, respectively, based on crystallite shape and EDS spectra. For both MCA-1 and MCA-2, the copper carbonate present was aggregated in isolated locations (Figures 5-5A and B, 5-6, and 5-7). The crystallites were always associated with larger particles. This is especially evident for the MCA-1 micrograph (Figure 5-5A). As previously discussed, the Whatman® Nuclepore® Polycarbonate Track Etched 0.45 μm membranes have a smooth surface and are designed for sample collection and subsequent microscopy analysis. The larger particles present in the micrographs do not resemble the SEM micrographs provided by the manufacturer, indicating the particles are bound/associated with cellulose dislodged from the wood surface during sample collection. The micrographs in Figure 5-5 of MCA-1 and 2 are very similar in appearance to those published by Matsunga and Kiguchi (Matsunaga *et al.*, 2009) who evaluated the distribution of copper carbonate in pressure-treated lumber. 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. As previously discussed, the difference in particle size between MCA-1 and 2 is immediately evident when comparing the images in Figures 5-6 and 5-7. The average particle length, width, and aspect ratio were determined for copper carbonate present in both micronized copper treated samples (Figures 5-6 and 5-7 and Table 5-2). The histograms in Figures 5-6 and 5-7 highlight the skewed size distribution of the copper carbonate, similar to the plots for the as-purchased materials. In comparison with the as-purchased material, the particle size and aspect ratio are very similar. The differences in the particle sizes are likely due to different imaging methods, BSE SEM versus TEM. The similarity in the shape and size indicates that after one month of exposure outdoors, very little transformation of the copper carbonate occurred.

Figure 5-6: BSE SEM micrograph of MCA-1 (A), EDS map of Cu from the same sample (B), and histogram and cumulative abundance plots for particle length, width, and aspect ratio (length/width) (C).

