Copper-silver ionization at a US hospital: interaction of treated drinking water with plumbing materials, aesthetics and other considerations

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ABSTRACT

Tap water sampling and surface analysis of copper pipe/bathroom porcelain were performed to explore the fate of copper and silver during the first nine months of copper-silver ionization (CSI) applied to cold and hot water at a hospital in Cincinnati, Ohio. Ions dosed by CSI into the water at its point of entry to the hospital were inadvertently removed from hot water by a cation-exchange softener in one building (average removal of 72% copper and 51% silver). Copper at the tap was replenished from corrosion of the building's copper pipes but was typically unable to reach 200 µg/L in first-draw and flushed hot and cold water samples. Cold water lines had >20 µg/L silver at most of the taps that were sampled, which further increased after flushing. However, silver plating onto copper pipe surfaces (in the cold water line but particularly in the hot water line) prevented reaching 20 µg/L silver in cold and/or hot water of some taps. Aesthetically displeasing purple/grey stains in bathroom porcelain were attributed to chlorargyrite [AgCl_(s)], an insoluble precipitate that formed when CSI-dosed Ag⁺ ions combined

with Cl^- ions that were present in the incoming water. Overall, CSI aims to control *Legionella* bacteria in drinking water, but plumbing material interactions, aesthetics and other implications also deserve consideration to holistically evaluate in-building drinking water disinfection.

Keywords: copper silver ionization; cold; hot; reduced silver; copper pipe; porcelain staining

1. Introduction

Hospitals in the United States (US) and world-wide are increasingly relying on in-building disinfection to control water-borne pathogens (e.g., *Legionella pneumophila*, *Mycobacterium avium* and *Pseudomonas aeruginosa*) and ultimately prevent or mitigate disease outbreaks in sensitive patients (Falkinham et al., 2015; Pruden et al., 2013). Systemic drinking water disinfection options for buildings include free chlorine, chlorine dioxide, monochloramine, UV radiation, ozone and copper silver ionization, with each option having different presumed or proven limitations and benefits (Rhoads et al., 2015; Pruden et al., 2013, Lin et al., 2011; 1998).

The implications of in-building water treatment are not fully understood (Rhoads et al., 2015; 2014). Information is gradually being collected as more disinfection technologies become commercially available, as buildings increasingly install such systems, and as researchers, policy-makers, building managers, manufacturers and water consumers assess the full impact of such installations on water quality. During a 2013 US Environmental Protection Agency (EPA) workshop, US state representatives requested more research on the effectiveness of each disinfection treatment against *Legionella* and on water quality evaluation after in-building disinfection is applied (Triantafyllidou et al., 2014).

Given that the primary objective of water disinfection in buildings is pathogen control, it is not surprising that its impact on general water chemistry and other potential consequences are often overlooked. But as with any type of water treatment, interactions of added disinfectants with the incoming water chemistry and with building plumbing materials can have other important effects (e.g., formation of disinfection byproducts and/or metallic corrosion) which could compromise the integrity of the plumbing system and even impact the efficacy of disinfection itself (Rhoads et al., 2015; 2014). In addition, possible aesthetic issues (water/fixture

discoloration, taste or odor) arising from in-building drinking water treatment may shape public perception of its effectiveness, whether they constitute sensory nuisances or true health threats (Dietrich, 2006). Assessment of in-building water disinfection should therefore include water chemistry impacts (non-microbiological) and public perception (aesthetics).

The efficacy of copper-silver ionization (CSI) to control *Legionella* in building plumbing systems has been studied, but little information has been gathered on water quality impacts, aesthetics and other factors associated with CSI installations. Most CSI case studies have been in hospitals or nursing homes, where only the hot water was treated and where treatment efficacy was based on microbiological indicators. Study findings have been mixed, with several reporting positive results of CSI in controlling *Legionella* (Dziewulski et al., 2015; Stout and Yu, 2003; Lin et al., 1998; 2002) while others did not have success (Demirjian et al., 2015; Rohr et al., 1999; CDC, 1997; Blanc et al., 2005). The reasons for this discrepancy were thought to include the development in *Legionella* of resistance to the disinfecting ions or inadequate ion concentrations (e.g., Rohr et al., 1999; Lin, 2000; Blanc et al., 2005).

CSI relies on the synergistic disinfecting capabilities of positively charged cupric ions (Cu^{+2}) and silver ions (Ag^{+}) (States et al., 1998; Lin et al., 1998). It consists of one or more flow cells, each equipped with two sacrificial copper:silver electrodes (Figure 1). The composition of the two electrodes (i.e., copper:silver ratio) can be customized. It is typically set to 70:30 copper:silver (weight %), but other ratios have also been reportedly used in various countries (i.e., 50:50, 60:40, 70:30 and 90:10) (Walraven et al., 2015). A direct electric current is applied across the electrodes to stimulate continual release of cupric ions and silver ions into the flowing water, causing the electrodes to be gradually consumed (Figure 1) and thus have to be replaced periodically.

In a CSI system the electric current can be adjusted through a controller, depending on water flow rate and condition of the electrodes, in order to achieve the manufacturer's recommended levels in water of 300-800 µg/L copper (optimum of 400 µg/L), and 30-80 µg/L silver (optimum of 40 µg/L) (Liquitech, Inc, 2014). Aside from this manufacturer's 2014 operations manual, some of the relevant scientific literature (e.g., Lin et al., 2011; 1998) as well as older manufacturer instructions as reported by States et al. (1998), report efficacy of CSI in controlling *Legionella* at even lower dosed minimum concentrations of 200 µg/L copper and 20 µg/L silver.

