DEVELOPMENT AND EVALUATION OF POINT-OF-USE WATER TREATMENT TECHNOLOGIES USING SILVER AS A DISINFECTION MECHANISM

A Dissertation

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Doctor of Philosophy

by

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ABSTRACT

Point-of-use water treatment technologies that use silver as a disinfectant have been shown to be effective by killing disease-causing bacteria and preventing potential recontamination during transport and storage in rural areas. However, current commercially available technologies require up to 8 hours for disinfection or use silver nanoparticles, which is not as efficient for disinfection as silver ions. In an effort to find solutions to these shortcomings, the release of silver and copper through electrolytic generation as a new point-of-use disinfection mechanism was examined. Electrolysis has previously been used in water treatment, but never in a low-resource, point-of-use setting.

In the laboratory a series of experiments were conducted to establish a proof of concept for an electrolytic point-of-use device. Two voltages common to commercially available batteries, 4.5 volts and 9 volts, were applied to a point-of-use apparatus with either two silver or copper wires submerged 1 inch into 10 liters of synthetic groundwater. In addition, the effects of wire diameter, ionic strength of groundwater, and other possible POU parameters on metallic ion release were examined. Silver levels measured over time by graphite furnace atomic absorption spectroscopy established a proof of concept that this kind of technology could be practically implemented in a point-of-use water treatment device in a rural setting. It was determined that the apparatus including only silver wire should be run for only 2 minutes at 9 volts to yield the target 50 ppb concentration for water treatment. Further, this conclusion was supported when 50 ppb electrolytically generated silver from the apparatus yielded up to a 5 log reduction of E. coli bacteria in synthetic groundwater. Copper was less effective in disinfection and also required 62 minutes to release the target 500 ppb for disinfection when 9 volts were applied to the system.

Based on this work, an electrolysis POU prototype was developed and evaluated in 20 households in Limpopo, South Africa over four weeks. The electrolysis prototype achieved a 2 log reduction in total coliform bacteria in household drinking water, which is comparable to field performance of other point-of-use devices in low-resource settings. It also consistently released enough silver sufficient for disinfection but below the WHO drinking water guideline. The use of electrolysis in a POU water treatment device is promising technology, and the field performance of the prototype suggests that such a technology could be incorporated into a low resource setting.

In tandem with the work on this new technology, the long-term performance of two established POU technologies were also evaluated. The first technology, a silver-impregnated ceramic tablet (MadiDrop), disinfect water by releasing silver ions into household water-storage containers. The second, a silver ceramic water filter, mechanically removes pathogens through filtration. It is also painted with a silvr nanoparticles solution that reduces live pathogens and provides a residual disinfectant to reduce the risk of recontamination in the lower reservoir.

404 homes in Limpopo, South Africa were randomized to receive a MadiDrop, silver ceramic water filter, safe-storage water container, or no intervention. The disinfection of total coliform and *E. coli* bacteria for each intervention was measured every six months over two years. The MadiDrop's disinfection of total coliform bacteria (3.22 ± 0.27 log reduction) exceeded the performance of silver ceramic water filters (1.80 ± 0.35 log reduction) and filters without silver (1.18 ± 0.25 log reduction). Safe-storage water containers did not improve water quality (0.01 ± 0.27 log reduction). After intervention adjustments, silver concentrations in treated water were 31.8 ± 36.7 µg/L for the silver ceramic filter intervention arm and 27.4 ± 39.1 µg/L for the MadiDrop intervention arm. These mean silver concentrations were less than the

100 µg/L World Health Organization guideline for silver in drinking water. MadiDrop longevity, based on consistent silver-ion release rate, was determined to be at least 12 months of daily use.

Results suggest that an electrolytic apparatus is promising technology for point-of-use water treatment and warrants further optimization of the device. Although copper by itself is not suitable for electrolytic disinfection, it still has potential to be introduced in a silver and copper system, as it would allow for more disinfection potential while still remaining under the EPA limit for metals in drinking water. In addition, this body of work affirms that MadiDrops and filters are effective in disinfecting household drinking water in low-resource settings, but there are opportunities to optimize the products by decreasing silver release.

