Bench- and Field-Scale Determination of Copper Speciation, Complexation, and Precipitation in Drinking Water Systems

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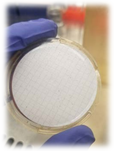
Background/Introduction

- Copper (Cu) is known to have antimicrobial properties, with cupric ion (Cu^{2+}) being the most biocidal form[1].
- The impact of Cu on growth of opportunistic pathogens, such as *Legionella pneumophila*, ranges from having the intended inhibitory effect, to having no impact, to facilitating their growth[1,2].
- Water conditions such as pH, alkalinity, and Cu ligands, such as natural organic matter (NOM) or phosphorus-based corrosion inhibitors have potential to mitigate Cu toxicity by decreasing presence of Cu^{2+}.
- Identifying environmental conditions that decrease or negate the biocidal capacity of Cu^{2+} is important for water quality management plans.
- The objective of this study was to identify factors associated with Cu^{2+} stability in drinking water.

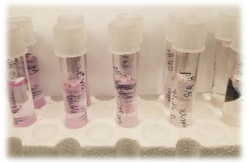
Materials & Methods

Bench-Scale Testing

Municipal water filtered by granular activated carbon (GAC), ferric oxide (Fe_2O_3), and a 0.22 µm filter.



-pH adjusted to target;
-Cu dosed (*10, 20, 30*, 50, 80, 100, 200, 300, 500 µg/L);
-pH re-adjusted (6.0, 6.5, 7.0, 7.5±0.02);
-Cu ligands dosed (PO_4^{3-}, NOM);



-Short term stabilization of the Cu^{2+} species occurs within 30 min; After 30 min.
-Measured total Cu, soluble Cu by HACH binchoninate reagents.*
-Measured Cu^{2+} using ion selective electrode (ISE).
-Measured pH at sampling time.

Field Testing

Three field were chosen to represent various ages of copper piping in order to quantify Cu speciation. System 1 has 9 year old pipes, system 2 represents brand new construction (no use), and system 3 is 2 years old. Samples were tested to determine amount of total Cu, soluble Cu, and Cu^{2+} in relation to the on-site parameters of use frequency (least used, LU, and most used, MU), pH, temperature, total and free Cl, ammonia, dissolved oxygen, and PO_4^{3-}.

*NOM was measured with ICPMS (Inductively coupled plasma mass spectrometry).

Results: Bench-Scale

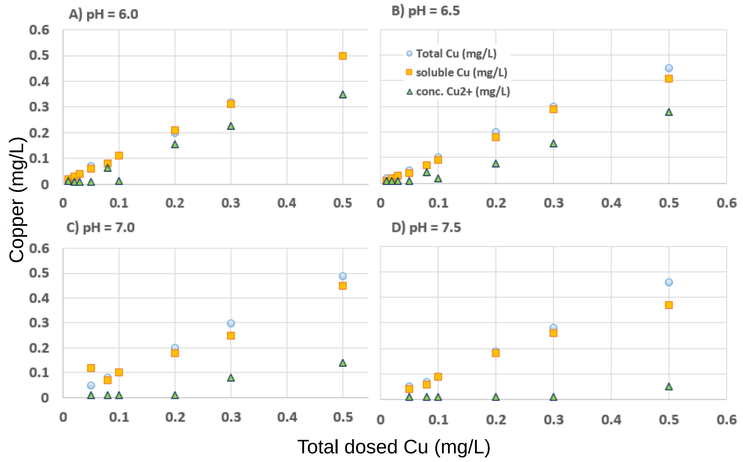


Figure 1. Cu species levels as a function of dosed Cu with different pHs

Table 1. Percent Soluble Cu & Cu^{2+} at various pH (dose 0.5 mg/L)

	pH=6.0	pH=6.5	pH=7.0	pH=7.5
Sol. Cu %	100%	91.1%	91.8%	80.4%
Cu^{2+} %	70.1%	61.6%	28.5%	11.6%

-pH=6 and 6.5 had quantifiable Cu^{2+} ion across total Cu concentrations of 200 µg/L and above, while pH=7 and pH=7.5 required more total Cu to have quantifiable Cu^{2+}.

-Figure 1, when Cu=0.5 mg/L from pH 6, 6.5, 7 to 7.5, reduced the levels of free Cu^{2+}. E.g. Cu^{2+} dropped from 0.35, to 0.28, to 0.14, to 0.05 mg/L.

-Referring to table 1, both soluble Cu and Cu^{2+} percentages dropped with the increase of pH.

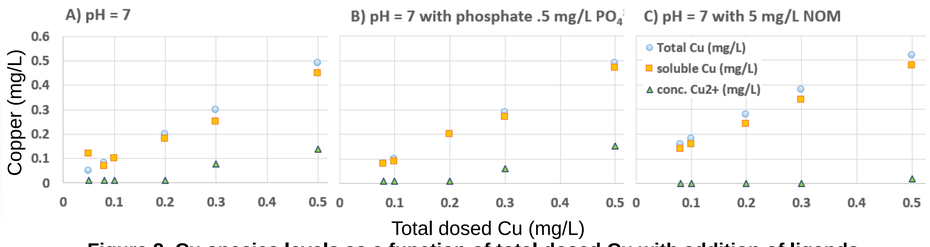


Figure 2. Cu species levels as a function of total dosed Cu with addition of ligands

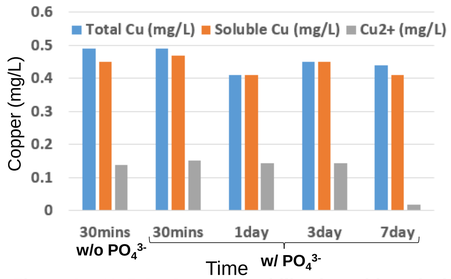


Figure 3. pH=7 Cu Species stabilization with and without PO_4^{3-}

-At pH=7.0, 0.5 mg/L PO_4^{3-} didn't change the levels of soluble Cu and Cu^{2+} (see figure 2). However, 5 mg/L NOM, was able to reduce Cu^{2+} levels below quantification limits even at total Cu=0.3 and 0.5 mg/L.