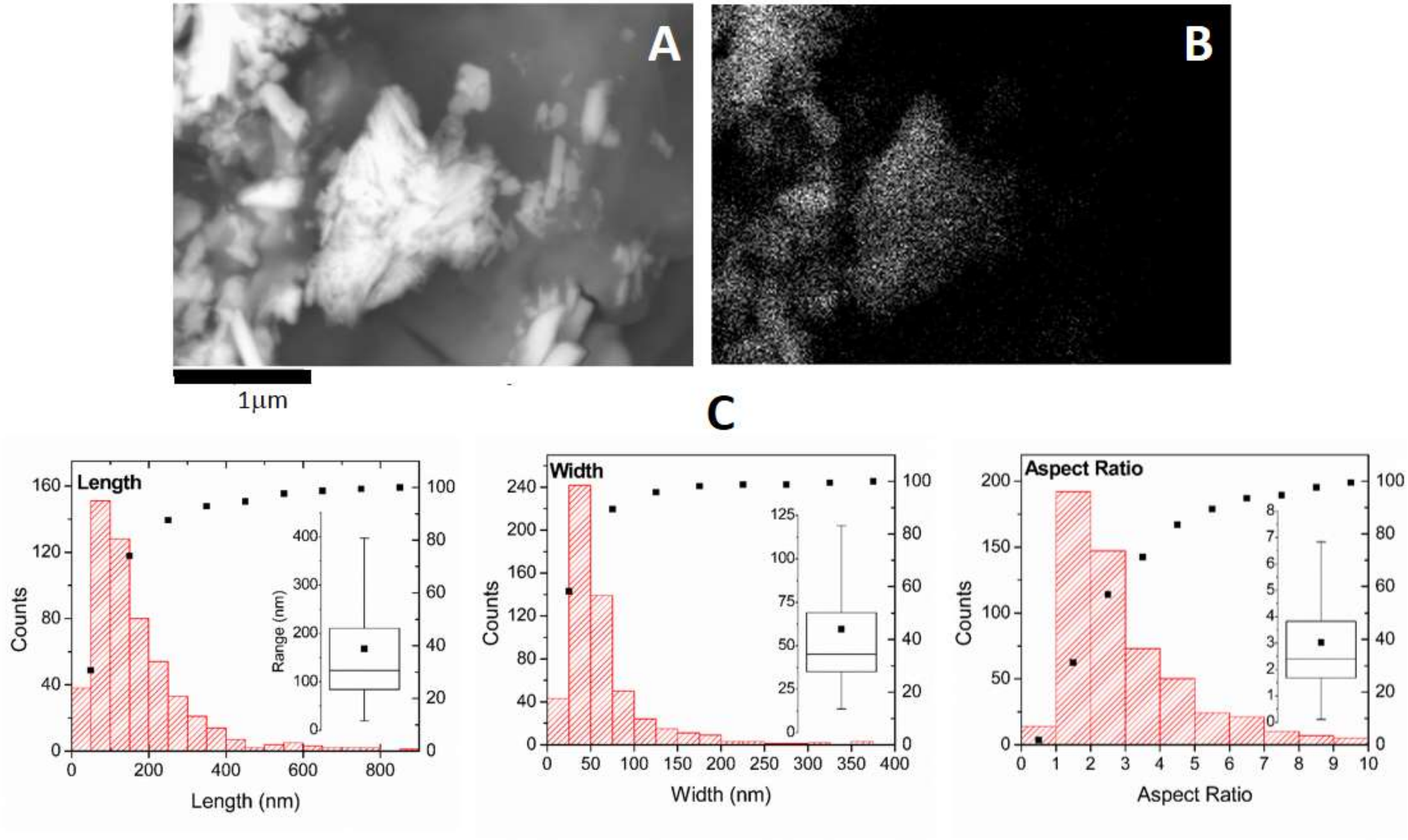


Figure 5-7 BSE SEM micrograph of MCA-2 (A), EDS map of Cu from the same sample (B), and histogram and cumulative abundance plots for particle length, width, and aspect ratio (length/width) (C).

