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**Quantifying metal migration from a deck constructed with copper
azole-treated lumber**

Gerald Presley and Matthew Konkler

Oregon State University
Department of Wood Science and Engineering
3180 SW Jefferson Way
Corvallis, OR, 97331
USA

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**IRG SECRETARIAT
Drottning Kristinas v. 61B
SE-114 86 Stockholm
Sweden
www.irg-wp.com**

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Gerald Presley, Matthew Konkler

Oregon State University, Department of Wood Science and Engineering, 3180 SW Jefferson Way, Corvallis, OR, 97331, USA. gerald.presley@oregonstate.edu , matthew.konkler@oregonstate.edu

ABSTRACT

Soluble copper or micronized copper wood preservatives are the most common available wood preservative systems for residential applications in the United States. Copper containing wood preservatives have been scrutinized for their potential negative impacts on the environment, across many jurisdictions. Concerns arise from the potential for preservatives to migrate out of treated wood upon water exposure into the environments. Because of this it is important to quantify chemical loss from lumber treated with available wood preservative systems so that their impact can be predicted for specific applications. This work describes an effort to measure the migration of copper from a newly installed deck made with hem-fir lumber pressure treated with copper azole-C (CA-C) to above ground contact retentions. The deck was constructed in 2021 and collection basins were installed beneath the deck at three locations. In each location basins were positioned so they would catch runoff from the deck surface boards only and where runoff would contact the deck surface and joists. Water samples were collected after each major rain event and analysed for copper concentration. Water was collected for an entire wet season in Western Oregon from October 2021 to May of 2022. Copper concentrations in runoff were highest in runoff collected after the second rain event of the season, averaging 2.61 mg/l for runoff from deck boards only and 4.92 mg/l for runoff collected from beneath the deck surface and a joist. Copper concentrations in runoff tapered off from there, reaching 0.11 mg/l and 0.19 mg/l for deck and joist runoff, respectively. Total copper lost from the deck over the first 7 months after installation was 44.48 mg/m² the deck surface alone and 71.12 mg/m² deck and joist. This level of chemical loss was not sufficient to result in copper accumulation in the soil beneath the deck two years after its installation. This work provides an excellent case study to test the robustness of a predictive model for treated wood's impact on the environment and efforts are currently underway to do so.

Keywords: Environmental impacts, leaching, metal migration

1. INTRODUCTION

Copper based preservative systems are widely used as preservatives for decking in the United States in residential and industrial applications. For all copper-based treatments limited amounts of copper can migrate into the surrounding environment from the wood's surface as it is exposed to precipitation while it is in service. This causes some concern about the potential for copper containing treated wood products to negatively impact sensitive aquatic environments near or under structures made with copper-containing treated wood (Brix *et al.* 2022). Quantifying metal migration rates from treated structures is essential for predicting their impact on the surrounding environment and can help ensure that treated wood structures are appropriate for the environment they are used in (Waldron *et al.* 2005).

Many studies of chemical migration have been done in the field and in laboratory conditions on pressure treated wood. Commodities treated with copper containing preservatives exposed to rainfall or simulated rainfall generally show their highest levels of copper loss upon the first few exposures. Copper concentrations in runoff typically rapidly decrease and stabilize at low levels after only a few months of natural rainfall exposure (Ruddick 2008) or a few hours of simulated rainfall (Morrell *et al.* 2005, Morrell *et al.* 2010).

For residential applications, the main treatments available in the United States are copper azole-C (CA-C) and micronized copper azole (MCA) and currently CA-C is the main treatment available in the western United States. CA-C is a soluble copper treatment containing propiconazole and tebuconazole as cobioicides equal proportions. The azoles are present only at roughly 4% of the mass of copper in CA-C, meaning the copper component of CA-C is the main active ingredient and the principal chemical of interest concerning migration into the environment (AWPA 2022).