Reported operational advantages of CSI include relatively low installation/ maintenance cost (Lin et al., 1998), relatively easy installation/ maintenance (Lin et al., 1998) with no reagents or complex monitoring (Swertfeger et al., 2014), and introduction to tap water of two metallic ions that are not expected to form disinfection byproducts (Swertfeger et al., 2014). Reported disadvantages of CSI include maintenance requirement to regularly remove accumulated scale from the electrodes (States et al., 1998; Lin et al., 1998), the possibility for ion deposition onto metallic pipes causing deposition corrosion (Pruden et al., 2013; Clark et al., 2011), possible interference of the background water chemistry (in particular of water pH>8.5) with the disinfecting ability of the added ions (Stout and Yu, 2003; Lin et al., 2002), and lavender discoloration of porcelain sink surfaces, and/or blackish discoloration of water if excessive ions are released into the water (Stout and Yu, 2003, Lin et al., 1998; States et al., 1998). Discoloration was believed to have occurred at the initial stages of CSI on surveyed hospitals' hot water lines, when silver ions exceeded the range of 20-40 µg/L (Stout and Yu, 2003). But aside from this survey result (Stout and Yu, 2003) or from brief qualitative

descriptions of aesthetic problems in passing (Lin et al., 1998; States et al, 1998), the discoloration/staining issue has not been thoroughly examined in the peer-reviewed literature.

This work investigated copper and silver levels generated by CSI and distributed spatially at a large hospital in Cincinnati, Ohio applying CSI to un-softened cold and softened hot water. This hospital offered a unique opportunity to obtain a range of information relevant to CSI applications, because CSI was applied for cold water disinfection in addition to hot water disinfection, because the incoming water has a chemistry of elevated pH and hardness, and because early access to the hospital allowed pre- and post-CSI comparisons. The interaction of dosed metals with hot and cold copper pipe surfaces and with bathroom porcelain surfaces were evaluated for the first time in a CSI installation, and the source of aesthetic implications was also examined for the first time.

2. Materials and methods

2.1 Incoming drinking water, CSI treatment and Ohio Environmental Protection Agency monitoring requirements

The hospital is centrally located within the city of Cincinnati's main distribution system and receives water from an adjacent water main. The hospital receives treated surface water of elevated pH (~8.6) and moderate alkalinity (~73 mg/L CaCO₃) that is considered hard (~128 mg/L CaCO₃) after conventional treatment followed by granular activated carbon filtration, free chlorine addition (~1.2 mg/L) and polyphosphate scale inhibitor addition (sodium hexametaphosphate at ~0.16 mg/L as P) at the Miller treatment plant (GCWW, 2014).

The hospital has two multi-floor patient buildings (designated as buildings A and B) and applied CSI treatment in February 2014 (i.e., 2/14) to both hot and cold water lines throughout these buildings. Three CSI cells were installed to treat the incoming drinking water (~0.11 million gallons/day for buildings A and B) at the point of entry (Figure 1). After passing through the CSI cells, water intended for hot water use was passed through pre-existing cation exchange softeners in each hospital building. The hospital has instantaneous water heaters (located on the highest floor 8 for building A and on the lowest floor R for building B). Building A relies on a single hot water recirculation line servicing all floors. Building B relies on 3 different hot water lines (a hot water recirculation line up to floor 4, a high-pressure line with electric heat tape for floors 5-7, and an un-tempered hot water line for surgery rooms of floor 3). Hot water at buildings A and B (with the exception of the un-tempered surgery line) is tempered through master mixing valves (floors A8 and BR respectively). Buildings A (built in 2002) and B (built in 1993) are plumbed with copper pipe and contain standard dual handle faucets at the rooms that were sampled.

No historical data on the occurrence of *Legionella* bacteria or Legionnaire's disease at this hospital were available, but a microbiological study parallel to this indicated that prior to CSI there was low background presence of *Legionella pneumophila* serogroup 1 in biofilms of buildings A and B (9 out of 64 shower hoses based on quantitative polymerase chain reaction) (Rodgers et al., 2014). Characterization of the composition of microbial communities in some shower hoses collected at this hospital prior to CSI has also been reported (Soto-Giron et al., 2016).

This Cincinnati hospital was the first facility to be regulated by the state of Ohio primacy agency after CSI installation. The hospital's management worked closely with the state of Ohio

primacy agency (i.e., the Ohio Environmental Protection Agency-OEPA) before installing the CSI treatment. After approval of the hospital's CSI treatment plans and subsequent installation, OEPA classified the hospital as a consecutive public water system (non-community, non-transient), which thus became subject to requirements of OEPA (Swertfeger and Haensel, 2014) under the Safe Drinking Water Act (e-CFR, 2016a). The OEPA set monitoring requirements for in-building water treatment, by considering how the nature of CSI treatment would be expected to impact regulated contaminants in the hospital's drinking water.