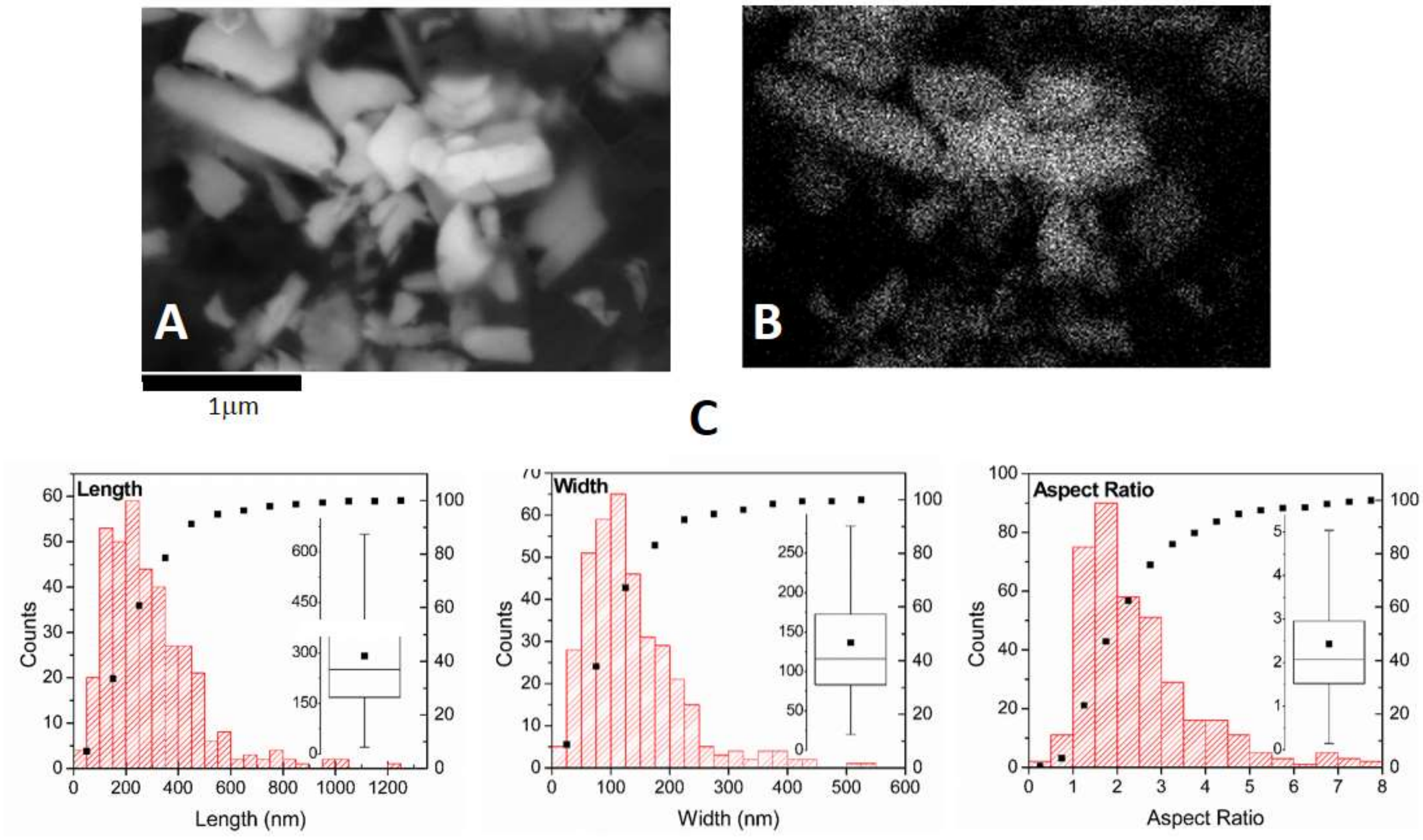


Table 5-2: Average particle size and aspect ratio of micronized copper particles dislodged from the wood surface after wiping with a polyester cloth as determined by analysis of BSE SEM micrographs. Previous data for the as-purchased pressure-treated lumber is presented for comparison. Aspect ratio is equal to the ratio between the particle length and width.

Wood Type	MCA-1		MCA-2	
	As-purchased	1 Month	As-purchased	1 Month
	Average/Standard Deviation			
Length	121/65	168/132	244/125	291/175
Width	56/42	65/52	105/58	136/83
Aspect	2.5/1.2	3.0/2.1	2.7/1.6	2.4/1.3
Number	314	537	370	378