Extensive studies have been done to measure preservative migration from CA-C treated wood both in service and in controlled laboratory and field experiments (Xu *et al.* 2020). Simulated rainfall exposure experiments show a pattern of chemical migration where copper concentrations in runoff are highest upon first few exposures to water and rapidly taper off thereafter (Kennedy and Collins 2001). Small test decks exposed to natural rainfall showed a similar pattern, but the location of the tests impacted the total copper loss from the decking (Morrell and Barnes 2015). Further study of full-scale structures can help generate data that can be used to test predictive model prediction on chemical migration from treated wood.

This study sought to quantify copper migration from a CA-C pressured treated deck from its construction through one season of weather exposure. Total copper loss from the deck in the first year of rain exposure was quantified and was used to identify trends in copper loss as the deck aged. This work serves as a case study for copper migration from decking in service and provides an excellent opportunity for predictive model testing.

2. EXPERIMENTAL METHODS

2.1 Deck construction and runoff collection

A deck was constructed with nominal 2 x 6 inch (5 x 15 cm) and 2 x 10 inch (5 x 25 cm) CA-C treated hem-fir lumber treated to above ground retentions in 2021. The deck surface was constructed with 2 x 6 inch lumber and joists were made incised 2 x 10-inch lumber. All decking material was sealed with a commercial pigmented sealer with a natural cedar colour prior to installation. The decking material was analysed for copper content using an x-ray fluorescence analyser according to the American Wood Protection Association A9 standard (AWPA 2022).

Three collection points were installed underneath the newly constructed portion of the deck, and these consisted of two collection basins each for a total of 6 collection basins (Fig. 1). Collection basins were 0.41 m wide x 0.61 m long x 0.15 m high. At each of three collection points, one basin was placed directly under the decking surface while a second basin was placed under decking and a joist. Water was collected from the basins with each significant rain event. At the time of sampling the mass of the filled basins was measured to measure the total volume of water in the basin for calculation of total metal lost from the deck.



Figure 1: Photo of the CA-C treated deck with three sampling locations and six sampling basis underneath the front of the deck.

2.2 Water collection and soil sample collection

A sample of water from each collection was reserved for metal analysis by ICP-MS. Samples were prepared for analysis according to EPA method 200.7 to measure total dissolved copper. Briefly, samples were acidified to a pH below 2 by acidifying 80 ml of each sample with 150 μ l of concentrated nitric acid. Samples were then filtered with a 0.45 μ m filter prior to being analysed for copper content Inductively coupled plasma mass spectrometry (ICP-MS).

Soil samples were taken at four locations around the deck two years after the construction of the deck. Five soil samples were taken from each location using a 2.5 cm diameter x 30 cm long soil corer. Samples were taken from underneath the newly constructed front end of the deck, 0.3 m downslope from the deck, 6.1 m downslope from the deck, and from behind Peavy Lodge, a location upslope from the deck.

Soil samples were homogenized, oven dried, and microwave digested according to EPA method 3052. Briefly, 0.25 g of soil or 0.5 g of plant biomass was placed into PTFE microwave extraction tubes and 10 mL of concentrated nitric acid was added. Samples were digested for approximately 9.5 minutes at 180 $^{\circ}$ C with a total microwave digestion time of about 15 minutes. The resulting digestate was rinsed from the tube with DI water and brought up to a volume of 35 mL with DI. Samples were then filtered with a 0.45 μ m filter prior to being sent for ICP-MS analysis.

2.3 Metal analysis with ICP-MS

Filtered water samples or soil extracts were analysed using the same procedure except soil samples were diluted to fall within the range of the standard curve for the analysis. Each analytical session began by allowing the ICP-MS to warmup for 30 minutes prior to being tuned first in standard robust (STDR) and then in kinetic energy discrimination robust (KEDR) modes utilizing a multiple element 1 part per billion (ppb) standard prepared in a 2% HNO_3 + 0.5% HCl matrix. Calibration standards were prepared from single element standards and were spiked with 0.5 ppb indium for use as an internal standards. Calibration curves were generated for ^{65}Cu and included nine standards and a blank. All standards and blanks were prepared using ultra pure 2% HNO_3 . Samples were spiked with 0.5 ppb indium as an internal standard and diluted 10-fold using laboratory grade water.