Based on that evaluation, the hospital was required to measure copper in water (daily with colorimetric hand-held meter and weekly at certified laboratory) so as not to exceed the copper action level of 1.3 mg/L set in the Lead and Copper Rule (e-CFR, 2016b). It should be noted that aside from the copper action level, a secondary maximum contaminant level (SMCL) of 1.0 mg/L has also been established for copper in the U.S. due to metallic taste and blue-green staining concerns (e-CFR, 2016c). The hospital was also required to measure silver in water (monthly at certified laboratory), so as not to exceed the silver SMCL of 0.1 mg/L, established due to skin discoloration concerns and graying of the white part of the eye (e-CFR, 2016c). The hospital contracted the Greater Cincinnati Water Works (GCWW) to fill the role of Operator of Record for the CSI treatment, and to conduct much of the sampling/reporting for copper and silver to OEPA (Swertfeger and Haensel, 2014).

The hospital was not deemed subject to the Disinfection By-Product Rule and to the Total Coliform Rule, partly because it is located in the center of the main distribution system with relevant sampling already undertaken by the public water utility (GCWW) in adjacent locations, and partly because the nature of CSI treatment was not thought to interfere with those regulated

contaminants in water. The hospital became subject to the Lead and Copper Rule monitoring requirements beginning 2016.

2.2 Research sampling

Sampling for this work was undertaken for purely research purposes, and did not fall under any OEPA monitoring requirements.

2.2.1 Water sampling to assess copper and silver levels

Nine nurse break-room faucets (5 in building A and 4 in building B) were periodically sampled over the course of ~1.5 years, both before CSI (5/13-1/14) and during CSI (2/14-10/14). The faucets were selected to represent various floors in each building (A1, A5, A6, A7, A8 in Building A and B1, B3, B4, B6 in Building B), proximal and distal to the CSI point-of-entry treatment (a higher floor number indicates a more distal sampling location). Water sampling was typically conducted once every month or once every other month [termed (bi)monthly herein].

Hot and cold 250 mL water samples were collected from the selected faucets in the early morning without prior flushing (termed “first-draw” samples). These samples approximate stagnant water due to infrequent overnight water use. However, given that sampling sites were in regularly-used nurse break-rooms with night shifts, stagnation time prior to “first-draw” sampling could not be controlled. Subsequent samples of hot and cold water after 3 minutes of flushing (termed “flushed” samples) were also collected from the two extreme floors of each building, closest (A1 and B1) and furthest (A8 and B6) from the CSI point-of-entry treatment. “Control” water samples were always collected from the incoming water main (i.e., before CSI),

immediately after the CSI unit, and also immediately after the softener of building A. Control samples were collected after a short flush (~10 seconds) to minimize the influence of the brass sampling port on water quality.

In addition, control weekly water samples (50 mL; 10-seconds flush to minimize the influence of a newly installed brass sampling port on water quality) were collected right after the CSI unit by its Operator of Record (i.e., by GCWW) for copper and silver analysis. Those control weekly copper and silver data supplemented the control bi(monthly) data.

2.2.2 Water sample analyses

Total copper and total silver in unfiltered water samples were analyzed in the laboratory using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) according to USEPA method 200.8 (USEPA, 1994). On two of the sampling dates, filtered water samples (0.2 μm filter) were also analyzed for dissolved copper and dissolved silver using ICP-MS. Temperature and pH of hot and cold water samples were analyzed on-site in water aliquots, using a portable meter (HACH MP-6). Water temperature was occasionally verified via a digital thermometer with a stainless steel probe (Fisher Scientific). Water pH was occasionally verified via two pH meters (Hach 40HDQ), each calibrated to account for hot and cold water temperatures according to Schock (2003). Free chlorine residual was also analyzed on-site with a portable meter (HACH Pocket Colorimeter II) using an equivalent method to USEPA Method 330.5 (USEPA, 1983).

Statistical comparison of pre-CSI versus post-CSI average measurements was conducted with 2-sided 2-sample t-tests at the 95% confidence level.

2.2.3 Solid sample analyses

The impact of CSI-treated water on copper pipe and bathroom porcelain surfaces was evaluated for the first time. A stained porcelain urinal was removed to be analyzed by powder X-ray diffraction (PXRD) five months after CSI activation. Stain material was scraped off the urinal and PXRD patterns were obtained with a diffractometer using Cu K α radiation at 1.8 kW (45 kV, 40 mA). Discussions with the facilities' management also offered insights to public perception of the porcelain staining issue.

Sections of copper pipe (~1.5 ft, 3/4 inch) were extracted five months prior to CSI and eleven months after CSI activation, from both the hot and cold water lines in a hospital bathroom that was easily accessible (building B, floor 1; proximal to CSI unit). The pipe samples were cut longitudinally, photographed and then analyzed by PXRD for scale mineralogy of the water contact scale layer following procedures detailed elsewhere (Schock et al., 2014). The pipe samples were also analyzed by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) for scale morphology.

3. Results and discussion

3.1 Baseline free chlorine residual in hot and cold water

Before CSI, free chlorine residual in the incoming water averaged 1.0 ± 0.1 mg/L, based on measurements at the water main (Table 1). By the time incoming water reached the building faucets, free chlorine residual had substantially decreased (Table 1). In particular, the average hot water free chlorine residual was only 0.1 ± 0.1 mg/L (building A) and 0.2 ± 0.2 mg/L (building B) and 3 minutes of flushing did not increase either residual (Table 1). These results confirmed the

expectation that chlorine residual can be nearly depleted in hot water lines of some large buildings (Pruden et al., 2013), possibly due to plumbing configuration (e.g., hot water recirculation) and longer residence time in conjunction with increased chlorine decay rates at warmer temperatures.