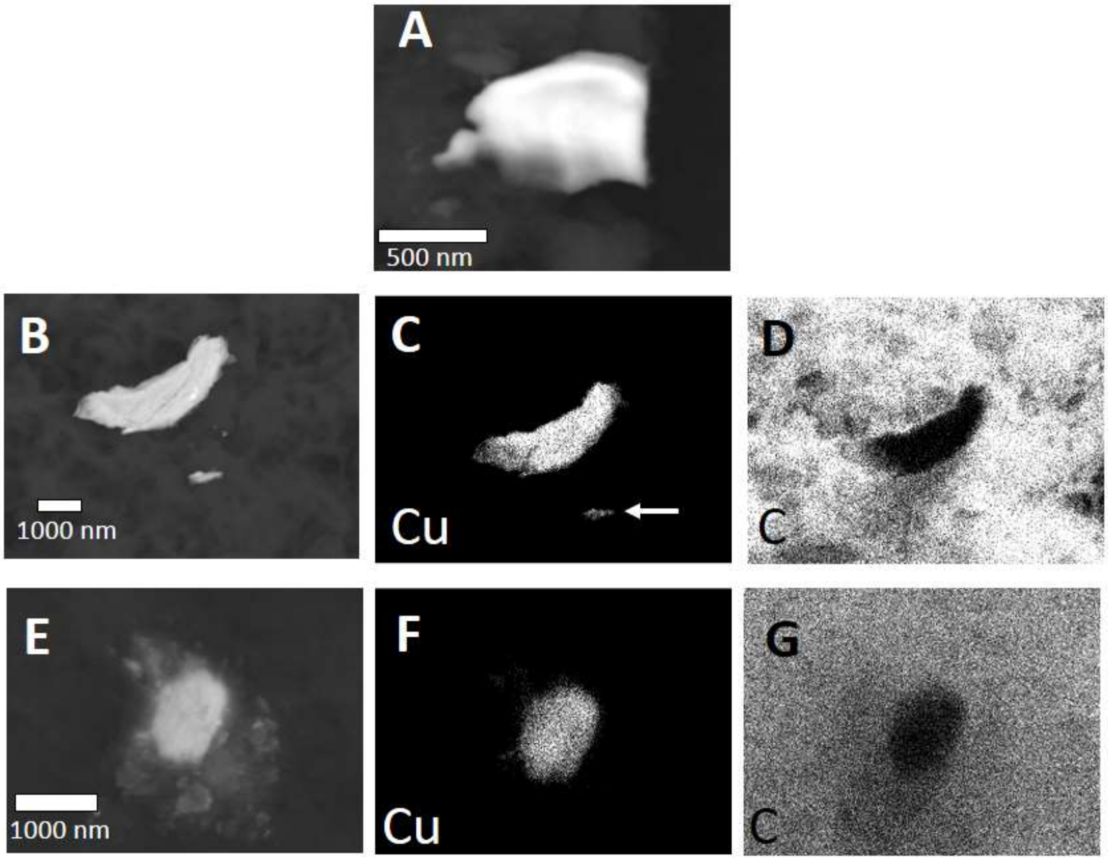
A second set of filters was analyzed after two months of exposure (Figure 5-8). As with the first set, there were no detectable particles associated with the wood matrix present on the 10 kDa filter papers. Copper particles were identified on the 0.45 μm filter papers. The relative abundance of particulates present was significantly less compared to the one-month sample. This is not unexpected given the reduction in the total copper that was dislodged from the surface (Figure 5-1). After the two-month time period the copper particulates collected were weathered/degraded (Figure 5-8). The well-defined rhombahedral crystals were degraded and it was no longer possible to identify or distinguish individual crystallites in the BSE images. A portion of the particulates present from the micronized copper treated lumber had also under gone changes in their chemical composition as evidenced in Figure 5-8C and D. The EDX maps of the chemical composition of the particles indicated there was no co-localization of Cu and C. The EDX map of O indicated co-localization of Cu and O ruling out the presence of a purely metallic Cu particle. Instead the images indicate that a portion of the malachite was transformed to either cuprite or tenorite (Cu_2O and CuO, respectively). The particle in Figure 5-8B appears to be a larger aggregate of smaller particles. However, it is not possible to rule out the possibility of changes in the surface morphology of a single crystal. It is important to note that not all of the copper carbonate was transformed to copper oxide. An example of this is evident by the arrow highlighting the particle in Figure 5-8C.

Copper particles were also identified in the ACA wood sample after two months of environmental exposure. It is difficult to determine if the particle in Figure 5-8E is a single crystal or an aggregate of smaller materials. As with the materials identified in MCA-2, there is evidence of a copper oxide particle. The number of Cu particulates identified in the ACA wood was less in comparison to the two micronized copper treated wood materials.

While not clearly visible in Figure 5-8, all of the copper particulates identified on the filter were associated with larger pieces of cellulose; again indicating that the copper particles are not present as individual particles, but associated with larger cellulose particles. As discussed in the leaching section there is evidence to support that copper is associated/bound to cellulosic materials and that copper carbonate exists as a free particle/aggregate. Identifying the species/form of copper is important when considering potential exposure pathways. From an inhalation perspective, the association of copper carbonate with cellulose will be integral in predicting whether penetration depth in the lung will be based on the particle size of the dislodged cellulose or the micronized copper particle size.

A third set of filters was collected after 3 months. However, however no copper particles were identified by SEM analysis.

Figure 5-8: 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 μm filter paper. MCA-1 (A), MCA-2 BSE micrograph and EDX maps (B, C, and D), respectively. ACA BSE micrograph and EDX maps (E, F and G), respectively.