-Relative long-term experiments demonstrated that PO_4^{3-} took much longer than 30 min to stabilize (see figure 3). This could explain the reason why adding PO_4^{3-} didn't change the levels of soluble Cu and Cu^{2+} in 30 mins of sampling. Longer stabilization time and/or higher PO_4^{3-} levels shall be investigated in the future.

Teaching Module

AP Chemistry and Pre-AP Chemistry students will be presented with the task of determining the ideal conditions for highest Cu^{2+} concentrations to impede the growth, or destroy microorganisms in water systems. Students will display their results via charts and plots within Excel and design their own set of parameters to measure and monitor in a water system with justification for their proposals.

Results: Field Test

Table 2. Water Chemistry Parameters for Different Field Sampling Systems

	pH range (Avg)	Total Cl_2 mg/L	Free Cl_2 mg/L	NH_3 mg/L	PO_4^{3-} mg/L	TOC mg/L (Avg)	DO mg/L
System 1	6.73-7.16 (7.00)	0.08(LUCS) - 2.3(LUCF)	n/a	0.3(LUCS) - 1.4(MUCF)	0.56(LUCS) - 1.48(MUCF)	7.44- 6.06 (6.55)	n/a
System 2	7.2-7.85 (7.64)	0.08(LUHS) - 0.25(LUCF)	0.07(LUHS) - 0.18(LUCF)	0.06(LUCS) - 0.09(LUHS)	0.15(LUHS) - 0.73(LUCS)	5.52 - 6.34 (5.93)	5.96(LUCF) - 7.95(LUHF)
System 3	7.46-8.01 (7.68)	0.78(LUHS) - 2.98(LUHF)	n/a	n/a	n/a	n/a	n/a

*LU- Least Use; MU- Most Use; CS-Cold Stagnant; CF-Cold Flushed; HS- Hot Stagnant; HF- Hot Flushed; DO- Dissolved Oxygen

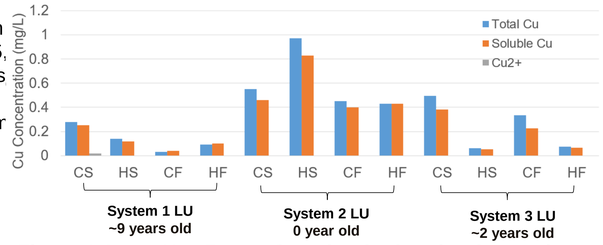


Figure 4. Least Use Faucet Samples Cu Species Comparison

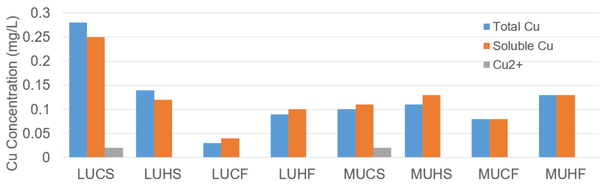


Figure 5. System 1 LU and MU Faucet Cu Species Comparison

-A substantial percent of Cu was found to be soluble in the field-scale systems, but tended to be complexed (i.e., not Cu^{2+}).
-Only System 1 cold stagnant samples had quantifiable Cu^{2+} probably due to low pH
-Stagnant samples generally had higher Cu concentration than flushed samples.
-Newer buildings/pipes tend to release more Cu than older ones.
-LU stagnant samples had more Cu than MU stagnant samples.
-Interestingly, MU stagnant sample also had quantifiable Cu^{2+}.

Conclusions/Recommendations

- Ideal environments for finding free, uncomplexed Cu^{2+} are low pH water systems, pH 6.5 or below or slightly higher pH systems of pH 7 with higher doses of copper or little/no phosphate added to achieve any free Cu^{2+} ion.
- Since 0.5 mg/L PO_4^{3-} did not affect the water systems of pH 6.5 and 7, investigations of higher phosphate levels will be conducted in the future.
- Stagnant and flushed water systems are both present in everyday, household/industrial/ hospital use, however flushed water samples were found to contain less Cu^{2+}, therefore more investigations are needed to design a method to deliver and maintain a high enough [Cu^{2+}] to inhibit pathogen growth.

Future Work and References

This work is one part of a larger project of finding water chemistry effects on bioavailable Cu^{2+} to inhibit the growth or possibly eradicate *Legionella pneumophila*.

Works Cited

[1] June, Stephanie; Dziewulski, David M., 2018. Copper and Silver Biocidal Mechanisms, Resistance Strategies, and Efficacy for *Legionella* Control. *Journal AWWA*, December 2018 110:12.

[2] Lin et al., 2002, Negative Effect of High pH on Biocidal Efficacy of Copper and Silver Ions in Controlling *Legionella pneumophila*.Applied and Environmental Microbiology); June 2002 68:6.

Acknowledgements

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