Compared to the hot water samples, cold water samples had higher first-draw free chlorine residuals of 0.6 ± 0.2 mg/L (building A, $p < 0.025$) and 0.5 ± 0.4 mg/L (building B, $p < 0.025$), and after flushing, free chlorine increased to 0.8 ± 0.1 mg/L (building A, $p < 0.025$) and 0.7 ± 0.1 mg/L (building B, $p < 0.025$) (Table 1). A substantial amount of free chlorine was therefore still available for disinfection in cold water lines and flushing further increased the free chlorine residual, unlike the situation in hot water lines.

3.2 Baseline temperature in hot and cold water

Prior to CSI, the temperature of hot water drawn from faucets was 28 ± 5 °C in first-draw samples and 38 ± 5 °C in flushed samples of building A, while it was 30 ± 5 °C in first-draw samples and 38 ± 5 °C in flushed samples of building B. Hot water at this hospital is tempered (i.e., blended with cold water to drop its temperature). Indeed, measured hot water temperatures were predominantly below 43°C, the upper limit for tempered water set by the state of Ohio Plumbing Code (Ohio Board of Building Standards, 2013). Flushed water samples were within the ideal temperature range of 32-42 °C for *Legionella* growth (Yee and Wadowsky, 1982).

Prior to CSI, cold water temperature in building A averaged 20 ± 4 °C in first-draw water and 19 ± 6 °C in flushed water. Cold water temperature in building B was similar and mostly below 25

°C, which is not considered optimal for *Legionella* growth but may sustain the pathogen (Bédard et al., 2015).

3.3 Copper and silver levels generated by CSI

The CSI flow cells in this hospital released variable levels of copper and silver during its first year of operation, based on weekly operator monitoring of water collected after the unit. Overall, copper levels exceeded 200 µg/L in 47% of the weekly samples (Figure 2A). If the more recent manufacturer recommendation of 300 µg/L minimum copper was considered, only 22% of samples would exceed the minimum. The occasional random spikes of copper fell within the manufacturer's current desired range (300-800 µg/L), but the majority of copper levels were below the minimum target dose (300 µg/L based on current manufacturer recommendation or 200 µg/L based on prior scientific literature).

Because the mixed electrodes in each flow cell were comprised of 70:30 copper:silver, fluctuations in copper release coincided with fluctuations in silver release, sometimes above the 100 µg/L silver SMCL (Figure 2B). Subsequent desirable reduction in silver release (Figure 2B) resulted in corresponding but undesirable reduction in copper release (Figure 2A). Silver release by the unit was above 20 µg/L in 86% of the weekly samples collected, and it was above the more recently established 30 µg/L minimum intended level in 75% of samples. Overall, the weekly data suggested that silver levels generated by the CSI mixed alloy electrodes were sufficiently high most of the time but exceeded the SMCL on 4 sampling dates. Copper levels were not sufficiently high and did not exceed the LCR AL.

These variable results may partly reflect certain initial challenges in unit operation (e.g., incorrectly balanced flow valves according to the CSI manufacturer, and electric current adjustments to reduce the occasional silver spikes to levels below the silver SMCL. States et al. (1998) also reported highly variable release of copper and silver into the water of another hospital, during initial operation of CSI. Such fluctuations in ion release could go un-noticed depending on the frequency of water sampling. To illustrate, monthly or bimonthly samples from the same sampling port missed the copper and silver spikes captured by weekly sampling. On average, (bi)monthly water samples leaving the CSI unit contained 196 ± 71 $\mu\text{g/L}$ copper and 35 ± 5 $\mu\text{g/L}$ silver, which were statistically similar ($p > 0.025$ for both copper and silver) but less variable than the weekly averages of 220 ± 136 $\mu\text{g/L}$ copper and 48 ± 32 $\mu\text{g/L}$ silver (Figure 2). All the data presented below reflect (bi)monthly sampling rather than weekly sampling, and are snapshots of those specific moments in time.

3.4 Copper and silver in first-draw cold water

Data from individual floors (Figure 3) provide an idea of spatial variability in the two sampled buildings. In building A, the sampling port closest to the CSI unit was A1 (i.e., building A, floor 1), with water averaging 46 ± 9 $\mu\text{g/L}$ copper before CSI and 131 ± 20 $\mu\text{g/L}$ copper thereafter (Figure 3A) ($p < 0.025$). The majority of data in both buildings (i.e., A5, A6, A7, B1, B3, B4 and B6) indicate similar trends for the rest of the sampled taps, with one exception. Copper in water drawn from the most distal sampling port A8 (i.e., building A, floor 8) was 104 ± 13 $\mu\text{g/L}$ on average before CSI, and increased to 121 ± 9 $\mu\text{g/L}$ during CSI treatment, suggesting only a slight improvement (Figure 3B) that was not statistically significant ($p > 0.025$).

Because maintenance work and renovations take place very often in such large buildings, it is possible that copper plumbing in this floor was newer (i.e., not yet passivated), and was thus already releasing more copper to the water due to copper corrosion compared to the other passivated pipes in the remaining floors. In addition, water use at this sampling port is believed to be lower compared to the other sampling ports (based on this room's distal location, as well as discussions with the hospital's facilities' management and with hospital staff on water use patterns), which may also have impacted copper release. For this sampling port, CSI did not substantially improve the level of disinfection protection from ionized copper.