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PUBLICATIONS AND PRESENTATIONS

This dissertation has resulted in the following publications:

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In Preparation: Hill, C., Smith, J., Gaylord, A., Hatley, M., Hardcastle, L., Renneker, K., "Incorporation of Electrolytic Release of Silver and Copper Ions into a New Point-of-use Drinking Water Treatment Intervention for Disinfection in Resource Limited Settings"

Under Review: Hill, C., et al, (2020) "Impact of low-cost point-of-use water treatment technologies on enteric infections and growth among children in Limpopo, South Africa," American Journal of Tropical Medicine and Hygiene.

Hill, C., Smith, J., (2019) "Electrolytic Release of Metal Cations in Water," Encyclopedia of Water: Science, Technology, and Society, 1-10.

Edokpayi, J., Rogawski, L., Kahler, D., Hill, C., et al, (2018) "Challenges to Sustainable Safe Drinking Water: A Case Study of Water Quality and Use across Seasons in Rural Communities in Limpopo Province, South Africa," Water Vol. 10, Issue 2.

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Beddow, T., Sutton, M., Taylor-Fishwick, E., Hill, C., "Developing and Implementing Sustainable Ceramic Technologies to Improve Water and Health in Developing Communities", Clinton Global Initiative University, Chicago, IL

Taylor, D., Wright, N., Hill, C., McCain, K., Rogawski, L., Frey, D., (2017) “A continuous objective metric for the usage of household water treatment and safe storage devices,” UNC Water and Health Conference, Chapel Hill, NC

McCarty, B., Hill, C., McCain, K., Lezmez, E., Kim, C., (2017) “Associations Between Drinking Water Source, Enteropathogen Prevalence in Child Stools, and Child Growth in rural communities in Limpopo Province, South Africa,” UNC Water and Health Conference, Chapel Hill, NC.

Hill, C., (2016) “Effectives of point of use water treatment technologies to prevent stunting among children in Limpopo, South Africa”, UNC Water and Health Conference, Chapel Hill, NC

Chapter 1: Introduction

1.1 INTRODUCTION

More than 2 billion people lack access to a safely managed drinking water source, which is defined by the World Health Organization as drinking water free of contamination that is available when needed.[1] Of these 2 billion, 844 million people lack access to basic a basic drinking water service, defined as having a protected drinking water source that takes less than 30 minutes to collect from[1]. Water sources that are not safely managed are at risk for contamination by harmful pathogens, and those who use these sources are at risk to contract water-borne diseases such as cholera, typhoid, and schistosomiasis.[2,3] Contaminated drinking water also causes diarrhea, which kills 361,000 children under 5 every year.[4] In addition, pathogens found in contaminated drinking water may contribute to cognitive impairment and growth stunting as a result of environmental enteropathy.[5]

In urban areas in high resource settings, large-scale, centralized water treatment is used that employs long-distance pipelines that deliver water to households with chlorine serving as a residual disinfectant.[6] This system is effective in protecting against pathogen exposure that cause the negative health outcomes previously described. However, this kind of system is not available in many low-resource settings or even in rural high-resource settings, as these systems are very expensive to maintain and there are many structural challenges to delivering centrally treated water to rural communities.[6] Because of this, many people in low-resource communities using untreated surface or ground water sources for drinking. If these communities do have centralized treated water treatment, it is often piped to a central collection point that requires long distances

for consumers to travel from their house.[7] This poses risk for recontamination during the transport of treated water from the collection point to their home and during the storage of that water before it is consumed.[8]

One solution in the effort to provide global access to clean water is point-of-use (POU) water treatment technologies. POU water treatment technologies are low-cost, effective devices that allow the user to treat water in the home before it is consumed, minimizing the risk of recontamination that can happen during transport and storage if water is only treated at a centralized source.[8] They are also not reliant on state- or community-run water infrastructure, which in low-resource settings can be unreliable and inefficient. These technologies have been shown to be effective in treating household water and reducing diarrhea prevalence in vulnerable populations.[9] Previous studies have shown that POU water treatment can be more sustainable than centralized treatment in resource limited settings.[10]