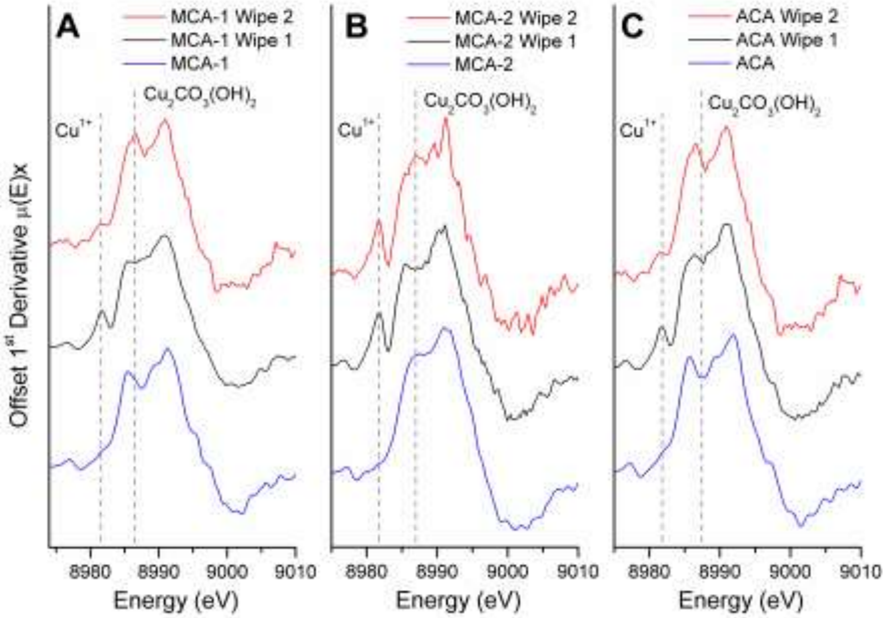


The change in particle size, shape, and chemistry with time is another important factor for risk assessment purposes. Based on the current data, the potential for exposure to micronized copper particulates from skin contact with the wood is greatly reduced after three months of environmental exposure. While the environmental conditions will vary, this data, in conjunction with the wipe results from the un-weathered lumber, suggests that particles in close proximity to the surface are readily dislodged. The strong correlation between copper particulates and cellulose would also indicate that migration of the malachite from within the wood structure to the surface is unlikely. Therefore a long term risk associated with the continued release of copper particles seems unlikely unless the surface is cleared of weathered materials exposing an un-weathered surface.

5.2.2 X-ray Absorption Fine Structure Spectroscopy (XAFS)

Copper speciation of the materials retained by the 0.45 μm and 10 kDa filters was assessed by XAFS. The concentration of copper retained by the 10 kDa filters was not sufficiently great enough to allow for a quantitative or even qualitative analysis of the XANES spectra. A copper edge was present, but it was not possible to further investigate the oxidation state or speciation of copper due to the poor signal to noise ratio. XANES spectra were obtained from the 0.45 μm filters for the 1 and 2-month wipe samples (Figure 5-9). Similar to the microscopy samples, after 2 months the total quantity of Cu retained on the 0.45 μm filters was not large enough to collect useful XAFS data. The 1 and 2-month spectra are presented with the XANES spectra from the as-purchased materials for comparison. The quality of the spectra for the two wipes is reduced compared to the original material and is a function of the total copper present. Hence, the reduced quality of the spectra between 1 and 2 months is due to a decreased quantity of copper dislodged/wiped from the wood surface. The dashed lines in Figure 5-9 highlight two areas where the transformation of the copper from the original composition is present. The first dashed line near 8980 eV indicates the location of the Cu(I) derivative peak, and the second dashed line near 8985 eV indicates the location of the malachite derivative peak. Immediately evident in all three wood types for both wipe events is the presence of Cu(I). 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). In previous research, 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. Also evident is the shift to lower energies of the derivative peak near 8985 eV. The shift in peak location is associated with the change in the Cu(II) species present.

Figure 5-9: Cu Kα XANES spectra for the as-purchased pressure-treated lumber and the material dislodged from the wood surface and retained on a 0.45 μm filter after 1 month (Wipe 1) and two months (Wipe 2). MCA-1 (A), MCA-2 (B), ACA (C). Dashed lines indicate the energy positions associated with Cu^{1+} and malachite.



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 either 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 5-3.

Table 5-3: Linear combination fitting results for Cu Kα XANES first derivative spectra for materials wiped off of the treated wood samples exposed to the environment after 1 and 2 months of exposure retained by a 0.45 μm filter.