The analytes ^{65}Cu was analyzed in KEDR mode. Each analysis consisted of five 80 sweep runs ^{65}Cu and ^{115}In analyzed with 10ms dwell times. Quality control and internal precision were monitored by repeated measurements of the prepared standards following every 25th sample. These are much improved from the previous core facility we used for sample analysis and we are assaying well above the limit of detection for the ICP-MS at their facility. Copper levels in the samples were measured and were used to calculate total μg of copper lost from the decking material.

3. RESULTS AND DISCUSSION

The copper retention levels measured in this study was about 0.75 kg/m³ for the 2 x 6-inch material and 0.60 kg/m³ for the 2 x 10-inch material. These were lower than the AWWA standard retention levels specified for UC3B, above ground contact exposed, of 1.0 kg/m³. Copper concentrations in deck runoff showed a predictable pattern of relatively higher concentrations in the first few water collections, followed by a steady drop off over time (Fig. 2). The highest copper concentrations were recorded in the second runoff collection and concentrations steadily declined thereafter. Copper concentrations in rainwater runoff tended to be higher in collections beneath joists, which is expected due to the higher wood surface area exposed to rainwater. The lowest average copper concentrations in runoff were found in the last five sampling points for both sampling locations (deck and joist), which suggests the copper loss rates started to settle to a more stable, lower value after 5 months of regular rain exposure.