POU drinking water treatment varies greatly and includes a variety of water treatment techniques and devices. Given that chlorine is an effective disinfectant in centralized systems, it has been proven to be an effective in-home option but it possesses an unappealing taste and odor for some consumers.[11] It has long been known that ionic silver is an effective disinfectant for waterborne pathogenic bacteria,[12,13] and it is currently employed in a variety of POU water treatment technologies, including the Folia Water paper filter, the MadiDrop, pot-shaped and candle-style ceramic filters, and more expensive filtration systems sold by Brita and Aquaphor[14–18]. Incorporating silver into POU technologies has been shown to disinfect bacterial pathogens in water just as well as chlorine, which is used widely in water purification, providing up to a 3.2 log reduction of total coliform bacteria in drinking water[16,19].

This dissertation focuses on the develop of a novel POU water treatment device that employs a new disinfection mechanism, electrolysis. Electrolysis (also known as electrolytic water disinfection) is the process of generating metal ions by inserting a negatively charged metal cathode and positively charged metal anode into water to be disinfected and applying an electric current. In this dissertation, the potential for electrolysis to be employed in a POU device using silver and copper ions, develops a POU prototype based on this work, and evaluates the technology in Limpopo, South Africa. In addition, this dissertation evaluates the performance two commercial POU technologies that employ silver as a disinfectant in households in the same location.

1.2 DISSERTATION AIMS

This research develops a novel point-of-use water treatment technology and assesses current technologies implemented in low resource, rural settings that incorporate ionic silver as a disinfection mechanism. Chapter 2 presents a literature review of the use of silver and copper electrolysis to date. Chapter 3 established a proof-of concept that electrolysis could be used in a point-of-use device in a low-resource setting. This was done by assessing the effects of device parameters on both silver and copper release, the disinfection efficacy of *E. coli* from electrolytically generated metal ions, and the potential of the technology to provide 50 ppb silver daily for one year. Chapter 4 evaluates an electrolysis prototype that was designed based on this proof of concept data. Prototypes were tested over four weeks in 20 households in Limpopo, South Africa. In Chapter 5, the long-term disinfection efficacy of *E. coli* and total coliform bacteria by silver-impregnated ceramic filters and the MadiDrop, a silver embedded ceramic

tablet, was assessed as part of a 2 year randomized control trial examining the health benefits of prolonged use.

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in Two Field Sites: Limpopo Province, South Africa and Dodoma Region, Tanzania. *Water* **2016**, *8* (3), 95. https://doi.org/10.3390/w8030095.

Chapter 2: Literature Review

The work presented in this chapter resulted in a published book chapter.

Hill, Courtney L., and James A. Smith. “Electrolytic Release of Metal Cations in Water.” In *Encyclopedia of Water*, 1–10. American Cancer Society, 2019. https://doi.org/10.1002/9781119300762.wsts0010.

2.1 ABSTRACT

Electrolytic water disinfection via metallic ions is a promising technology for water and wastewater treatment. This approach has relatively limited detrimental environmental effects and does not change the taste or odor of the treated water. The mechanisms of electrolytic silver and copper release were investigated, including the current efficiency, the relation between ion generation and current in the systems, and previously examined water chemistries. A comparison of pathogen inactivation rates and pathogen reduction for various combinations of free chlorine and electrolytically generated silver and copper ions have been previously reported. Silver and chlorine do not disinfect as well as free chlorine, but it can be used in combination with low levels of free chlorine to produce disinfection rates comparable to higher levels of free chlorine. These results lay a strong foundation to investigate the use of electrolytic systems in a developing world context, particularly where water from the municipal tap contains chlorine but is at risk for recontamination during storage. Upon review of the literature, it was found that more research should be conducted to understand how organic loads and water chemistry affect ion generation and disinfection kinetics in these systems.