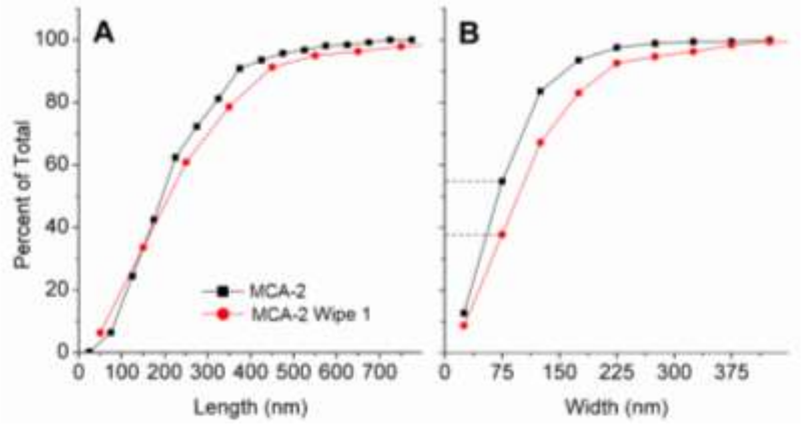
Sample	Month	Cu-Organic	Cu_2O	$Cu_2CO_3(OH)_2$	$CuCl_2$ (aq)
	Average/Standard Deviation %				
MCA-1 as-purchased	0	88/1		12/1	
MCA-1 Wipe 1	1	49/4	10/1	41/4	
MCA-1 Wipe 2	2	20/5	5/2	76/8	
MCA-2 as-purchased	0	42/3		58/2	
MCA-2 Wipe 1	1	52/5	14/2	34/5	
MCA-2 Wipe 2	2	16/5	14/3	70/5	
ACA as-purchased	0	90/5		10/2	
ACA Wipe 1	1	73/3	10/1		18/2
ACA Wipe 2	2	67/5	5/2		28/4

*The summation of Cu-Acetate and Cu-Oxalate

The Cu(I) in the sample is likely present as a solid species based on the microscopy and LCF results. The microscopy data indicated that Cu particulates were not co-localized with carbon, ruling out malachite as a potential species. The LCF results did not indicate that CuO was present in the samples; therefore, it stands to reason that the Cu(I) species is Cu_2O (cuprite). Additional Cu(I) present as an adsorbed phase cannot be ruled out, but there is evidence supporting the formation of cuprite. The *in situ* formation of cuprite in pressure-treated lumber has not previously been reported in the literature, and current available data does not allow for the formulation of a mechanism to describe Cu(II) reduction and subsequent precipitation. Copper (I) is meta-stable under ambient conditions and will eventually oxidize to Cu(II) as seen in the decrease in the relative abundance of Cu(I) from 1 to 2 months for MCA-1 and ACA.

Over the two month time period the relative abundance of the Cu-organic complexes decreased while the relative abundance of malachite increased for the two micronized copper treated samples. The biocidal mechanism for micronized pressure-treated lumber is based on the slow dissolution and subsequent release of aqueous Cu. Therefore, with time the ratio of malachite to ionic copper should increase as Cu is released from the wood surface. The change in speciation of Cu in the two micronized wood samples supports the biocidal mechanism. The reason for the increase in Cu-Organic fraction and decrease in malachite fraction after one month for MCA-2 is unclear. The initial distribution of Cu species at the wood surface may be different than the bulk composition (enriched in Cu-organic complexes) or it could be attributed to rapid dissolution of nano-sized malachite crystals. Comparing the percent distribution of particle sizes between the as-purchased MCA-2 and the MCA-2 wipe 1 reveals that there is little difference between the relative abundance of particles for a given length (Figure 5-10). For particle widths there is a 10-25% reduction in the relative abundance of particles of a given width between 50 and 100 nm (Figure 5-10). This shift to a lower percentage of particle less than 100 nm after 1 month would indicate that a portion of the nano-sized material underwent rapid dissolution. It is impossible to fully attribute the subsequent decrease in malachite and increase in Cu-organic species totally to dissolution of nano-phases. Instead, a change in the distribution of Cu species at the wood surface in combination with particle dissolution is likely responsible.

Figure 5-10: 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).