Silver in cold water was sufficiently high (i.e., $>20\text{ }\mu\text{g/L}$) in sampled taps of buildings A and B after CSI activation, with the exception of remote floors A8, A5 (Figure 3B) and B6 (data not shown) where it was insufficient 100%, 80%, and 40% of the time, respectively. Sampling port A8 appears to be the "worst-case", with silver levels never reaching desirable levels. In addition to proximal sites, this type of analysis emphasizes the need to identify and sample distal sites that are used infrequently, and/or that otherwise receive lower levels of disinfectant.

3.5 Copper and silver in hot water removed by softening

Pre-existing softening at the hospital aimed to remove divalent calcium cations (Ca^{+2}) and divalent manganese cations (Mg^{+2}) from the incoming hard water intended for hot water use, in order to prevent their deposition and potential clogging of plumbing components. Depending on the selectivity of the ion exchange resin, this cation-exchange process can also remove desirable cations, such as Cu^{+2} and Ag^{+} generated by CSI. While detailed investigation was outside the scope of this work, cation-exchange softeners have the potential to remove positively charged

ions to a certain extent, depending on the affinity of the cation-exchange resin for a given cation as governed by the specific resin material and resin structure (Edzwald, 2011).

Indeed, cupric ions dosed by the CSI unit into the water were inadvertently removed by the softener of building A (located on floor A2), as evidenced by only 30-65 µg/L copper measured in water coming out of the softener, a decrease ranging 50-85% (average decrease of 72%) compared to the copper content of CSI-treated water (Figure 3C). Control water samples were collected after the CSI unit and after the softener, but not right before the softener. Therefore percent removal of copper (and silver) by the softener are estimates based on available data.

Copper levels removed by the softener were replenished by the time hot water reached the sampled taps. This was probably due to corrosion of the abundant copper pipes distributing that hot water within the building. Still, levels of copper measured at the taps were below 200 µg/L (Figure 3C).

Similarly to the removal of copper by the softener, 10-90% (average of 51%) of the added silver was also removed by the softener of building A, depending on sampling date (Figure 3D). While the lost silver could not be replenished in water by the plumbing materials as could copper, some taps in building A occasionally had higher silver levels than what was measured after softener A. This could be due to silver ions already present in the hot water line due to their previous dosing by CSI. It could also be due to the tempering of hot water, by blending it with un-softened cold water which had higher silver concentrations.

Overall, positioning the CSI unit before the softener countered the purpose of CSI treatment for hot water, by removing a large fraction of the added beneficial ions. The removal of copper and silver by softening in other CSI hot water systems has not been reported, possibly because CSI was installed after the softener, thereby avoiding the complication experienced here.

3.6 Copper and silver levels at hospital taps

Based on first-draw cold water samples collected periodically on various hospital floors during the nine months preceding CSI activation, total copper levels were 55 ± 30 $\mu\text{g/L}$ for building A and 50 ± 18 $\mu\text{g/L}$ for building B (Table 1). These levels represent the average baseline copper in the water due to copper pipe corrosion throughout both buildings. After CSI activation and based on similarly collected first-draw samples during the first nine months of CSI treatment, copper levels increased to 132 ± 21 $\mu\text{g/L}$ ($p < 0.025$) in building A and 132 ± 29 $\mu\text{g/L}$ ($p < 0.025$) in building B (Table 1). The contribution of CSI to copper levels in cold water was therefore in the range of 50-100 $\mu\text{g/L}$, and copper was never able to reach the intended level of >200 $\mu\text{g/L}$ (or the newly established intended level of >300 $\mu\text{g/L}$) at any sampled hospital tap.

The inability to reach desirable copper levels could be theoretically explained by restrictions to copper solubility at this water's pH, if chemical equilibrium is assumed. For example, in the best case scenario of the most soluble copper solid formation (fresh cupric hydroxide solid- $\text{Cu}(\text{OH})_{2(s)}$), copper solubility would be less than the CSI target minimum of 200 $\mu\text{g/L}$, based on theoretical modeling predictions (pH=8.5, Dissolved Inorganic Carbon=20 mg C/L, T=25 °C) relying on chemical equilibrium simulations that were conducted by Schock et al. (1995). Assuming chemical equilibrium helps identify thermodynamic tendencies, but the fairly new CSI installation at this hospital likely deviates from this assumption since the constant supply of fresh cupric ions may compete with their thermodynamic tendency to precipitate out of solution. Dissolved copper data collected on 2 sampling dates suggest that the majority of the copper was dissolved shortly after CSI was activated (on sampling dates 3/14 and 5/14) (Table 1). These

limited dissolved copper data collected during early CSI operation, the absence of background dissolved copper data prior to CSI operation (Table 1), and inherent limitations of modeling predictions do not allow drawing definitive conclusions.

For hot water, the deliberate addition of cupric ions through the CSI unit was unable to increase the previous baseline copper levels to more than 114 ± 17 $\mu\text{g/L}$ (building A, $p < 0.025$) and 103 ± 16 $\mu\text{g/L}$ (building B, $p < 0.025$) in first-draw samples (Table 1), with copper possibly further restricted by the higher water temperature.