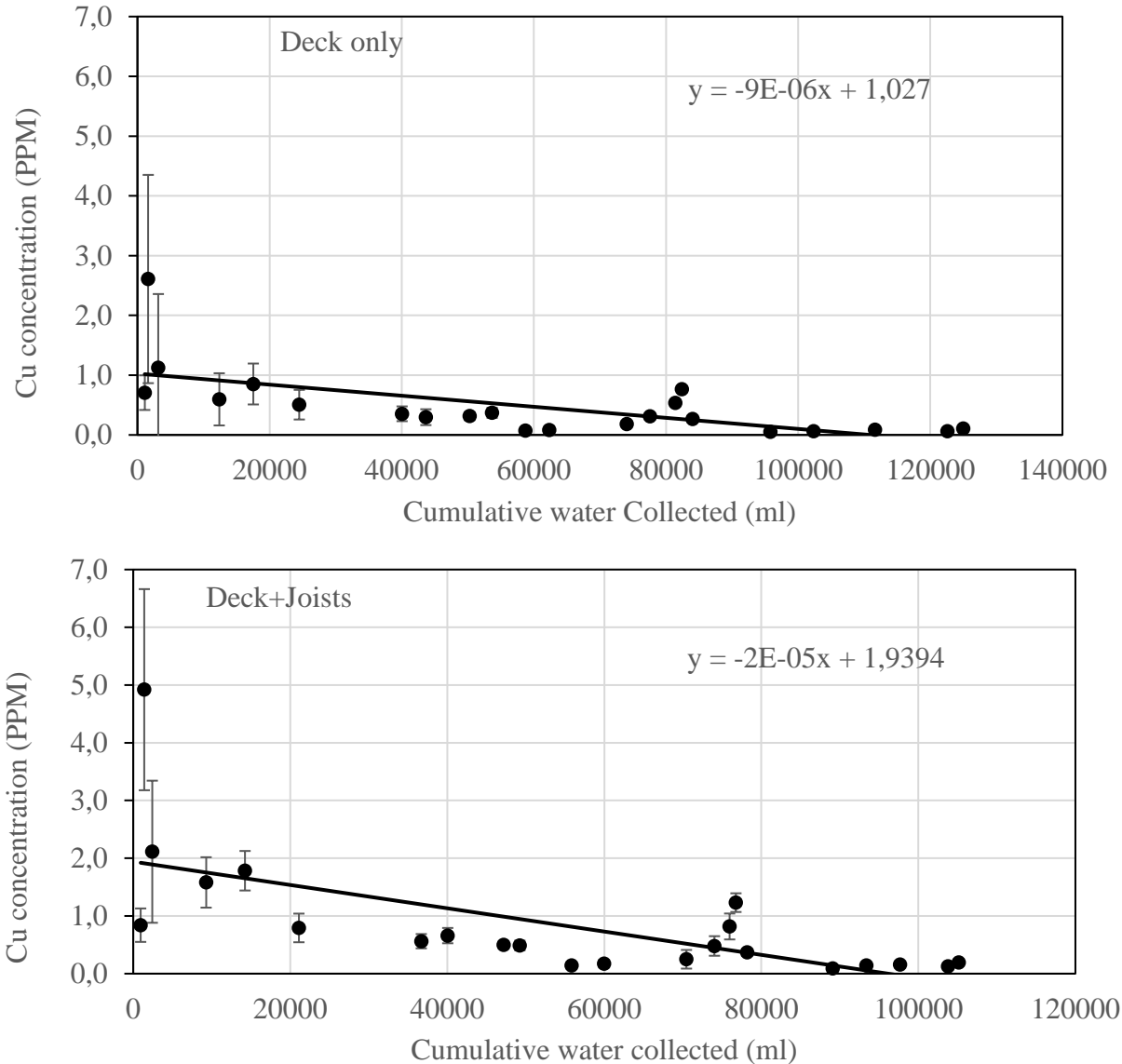


Figure 2: Average copper concentrations measured in deck runoff from collection points below decking alone (Top), decking+joists (Bottom). Error bars are standard deviations of three replicate collections.

Cumulative copper increased rapidly initially as high collection volumes coupled with relatively higher copper concentrations added to the total quickly (Fig. 3). Copper concentrations in the runoff tended to decrease over the wet season with decreasing copper migration rate from the decking. After about 5 months of rain exposure, the cumulative copper tended to stabilize at both sampling locations and successive copper increases dissipated to less than 1.0 mg/m² for each rain event. More cumulative copper was detected from detection points under joists as opposed to deck surface alone. This was expected because of the larger surface area of wood. Total copper loss in runoff over the 7-month collection period totalled 44.5 mg/m² for decking only and 71.1 mg/m² for decking+joist.

