Form and toxicity of copper released into aquatic systems from conventionally and nano-sized copper treated lumber

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The fate and effects of pristine engineered 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, such as lumber 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. In this work, the goal was to determine the form of copper released from several commercially available pressure-treated lumber samples immersed in 0, 1, 10, and 30 ppt seawater and whether the resulting leachate poses an unexpected toxicity risk. Untreated Southern Yellow Pine (SYP) and 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 were evaluated at each salinity. Of the different treatments, only MCA included nano-sized copper complexes. The experimental system utilized 8 cm^3 blocks cut from the outer surface of the lumber submerged in 250 mL of media (0, 1, 10, and 30 ppt reconstituted seawater). Water was sampled at 0.33, 1, 2, 7, 14, 28, and 133 days. 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 approaching ionic copper (<3000 Dalton subsample) concentrations. Within 28 days, most treatments reached a steady state of copper release with no significant difference between subsamples within a treatment. This suggests that all the copper released was accounted for in the approaching ionic copper fraction. The results of the long term leaching study were confirmed by comparison of ion selective electrode measurements to subsamples analyzed via ICP-AES. The leachate was also used in parallel with a copper ion positive control ($CuSO_4$) to perform a 96 hour toxicity study with the marine mysid, *Americamysis bahia*. The resulting dose response curves and calculated LC_{50} values were not significantly different, further supporting the previous results. Overall, these results demonstrate that the copper form released from treated lumber was ionic and not nanocopper. This finding suggests the risk associated with nanocopper treated lumber can be addressed with existing copper ion modeling approaches.