After CSI activation, silver levels in water were 26 ± 14 $\mu\text{g/L}$ (cold water) and 18 ± 11 $\mu\text{g/L}$ (hot water) in building A, and 28 ± 10 $\mu\text{g/L}$ (cold water) and 20 ± 10 $\mu\text{g/L}$ (hot water) in building B (Table 1). These concentrations were mostly above the minimum intended level of 20 $\mu\text{g/L}$ established in the literature, but below the minimum intended level of 30 $\mu\text{g/L}$ recently adopted by the manufacturer. Unlike copper and based on prior silver solubility modeling by Lin et al. (2002), silver solubility was not expected to be restricted at the water conditions (pH 8.5, approximate 40 mg/L chloride, and $T = 25$ °C), if chemical equilibrium is assumed. Even though unrestricted by the high water pH, silver concentrations measured at this hospital's taps were lower than what was actually dosed and occasionally lower than the recommended minimum dosage, which will be further explored later on.

3.7 Copper and silver levels in flushed water samples

First-draw samples from each tap are thought to represent water stagnating within that short piping branch. Flushed samples are thought to represent water distributed from the CSI unit to the hospital's main plumbing lines. Compared to the (un-flushed) first-draw data, total copper

after flushing was higher in cold water of building A (statistically significant, $p < 0.025$) and higher in building B (not statistically significant, $p > 0.025$) (Table 1). Total copper after flushing was lower in hot water of building A (statistically significant, $p < 0.025$) and of building B (not statistically significant, $p > 0.025$) (Table 1).

As was observed for copper in cold water, flushing is generally expected to increase disinfectant levels compared to the initial (un-flushed) first-draw sample. But it is possible that the substantially warmer temperatures of flushed water in the hot lines (about 10° C higher compared to the first-draw hot water samples, see Table 1) restricted the amount of copper available in hot flushed water (compared to the hot first-draw sample). It is also possible that the effect of the softener in removing dosed ions was more evident in flushed water than in relatively stagnant water, since the removed copper could potentially be at least partly replenished by copper corrosion during stagnation of water within the copper piping branch/brass faucet. Compared to the first-draw samples, total silver after flushing was higher in cold water of buildings A and B (Table 1) ($p < 0.025$ in both buildings).

The CSI manufacturer for this specific hospital recommends to flush distal sites at least twice a week, in order for sufficient copper and silver to reach those taps (Liquitech, 2014). The hospital was not implementing such a flushing protocol when the study was conducted, but results indicate some benefits of a 3-minute flush for cold water only, in increasing copper, silver and even free chlorine levels reaching the taps (Table 1). The similar or lower copper, silver and free chlorine levels measured in flushed hot water (compared to first-draw samples) do not make obvious the benefit of a 3-minute flush for hot water.

3.8 Extensive staining of bathroom porcelain

Approximately two months after CSI activation, observations of aesthetically displeasing purple/grey stains on bathroom porcelain across hospital buildings A and B were brought to the attention of the facilities' management. The stains were consistently observed on the porcelain of urinals and toilets (Figure 4), but rarely on porcelain sinks. Analysis by PXRD identified the purple/grey urinal stains as comprised of chlorargyrite [AgCl_(s)] (Supplemental Figure S1). Chlorargyrite is an insoluble precipitate that formed when the dosed Ag⁺ ions combined with the Cl⁻ ions that were already present in Cincinnati tap water (Cl⁻=36 mg/L on average for treated Miller plant water (GCWW, 2014)), based on the following reaction:

Even though the stained urinal porcelain sample was overwhelmed by other background porcelain constituents (Supplemental Figure S1), mineralogical identification of chlorargyrite is visually consistent with the color observed on the porcelain, because photodecomposition of the normally white AgCl_(s) results in appreciable grey/purplish coloration (Peters et al., 1974).

The silver precipitate was observed on bathroom porcelain that solely receives cold water for flushing. It rarely formed on bathroom sinks, which utilize hot water along with cold water. Thermodynamics indeed favor formation of the precipitate at colder rather than warmer temperatures, based on temperature correction of the precipitation reaction's equilibrium constant through the Van 't Hoff equation (Stumm and Morgan, 1996), which yields $K=1.06 \times 10^{10}$ at 18 °C versus $K=2.21 \times 10^9$ at 36 °C. It is also possible that silver levels were sufficient in cold water for formation of the silver chloride precipitate, but were not sufficient in tempered hot water due to silver removal by softening (see Table 1).

Discussion with the facilities' management revealed that the stains were resistant to the common cleaners used by the hospital's cleaning crew, became more visible as time passed, and created concerns to patient families and clinical staff about the safety of water for consumption/use by immuno-compromised patients and for laboratory analyses. Taste, odor or black water complaints were not reported. After the hospital's Occupational Safety and Employee Health Office issued a notice to assure of an aesthetic nuisance only, concerns were reportedly minimized.

The porcelain staining problem at this hospital persisted for the first nine months of CSI operation and, in the absence of any known *Legionella* illnesses at the time, partly led to temporary inactivation of the CSI treatment. Inactivation stopped the staining of bathroom porcelain that had been previously cleaned with an aggressive hydrofluoric acid cleaner. Once CSI treatment was indefinitely inactivated, sampling for this project was terminated.