2.2 BACKGROUND

The final step in water treatment processes is disinfection which inactivates disease-causing organisms in a water supply. This is accomplished through two mechanisms: the provision of primary disinfection that removes or deactivates pathogens in the water and the supply of a residual disinfectant in distribution systems.[1] Inadequate disinfection of drinking water results in a variety of water-borne diseases such as cholera, typhoid, schistosomiasis, and diarrhea.[1] This is important in the context of diarrheal disease being the leading cause of

mortality in children under the age of 5 and is particularly prevalent in low and middle income countries that lack access to adequate water treatment.[2] Effective water disinfection also has implications on providing safe water for medical, food safety, recreational purposes such as swimming pools and even reducing corrosion-inducing bacteria in cooling systems.[2,3]

Chlorine is widely used to achieve both primary and residual disinfection of pathogenic microorganisms. However, while it is highly effective, it possesses an unappealing taste and odor for some consumers, an inability to disinfect certain resistant microorganisms, and contributes to the formation of hazardous products such as chloroform.[1] In addition, the concentrations of hypochlorites required to effectively inactivate *Legionella* could cause corrosion in plumbing systems.[4] Chlorine also has security issues with storage and handling, a high toxicity to non-targeted microorganisms during disinfection, an efficiency dependent on pH and temperature, and a reactivity with ammonia and nitrogen to form chloramines and organic chlorine compounds, reducing potential for disinfection. These issues also affect chlorine's efficiency and safety in disinfecting water for recreational purposes, as organics and bodily fluids from swimmers effect levels of free chlorine in the water, and trihalomethane compounds formed have the potential to absorb through skin.[5]

Due to these concerns, various disinfection alternatives to chlorination have been developed. Electrolytic water disinfection has been developed as one of these alternatives and has been examined for a variety of water treatment applications, as it is a promising tool to treat water without detrimental environmental effects.[3] Specifically, copper and silver electrodes have previously been studied as viable electrode materials as a means for electrolytic disinfection.[3] Ionic copper and silver are slower than chlorine in deactivating microorganisms, but they disinfect in smaller concentrations and are safe, odorless, and provide residual effect.[5] Copper

has been shown to more severely harm coliform than chlorine and cause longer recovery times.[6] Silver ions have the potential to be recovered, rendering electrolytic silver disinfection both economical and environmentally friendly.[7] Silver has also has been incorporated into point-of-use water treatment technologies such as ceramic water filters that treat water in the home when households lack access to a continuous, reliable water source.[8] Both metals have the potential to adsorb to materials' surfaces to potentially provide contact residual against the formation of biofilms that could contain pathogens.[3] There may be ways to treat water in a developing world setting using electrolytic silver/copper alone or in combination with chlorine to provide resilient and sustainable treated water.

While there may be some hesitation about the health effects of ingesting copper and silver, the Environmental Protection Agency (EPA) has established copper and silver maximum of 1000 and 100 parts per billion to be safe in drinking water, respectively.[9] To date, the only detrimental health effect due to silver discovered is argyria, irreversible skin discoloration that occurs due to the administration of high concentrations to individuals, which would require more than 10 g of silver to be ingested over a lifetime.[9]

2.3 ELECTROLYTIC SILVER AND COPPER RELEASE

In this process, metal ions are generated by inserting a negatively charged cathode made of the metal of interest and a positively charged anode made of the metal of interest either directly into the water to be disinfected or into a separate reservoir that is released into the water system.[5] A DC voltage is applied between the electrodes, enabling the release of metal ions from the anode. A schematic of this process is depicted in Figure 2.1.

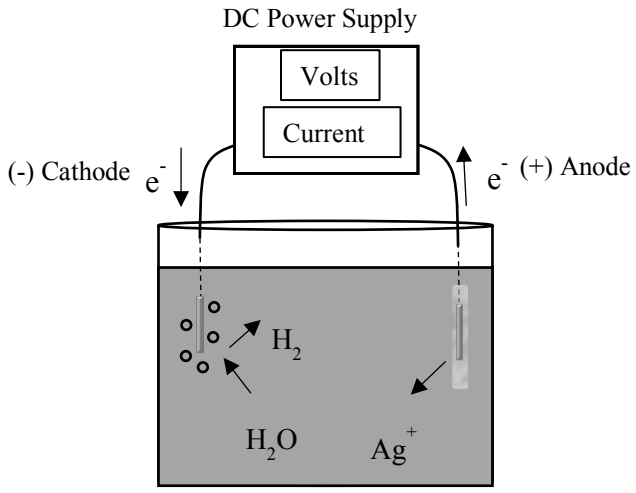

Figure 2.1: Configuration of an electrolytic cell with a metal cathode and anode

In the case of electrodes that are both made of one metal, the following reactions occur:

(a) Silver ions:

At the anode:

$$Ag \rightarrow Ag^{+} + e^{-}$$

At the cathode:

$$H_2O + e^{-} \rightarrow 0.5H_2 + OH^{-}$$

(b) Copper ions:

At the anode:

$$Cu \rightarrow Cu_2^{+} + 2e^{-}$$

At the cathode:

$$H_2O + e^{-} \rightarrow 0.5H_2 + OH^{-}$$

The electrolytic release of copper and silver ions can be described through Faraday's first and second laws of electrolysis. The first law states that the chemical transformation due to the flow of a current through an electrolyte solution is directly proportional to the quantity of electricity passed through it. In accordance with this, the second law states that when the same quantity of charge is passed through the electrolytic cell, the mass of the substance transformed is proportional to the respective equivalent mass or equivalent weight of the substance being transformed. Equivalent weight is defined as being equal to atomic weight of the substance per valency of an individual atom of the substance.[10]

These two laws can be summarized with the following relation[10]:

$$n = \frac{Q}{F} * \frac{1}{z} \qquad \text{Equation 1}$$

where:

n is the number of moles electro-transformed

Q is the total charge passed through the cell

F= 96485 charge/mole of electrons is the Faraday's constant

Z is the ion valency

2.3.1 CURRENT AND METAL ION RELEASE

If the current is constant, *Q* is equivalent to the current applied multiplied by the total time of current application. If it varies, the total charge must be found by integrating the electric current over time.[10] Because electrolytic disinfection adds conductive ions to the electrolyte solution while the current in being applied, resistance in the solution would decrease, and would

theoretically cause an increase in current over time. This increase over time would in turn result in higher ion release, as Equation 1 shows that the total charge passed through the cell is directly proportional to the number of moles of the substance electrotransformed.

While many studies have investigated the efficacy of these systems for inactivation of viruses and bacteria, there has been little previous work that investigates the effect of silver release or copper release on the rise of current in an electrolytic system.[10] Of these studies, one discussed monitoring the current over time.[3] In this experiment, electrolytic silver release from 1 mm thick plates and current data was monitored in distilled water for 50 minutes and yielded an exponential increase in silver over time, representing the synergistic relation between ion and current increase and suggesting that the current be integrated over time in order to accurately predict ionic release (Figure 2.2a). Additionally, data has been collected for current release from 1 mm thick wires over 120 minutes in an electrolyte solution for synthetic groundwater (Figure 2.2b). This experiment yielded a constant current consistent with the original conductivity of the solution, suggesting that current could be assumed as constant over time. The discrepancy between these experiments is likely not because there is a different relation between ionic release and current, but of the electrolyte solution was less conductive in the first experiment. This caused the addition of silver to make a greater impact on the system's conductivity in Figure 2.2a when compared to Figure 2.2b. While silver release and the volume of distilled water for Figure 2.2a is not documented, it is likely the silver release was also far more concentrated in Figure 2.2a, as the first experiment employed 1mm silver plates in contrast to 1 mm wires used in the second.