For ACA, there was a marked decrease in the Cu-orgainic phase coupled with an increase in ionic Cu(II). The increase in ionic Cu is not associated with the MCA samples. The specific reason is unclear, but may be related to the formulation of the initial treatment solution.

5.3 Copper Toxicity Assessment

A 2003 Consumer Product Safety Commission report pertaining to CCA wood provides a detailed review of the potential toxicity of copper to humans (Osterhout, 2003). 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, 2003). The report summarizes several case studies and lists the acute and chronic levels of copper that could produce adverse effects in humans if ingested. Table 5-4 details the most relevant copper levels as they relate to the above results. Also shown in Table 5-4 are results from other published studies as well as the Institute of Medicine of the U.S. National Academy of Sciences' list of tolerable upper intake levels (TUIL) for copper for children, young adults, and adults, based on age (IOM, 2001; Stern, 2010). Above these tolerable levels, mild symptoms, such as nausea, vomiting, and abdominal pain, may be observed. More significant effects of copper exposure are possible. For acute effects, intake amounts are extremely high (>100 mg per dose), which causes more severe symptoms and potentially death. For chronic effects, doses over 20 mg d^{-1} have resulted in liver failure, requiring a transplant (Stern, 2010). These levels are very high and likely not obtainable from PTL outside of extreme cases (i.e., direct consumption of large quantities of PTL). Based on the reported toxicity levels, children between the ages of 1 and 13 are likely the most at risk to copper toxicity from contact with PTL.

Table 5-4: Summary of Copper Toxicity Levels.

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

To equate the exposure levels to the gathered data, Thomas et al. (2004) determined that the surface area a child would come into contact with during a typical visit to a playground, the most likely place for a child to encounter PTL, to be 1.29 m^2. Using this area as an upper limit on typical contact with the treated wood, an estimate can be made on how much copper could be wiped off and potentially ingested during a playground visit. At 2 mg m^{-2}, a value at the upper range found during testing, the amount of copper released onto the hand would be 2.58 mg. The relative abundance for copper carbonate for the 2 MCA samples after two months was ~70% copper carbonate. Converting the total copper released to micronized copper released onto the hand (70% of 2.56 mg) would equal 1.8 mg of particulate copper carbonate. Comparing to the toxicity levels in Table 5-4, only children 3 years old and younger would be effected, their TUIL being 1 mg d^{-1}. Children ages 4 – 8 could be at risk if they consume more than 3 mg of copper in their regular diet. At 2.56 mg of copper per visit, mild symptoms, such as nausea, vomiting, and abdominal pain, could be observed.

Other factors may increase or decrease the toxicity. For instance, the area determined by Thomas et al. (2004) assumes only three visits per week though the exposure and TUIL levels 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. In order to arrive at a single value for the wiped area, they make several assumptions about the average area of a child's hand and how much of it is contacted with 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. The levels also assume complete ingestion of the transferred copper, which is unlikely. The TUIL values used for comparison are also general recommendations and not known limits that guarantee symptoms will occur. Finally, the micronized copper formulations release comparable amounts of copper to the aqueous formulation, which has been on the market and in use for several years.

The above comparison focuses solely on the ingestion of total copper, regardless of form (ionic v. particulate). A study conducted in parallel to this work examined the fate of micronized copper particles after ingestion. They determined that the copper particles dissolved completely upon coming into contact with stomach fluids and the copper was ~90% bioavailable (Lenibel et al, 2015). This indicates that the toxicity of the particles is not significantly different than the ionic copper. However, their study is not a comprehensive investigation on the toxicity of micronized copper versus ionic copper.

6 Conclusion

Representative micronized copper azole (MCA) and aqueous alkaline copper azole (ACA) pressure-treated wood products were extensively characterized to determine the total copper and particle concentration, the speciation of copper present in the wood products, and the particle size distribution. The three pressure-treated wood types and an untreated wood sample were assessed for copper release during typical use: transfer from hand contact and leaching from solution contact.