3.9 Plating of reduced silver onto copper pipes

Hot and cold water copper pipes collected from the hospital before CSI treatment had various copper mineral formations identified via PXRD (Figure S2). There were no silver solids identified in either hot or cold water pipes before CSI, as expected (Figure S2). Copper orthophosphate solids, presumed to interfere with copper efficacy in eradicating *Legionella* (Lin et al., 2006), were not identified by PXRD on any of the analyzed pipes.

For hot and cold water pipes collected after CSI treatment, $\text{AgCl}_{(s)}$ was not identified by PXRD on any of the pipe samples (Figure S2), unlike the situation with the urinal porcelain samples (Figure S1). Instead, elemental silver (Ag^0) was identified both in hot and cold water

lines by PXRD analysis (Figure S2). This suggested that Ag^+ ions from the more cathodic silver metal were reduced to Ag^0 and were directly deposited and plated onto the surface of the more anodic copper pipe. Similar silver deposition was observed unexpectedly during a nanomaterials' synthesis experiment (Nadagouda and Varma, 2008) when a dilute aqueous solution of Ag^+ was placed on the surface of a copper grid to obtain TEM (transmission electron microscopy) images.

In the context of potable water systems, based on the electromotive force series (Table 2), when soluble ions from a more noble metal (such as silver) are present in the drinking water flowing through a copper pipe, they can be directly deposited and plated onto the copper surface, potentially corroding the underlying copper metal due to deposition corrosion. Metallic deposition has previously been observed between common plumbing materials like copper-galvanized steel and copper-lead (Clark et al., 2015), and the same electrochemical theory would apply to copper-silver in potable water plumbing.

SEM analysis of the copper pipes reinforced the PXRD finding of silver plating onto the copper pipes, by revealing impressive silver dendrite structures deposited on the copper pipe surfaces (Figure 5). Such elemental silver deposits were observed at various locations throughout the pipe surfaces (Figure S3), were confirmed to consist of silver based on EDS mapping (Figure S4) and made the pipes glitter to the naked eye. Deposition of reduced silver can help explain the occasionally lower silver levels measured in water samples, compared to the levels supplied by the CSI unit.

Obviously, silver deposition from the water onto the pipes will have implications on its disinfecting ability for bulk water and for biofilms, and this aspect needs to be critically examined by microbiologists. Secondly, deposition corrosion of the underlying copper pipe

could in theory damage the integrity of the pipe and increase copper contamination of the water (Rhoads et al., 2014; Pruden et al., 2013; Clark et al., 2011).

Deposition corrosion of copper in this instance was not evident, because the copper levels measured in water of hospital taps did not increase, and because SEM imaging revealed smooth rather than disturbed surfaces of copper pipe around the deposited silver (Figures 5 and S3). This may be due to the vast surface area of the copper pipe (anode) compared to the deposited silver (cathode), copper solubility restrictions dictated by this water's elevated pH, the crystalline form of the newly deposited silver, or other parameters that did not (yet) activate the micro-galvanic corrosion cells to trigger deposition corrosion of copper.

This is the first time that silver deposition onto copper pipes was definitively confirmed by PXRD and SEM/EDS. Analysis of copper pipes at other hospitals with years of CSI treatment is strongly encouraged, to build upon this first documented field experience and to offer longer-term insights to its implications.

4. Conclusions

A tap water sampling approach (hot and cold water, first-draw and flushed, two different buildings and different floors within each) was supplemented with copper pipe surface analysis and bathroom porcelain surface analysis, in order to explore the fate of copper and silver ions during the first nine months of CSI water disinfection at a large US hospital:

- Copper and silver levels generated by CSI were variable during the first nine months of treatment.

- Silver released by CSI occasionally exceeded the SMCL during weekly sampling while copper never exceeded the LCR AL.
- Mostly sufficient silver ($>20 \mu\text{g/L}$) and mostly insufficient copper ($<200 \mu\text{g/L}$) reached hospital taps during (bi)monthly sampling.
- The cation exchange softener installed in building A for hot water treatment countered the CSI treatment, by removing an average 72% of the added copper and 51% of the added silver ions. CSI treatment for hot water systems should therefore be installed after softening.
- Visually displeasing purple/grey staining in bathroom porcelain after CSI activation was attributed to $\text{AgCl}_{(s)}$.
- Negative reactions to the staining underscore the importance of public perception, and led the hospital to consider alternatives that would eliminate the staining.
- Deposition of metallic silver onto copper pipes after CSI activation was verified for the first time and could be explained by electrochemical interaction between dosed silver ions and metallic copper.
- Overall, supplementing a tap water sampling approach with pipe analyses and with bathroom porcelain helped to better understand the interaction between CSI-treated water and building plumbing materials.
- The copper pipe observations in particular emphasize the importance of extracting and analyzing pipes hidden inside walls, in order to proactively identify interactions not visible to the naked eye.

5. Practical Implications

It is critical to note that the aesthetic and other implications of CSI observed in the sampled hospital during early operation (<1 year of CSI) do not reflect every other CSI installation. The incoming water's pH=8.5, the CSI treatment location at the point of entry as complicated by subsequent softening, and possibly other factors resulted in certain challenges that may not be encountered in other facilities, but that should be considered when evaluating in-building disinfection options.