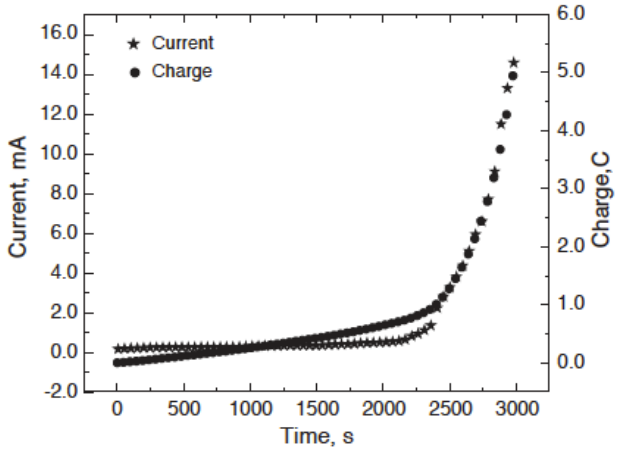

Figure 2.2a: A plot of the current and charge variation as a function of time of silver generation at 5 V in distilled water at room temperature.[3]

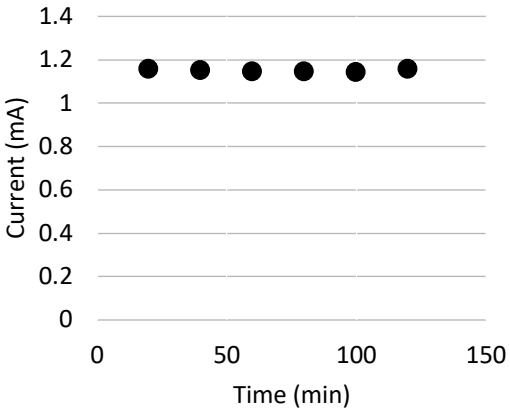

Figure 2.2b: Current and charge variation as a function of time of silver generation at 5 V in synthetic groundwater at room temperature (original data).

2.3.2 PARAMETERS AFFECTING ELECTROLYTIC RELEASE OF METALLIC IONS

It can be seen from Equation 1 that an increase in the total electric charge passed through the cell results in a proportional increase in metallic ion release. As previously described, total electric charge is both a function of time and current (Q=current*time), and so an increase in either parameter would result in a proportional increase in electrolytic release of ions. A study that compared silver ion generation in tap water, a sodium nitrate electrolyte solution, a sodium sulfate electrolyte solution, and distilled water found that distilled water was best for silver production because the other solutions tested formed precipitates with the silver ions (AgCl, $AgSO_4$, etc.) which decreased the amount of silver in the water for disinfection.[3] There is also documentation that electrodes developed oxidized surfaces over time, requiring either electrode cleaning or replacement. Studies discussed different thresholds of parameters to indicate the need for cleaning electrodes: a specified interval of time (30 days), minimum amperage (2 amperes) in the cell, or minimum copper concentration in the cell (0.1 ppm).[11] One study cleaned electrodes

very frequently, every 3000 seconds.[3] These parameters were dependent on the electrolytic cell configuration, required ion generation, and the cell's potential to meet the demands for ion generation.

2.3.3 CURRENT EFFICIENCY

The Faradaic or current efficiency of an electrolytic cell describes the efficiency with which electrons are transferred into the cell.[12] Losses in efficiency occur due to ions used in unintended reactions other than disinfection. This can either be due to heat or the formation of by-products of the solvent as shown by the cathode reaction equations previously for the electrolytic release of silver and copper ions.[13] Current efficiency in electrolytic systems can be described by Equation 2:

$$\phi = \frac{n}{N} \qquad \text{Equation 2}$$

where:

ϕ is the current efficiency of the electrolytic cell

n is the number of moles of the substance theoretically liberated

N is the number of moles of the substance actually liberated

The term n is determined through Equation 1 and N should be determined through analytical methods. The efficiency by which electrons are transferred during electrolysis has rarely been discussed in the literature. However, one study reported silver and copper electrolysis provided current efficiencies of 50% and 65% in distilled water, respectively.[3] This poses a challenge in calculating the amount of silver or copper being dosed into the water, and that more

study of water parameters and electrolytic cell configuration effects on current efficiency should be conducted to better understand metallic ion release mechanisms. This is important because silver and copper must be delivered under the Environmental Protection Agency regulations of 1000 parts per billion copper and 100 parts per billion silver, otherwise the electrolytic cells would be unfit as a drinking water treatment method.

