Concentration and form of copper released into aquatic systems from commercial liquid and micronized pressure treated lumber

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The fate and effects of pristine engineered metal nanomaterials (ENMs) in simplified systems have been widely studied; however, little is known about the potential release and impact of metal ENMs from consumer goods, especially lumber which has been treated with micronized copper. Micronized copper treatment solutions contain copper complexes predominately in the 10-700 nm size range, and are used in lumber to prevent microbial degradation and fouling. In this work, the goal was to determine the rate, concentration, and form of copper released from several commercially available pressure-treated lumber samples exposed to an aqueous system at 0, 1, 10, and 30 ppt seawater. Lumber tested included untreated Southern Yellow Pine (SYP) as the control, SYP treated with micronized copper azole (MCA) at 0.96 and 2.4 Kg/m^3, alkaline copper quaternary (ACQ) at 0.30 and 9.6 Kg/m^3, and chromated copper arsenate (CCA) at 40 Kg/m^3. Of the different chemical treatments, only MCA included nano- and micro-sized copper complexes. The experimental system included 2 cm wood cubes cut from the outer surface of the lumber submerged in 250 mL of media (0, 1, 10, and 30 ppt reconstituted seawater) in high density polyethylene bottles, and mixed on a shaker table at 120 rpm for 6 months. Water samples were taken at 8 hours, and on days 1, 2, 7, 14, 28, 133, and 210. Subsamples included unfiltered water, and water filtered through a 0.1 µm polyethersulfone (PES) syringe filter and a 3000 Dalton centrifugal filter, which were analyzed using ICP-AES to determine the total, nano+ionic copper (< 0.1 µm subsample), and presumably ionic-only copper (<3 KDa subsample). Results showed that within 28 days, most treatments reached a steady state of copper release. Lumber treated with higher copper concentrations released more copper into the water, and all treatments released ionic copper rather than particulate copper (nano or micro). Ion selective electrode measurements and the magnitude of toxicity to marine mysids (*Americamysis bahia*) were used to confirm the results of the size-based analyses. Overall these results suggest that the form of copper released from treated lumber is ionic and that little free nanocopper is present. This finding suggests the risk associated with nanocopper treated lumber can be addressed with conventional existing copper ion modeling approaches.