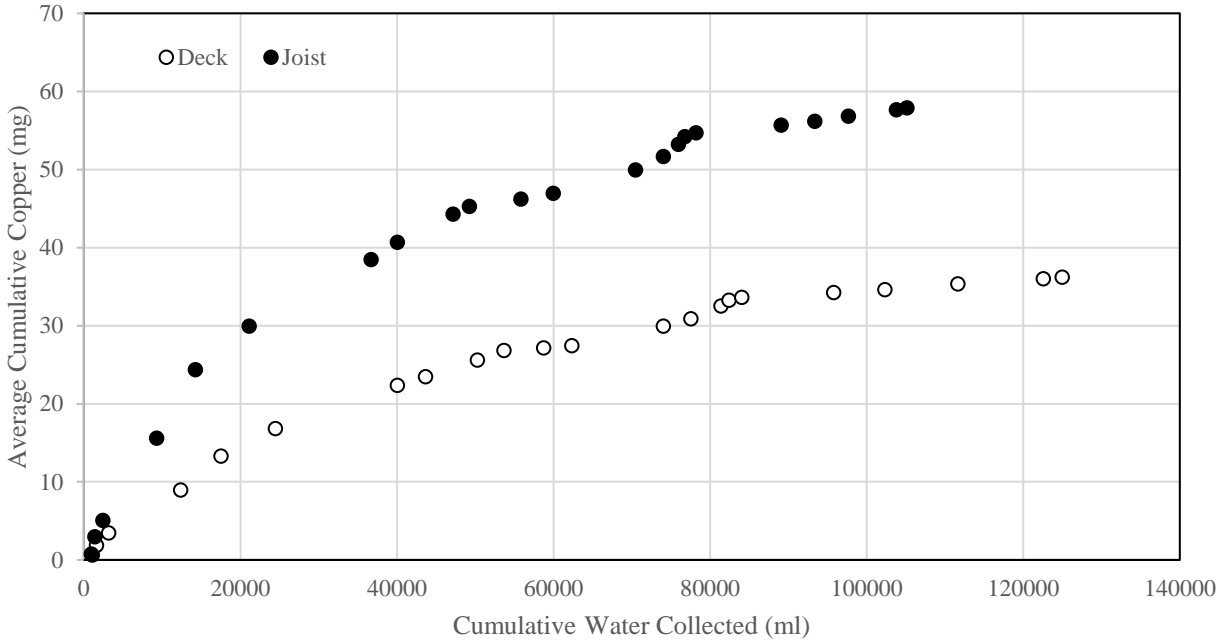


Figure 3: Cumulative mg copper collected in rainwater runoff versus cumulative rainwater collected in ml for water collected beneath decking only and decking+joists.

Copper levels in soils collected in 2023 directly beneath the treated deck were indistinguishable from copper levels found downslope or upslope from the deck. Average copper levels in soils ranged from about 50.3 PPM to 54.4 PPM and the average levels beneath the deck were the lowest observed, although they were not statistically different than the other average levels (p>0.05). All values measured were well within the normal background copper levels for the Willamette Valley which are not considered elevated until they exceed 140 PPM (DEQ 2013). This data indicates that after two years of service, copper migration from the Peavy Lodge deck was insufficient to produce a measurable increase in copper concentrations in soil.

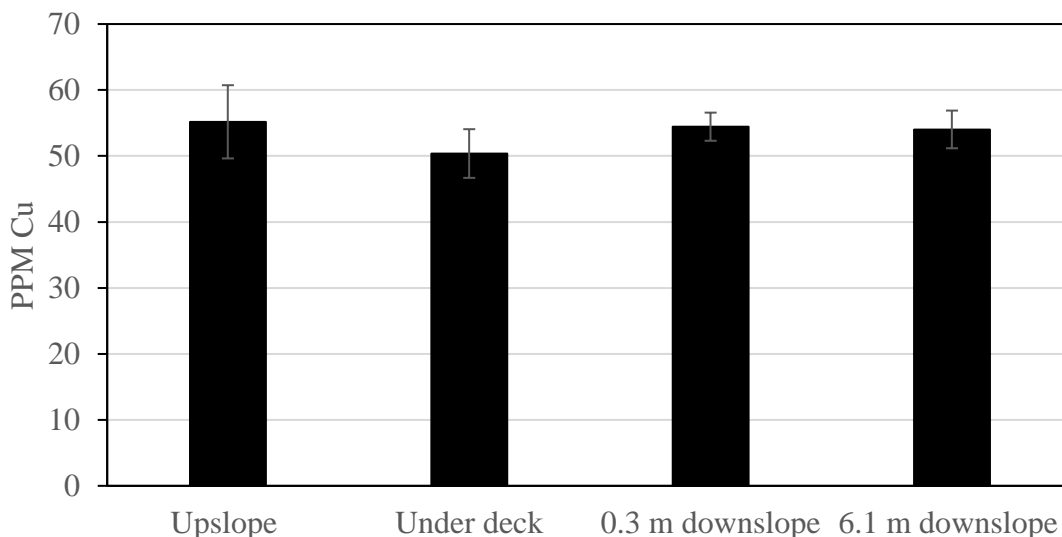


Figure 4: Copper concentrations in soils collected underneath, upslope and downslope from the pressure treated deck sampled in this study two years after it was constructed.

4. CONCLUSIONS

Copper migration rates from a copper azole treated deck followed a familiar pattern of relatively high copper loss with the first few exposures followed by a rapid decrease in copper loss rates over about 5 months of rainfall exposure. After 5 months of exposure, copper loss stabilized to a low level of less than 1.0 mg/m² of decking for each significant rain event. Total copper loss over 7 months of rainfall exposure totalled 44.5 mg/m² for the decking surface alone and 71.1 mg/m² for decking plus joist. This level of copper loss was not sufficient to register a measurable increase in copper in soil underneath the deck two years after installation. This study provides data that can be used to test predictive models for chemical loss from treated wood.

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