2.4 DISINFECTION KINECTICS

Ideally, microorganisms of the same species are distinct units equally susceptible to a single type of disinfectant, both microorganisms and the disinfectant are evenly dispersed, and the disinfectant remains unchanged in chemical composition and constant in the concentration in water with no interfering substances. When there is uniform dispersion, constant chemical composition, no interfering substances, and equal susceptibility, the rate of disinfection is first order as a function of contact time, disinfectant concentration, and water temperature.[14] Many studies only present results through reports of $\log_{10}$ or percent reduction and do not demonstrate that first order kinetics were observed. However, first order kinetics were confirmed for *Staphylococcus* sp. when exposed to free chlorine alone and in combination with electrolytically produced silver ions and copper ions in tap water containing urine and bath water and in well water.[5] A swimming pool simulation experiment did not release data over time, but indicated first order inactivation of *Legionella pneumophila, Staphylococcus aureus, Staphylococcus* sp., *Escherichia coli,* and *Streptococcus faecalis* exposed to combinations of copper ions, silver ions, and free chlorine. The disinfection of *Legionella pneumophila* was also confirmed to be first order in 100 mL of filtered well water.[4] In addition to bacteria, first order disinfection rates for the amoeba form of *Naegleria fowleri* and MS-2 virus in well water were reported for different

combinations of free chlorine, copper ions, and silver ions as well.[15,16] A summary of these values are provided in Table 2.1 in descending order of inactivation rate (*k*), for each pathogen reported in the literature.

Table 2.1: First-order disinfection rate coefficients reported in the literature for different microbial pathogens at different free chlorine, copper, and silver concentrations

Pathogen	Source	Free Chlorine (ppm) / Copper (ppb) / Silver (ppb) concentration	Inactivation Rate, *k* (min^{-1})
Staphylococcus sp.	(7)	0/491/52	$9.0x0^{-4}$
	(7)	.8/0/0	1.7
	(7)	.25/595/85	2.8
	(15)	.2/0/0	2.8
	(15)	.2/400/40	3.0
L. pneumophila	(4)	0/200/20	$9.8x10^{-4}$
	(4)	0/400/40	$2.9x10^{-3}$
	(4)	0/800/80	$7.5x10^{-3}$
	(15)	.1/0/0	.31
	(15)	.1/400/40	.49
	(15)	.2/0/0	.90
	(4)	.2/0/0	1.1
	(4)	.2/400/40	1.3
	(4)	.3/0/0	1.6
	(4)	.2/800/80	2.0
	(15)	.2/400/40	2.2
	(4)	.3/400/40	2.3
	(15)	.3/0/0	2.3
	(4)	.3/800/80	2.6
	(15)	.3/400/40	2.7
	(15)	.4/0/0	5.0
	(15)	.4/400/40	5.8
Streptococcus faecalis	(15)	.2/0/0	3.8
	(15)	.2/400/40	6.2
	(15)	0/391/0	.31
E. coli	(15)	0/0/62	1.8
	(15)	0/530/67	2.9
	(15)	.2/0/0	3.2
	(15)	.2/400/40	7.4
Pseudomonas aeruginosa	(15)	.2/0/0	8.9

	(15)	.2/400/40	9.8
MS-2 virus (14)	(15)	.3/0/0	11.2
	(15)	.3/400/40	13.4
Naegleria fowleri	(16)	.1/0/0	.33
	(16)	1/400/40	.48
	(16)	1/800/80	.52

There is little overlap between the type of pathogens tested in the literature as can be seen in Table 2.1. However, some comparisons can be made. Overall, it can be seen that the concentration of the free chlorine dose added to each system was most influential on the inactivation rates compared to the concentration of silver or copper ions. This trend is consistently seen within individual experiments and when comparing inactivation rates of *Legionella pneumophila* from different experiments.[4,15] In the same trend, it can be observed that copper and silver ions added to a given amount of free chlorine consistently increase the inactivation rates, and often were added to a lower dose of chlorine to produce the inactivation rates comparable to a higher dose of free chlorine alone.