Overall, although the primary aspect of CSI in this and other hospitals is the effect on controlling *Legionella* and other pathogens in water, non-microbiological implications such as the plumbing material interactions and aesthetic implications presented herein are also new territory and deserve exploration to holistically evaluate in-building drinking water disinfection.

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Figures and Tables

Figure 1. Three Copper-Silver Ionization (CSI) cells with three corresponding controllers (left) treated incoming water intended for both hot and cold uses. Inside a CSI cell with “fresh” (unused) 70% Cu-30% Ag electrodes (middle). Inside a CSI cell with used electrodes (right).

Figure 2. Total copper (A) and total silver (B) in hospital water during the first year of CSI. Levels after the CSI unit are compared to levels before the unit (i.e., from the water main).

SMCL: Secondary Maximum Contaminant Level; LCR AL: Lead and Copper Rule Action Level; Min. Intended refers to the minimum concentrations typically required for *Legionella* control, based on the literature.

Figure 3. Copper and silver in cold tap water (A, B) and hot tap water (C, D) before/after CSI, in different floors of hospital building A. Cold water intended for the hot water line passed through a softener after CSI (i.e., Softener A), but cold water from the CSI blend intended for the cold water line did not.

Table 1. Temperature, pH, chlorine, copper and silver levels in water measured at the water main versus at hospital faucets pre-CSI (5/13-1/14) and post-CSI activation (2/14-10/14).

Mean±STDEV	Water Main		CSI Blend	Building A 5 faucets combined (A1, A5, A6, A7, A8)				Building B 4 faucets combined (B1, B3, B4, B6)			
	Pre-CSI N=4	Post-CSI N=5	Post-CSI N=5	Cold Water N=45		Hot Water N=45		Cold Water N=36		Hot Water N=36	
				Pre N=20	Post N=25	Pre N=20	Post N=25	Pre N=16	Post N=20	Pre N=16	Post N=20
T (°C)	18±9	17±7	15±8	20±4 <i>19±6</i>	22±4 <i>17±8</i>	28±5 <i>38±5</i>	35±5 <i>42±4</i>	24±5 <i>21±6</i>	21±4 <i>19±2</i>	30±5 <i>38±5</i>	32±5 <i>44±4</i>
pH	8.5±0.2	8.5±0.1	8.5±0.1	8.4±0.2 <i>8.4±0.3</i>	8.5±0.1 <i>8.6±0.1</i>	8.6±0.2 <i>8.6±0.2</i>	8.6±0.1 <i>8.5±0.2</i>	8.4±0.2 <i>8.4±0.1</i>	8.5±0.2 <i>8.5±0.1</i>	8.5±0.2 <i>8.6±0.2</i>	8.7±0.2 <i>8.5±0.2</i>
Free Cl ₂ (mg/L)	1.0±0.1	1.0±0.1	0.8±0.1	0.6±0.2 <i>0.8±0.2</i>	0.5±0.3 <i>0.8±0.1</i>	0.1±0.1 <i>0.1±0.1</i>	0.2±0.2 <i>0.1±0.1</i>	0.5±0.4 <i>0.8±0.1</i>	0.6±0.2 <i>0.7±0.1</i>	0.2±0.2 <i>0.1±0.1</i>	0.1±0.1 <i>0.1±0.1</i>
Cu _{total} (µg/L)	9±8	7±7	196±71	55±30	132±21 <i>187±27</i>	67±15	114±17 <i>90±4</i>	50±18	132±29 <i>210±60</i>	64±17	103±16 <i>70±36</i>
Ag _{total} (µg/L)	BD	BD	35±5	BD	26±14 <i>37±1</i>	BD	18±11 <i>6±3</i>	BD	28±10 <i>39±3</i>	BD	20±10 <i>21±10</i>
Cu _{dis} (µg/L)*	-	-	-	-	119±23 <i>158±23</i>	-	117±15 <i>85±3</i>	-	119±10 <i>158±15</i>	-	99±6 <i>66±36</i>
Ag _{dis} (µg/L)*	-	-	-	-	22±16 <i>32±3</i>	-	22±9 <i>5±3</i>	-	23±4 <i>36±4</i>	-	15±10 <i>19±8</i>

BD Below Detection of 0.05 µg/L

- Not measured

Italics (where available in the second row) represent flushed water samples (3 minutes) for combined faucets A1/A8 and B1/B6 only.

* N=10 for dissolved metals after CSI (measured on 2 sampling dates only-3/14 and 5/14-, as opposed to 5 sampling dates for total metals)

Figure 4. Purple/grey staining was consistently observed in bathroom porcelain of buildings A & B, specifically on toilets (left) and urinals (right), but rarely on porcelain sinks, soon after CSI was activated. The stains followed the streaks of cold water flowing through the porcelain during water flushing.

Table 2. Standard electrode potentials for copper and silver in aqueous solutions at 25 °C vs. standard hydrogen electrode (Jones, 1996)

Reaction	Potential, V	Implication
$\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag}^0$	+0.799	More Noble (Cathodic)
$\text{Cu}^{+2} + 2\text{e}^- \leftrightarrow \text{Cu}^0$	+0.342	More Active (Anodic)

Figure 5. Impressive silver dendrite structure deposited onto copper pipe (hot water line) at different SEM magnifications (x200 to x4,000). The copper pipe was removed from the hospital after 11 months of CSI. The reduced silver that deposited onto the copper pipe surface made it glitter to the naked eye (not shown here).