- The total concentration of copper present in the MCA treated lumber samples were similar and significantly less than the ACA treated sample. Copper carbonate was identified as the solid phase present in the MCA treated samples. Additionally, trace quantities of copper carbonate were identified in the ACA samples by XRD and XAFS analysis. The copper speciation of the three pressure-treated samples differ greatly. The MCA-2 sample was dominated by copper carbonate (88%), the ACA sample by copper complexed with organics (90%), and a mixture of copper carbonate and organically complexed copper in MCA-1.

- Microscopy data showed that the copper carbonate present in MCA-1 was approximately half the size of the material present in MCA-2. Histograms, total count, and box plots of the particle width and length indicated the data was not normally distributed but skewed towards smaller values. Previous research has demonstrated that micronized copper is distributed on the cell walls. Copper present in the BSE SEM images was always associated with cellulosic material and not present as isolated particles or aggregates. Further, the appearance of the copper carbonate and physical distribution was similar to the distribution of copper in the wood micro structure.

- The total quantity of solution copper released, during leaching, from the two MCA samples was similar and significantly less than the total copper leached from the ACA treated sample. Based on the solution concentrations, greater than ~95% of the copper leached from the blocks was in ionic form. The total solution concentration of copper leached from the three lumber types was similar for the three different solution chemistries examined.

- Solid phase data from the leaching studies showed that the majority of the copper that was captured during filtration was retained on the 2.5 μm filter membrane with significantly less material retained by the 0.45 μm and 10 kDa membranes. XAFS speciation data showed different trends for the two MCA samples. For MCA-1, the relative abundance of copper carbonate increased with smaller size fractions while the reverse was true for MCA-2. In all three pressure-treated wood samples a Cu^{1+} species was present in the material retained on the 2.5 and 0.45 μm membranes. SEM BSE images of the materials retained on the 2.5 and 0.45 μm membranes showed a decrease in the particle size from the 2.5 to 0.45 μm membrane. A single particle was detected on the MCA-2 10 kDa membrane. The aggregate was several microns in size and suggested that the copper carbonate had aggregated on the membrane.

- Comparing the MCA wood to the ACA wood, MCA released substantially less copper than the ACA, leading to a lower potential impact on the environment. ACA has already been shown to have little impact on soil environmental communities in close proximity to PTL surfaces, indicating the MCA would have a negligible impact.

- MCA treated wood, as well as ACA treated wood, released a large quantity of copper during the initial wipe sampling events, and decreased with each additional sampling event. During the initial period of high release, contact with the wood causes far more depletion of the copper than any type of environmental exposure. During testing, MCA-1 released slightly more copper than MCA-2, possibly due to the smaller size of the copper particles in the MCA-1 formulation or the increased concentration of organically complexed copper. The total quantity of copper released for all of the wipe experiments exhibited the same trend of decreasing copper concentration followed by a steady state after 3 to 4 sampling events. Light sanding of the weathered surface after a year of exposure to ambient environmental conditions did not result in an increase in the amount of copper transferred during subsequent wipe sampling events.

- Copper speciation by XAFS analysis was only possible for the first two months of the Outdoor experiment. After three months the total quantity of copper retained on the filter membranes was too low for bulk XAFS analysis. Both MCA samples of materials retained on the 0.45 μm membrane increased in the relative abundance of copper carbonate after two months. Indicating that organically complexed copper was the primary species released from the wood samples.

- After one month of environmental exposure there was no change in the particle length of copper carbonate, however, there was an increase in the average width of the particles indicating active dissolution of the nano-size copper carbonate. After two months of exposure the particles were heavily weathered, and the presence of a Cu(I) oxide phase was identified. After three months copper carbonate particles were not identified by microscopy analysis.

- The risk of copper exposure is low for older children (>8 y) and adults, but younger children (<8 y), particularly toddlers (1-3 y), may encounter quantities above the recommended thresholds, resulting in mild symptoms of nausea, vomiting, and abdominal pain. This would only be a potential in the upper bound of possibilities where a child had significant contact with the wood three times a week and then ingested most of what accumulated on the contacted skin. Severe acute and chronic symptoms are very unlikely during normal use.

- In summary, the particulate copper released from micronized copper PTL constituted a small fraction (< ~5%) of the total released. The total copper released was less than or comparable to the current ACA formulation available to consumers.

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