With the exception of one experiment, all inactivation rates found in the literature were measured in groundwater at room temperature in various water chemistries. Many studies failed to report water chemistry parameters, making a true comparison of inactivation rates difficult. One study found that the effects of pH and temperature have no appreciable effect on the performance of biocide systems.[3] In contrast, it has also been observed that copper and silver disinfection can be influenced by pH, chlorides, phosphates, and calcium ions.[17] Another study found that copper and silver release increased with increased water temperatures.[4] However, this association was not statistically significant (disinfection rate (k)=1.077 and 1.322 in lower temperatures compared to 1.186 and 2.559 for free chlorine and free chlorine in combination with silver and copper, respectively).[4] The reported physiochemical characteristics of the water from the literature are included in Table 2.2.

Table 2.2: Physiochemical Characteristics of Water Used in Disinfection

	Source						
Physiochemical Characteristics of Water	**4**	**5**	**5**	**7**	**7**	**9**	**9**
pH	7.9	8	7.8	7.72	7.53	7.6	7.77
Alkalinity (mg $CaCO_3$/L)	110	390	98	53.1	49.3	X	X
Turbidity (NTU)	0.21	X	X	1.13	4.73	0.77	0.91
Total Hardness (mg CaCO3/L)	92	X	X	213	X	X	X
Nitrate (mg/L)	3.5	X	X	2.58	4.22	5.754	X
Conductivity (mS/cm)	0.414	X	X	X	X	.672	.709
Ammonia (mg/L)	0.31	X	X	X	X	0.643	X
Phosphate (mg/L)	X	19	6	X	X	1.1	X
Magnesium (mg/L)	X	120	32	X	X	X	X
Sulfate (mg/L)	74	20	22	X	X	X	X
Chloride (mg/L)	30	110	75	X	X	X	X

In one of the studies included in Table 2.1, bath water and urine were added to the experimental apparatus in order to simulate the organic loads from swimmers in pools.[5] It can be seen that the inactivation rates of *Staphylococcus* sp. determined from this experiment are much lower than the rates reported for well water only. This was due to organic demands from urine and bath water introduced to the system,[5] which highlights the need to further study the effect of increased organic loads on silver and copper disinfection. With the exception of this study, this relation has not been previously studied, and is vital in order to understand the applicability of silver and copper ions for disinfection in drinking and recreational water treatment. This is particularly important if this technology were to be used as a water treatment method in developing countries, given that the organic loads of water disinfected immediately after collection from the source and/or stored in the home would be far higher than water reaching the disinfection stage in a conventional wastewater treatment plant.

One advantage of disinfection with silver and copper when compared to free chlorine is

that chlorine concentrations were shown to decrease dramatically during disinfection.[5,13] In a continuous flow water system loaded intermittently with bath water and urine in an outdoor atmosphere, there was no free chlorine detected 3-4 hours due to organic demands previously discussed, exposure to high temperature, and solar radiation. An identical indoor system observed similar but slower decreases with some residual up to the next morning.[5] In a study of the disinfection of various human enteric viruses, values of free chlorine were 79%, 35,%, and 29% of original values of 0.94, 0.51, and 0.17 mg/L of free chlorine, respectively, after 30 minutes. In the same study, 75% and 44% percent of electrolytically generated copper and silver remained after 60 days, respectively.[13]

Theoretical first order disinfection kinetics were easily replicated in experiments for bacteria, *Naegleria fowleri,* and MS-2 virus over short periods of time. However, an experiment investigating the disinfection of various human enteric viruses in well water by copper, silver, and free chlorine yielded inactivation kinetics that ceased to be truly first order when carried out over longer periods of time.[13] This phenomenon is depicted in Figures 2.3a-b. Figure 2.3a was taken from a disinfection experiment of *Staphylococcus* sp. in well water over 2 minutes with 0.8 mg/L of free chlorine alone and 0.25 mg/L free chlorine in combination with 595 and 85 ug/L copper and silver, respectively.[5] Figure 2.3b displays the disinfection of a variety of human enteric viruses in well water with exposure to 0.2 mg/L free chlorine in combination with 700 ug/L and 70 ug/L copper and silver, respectively. It can be seen that the data in Figure 2.3a fit a first-order kinetic model. In Figure 2.3b, similar doses of free chlorine/silver ions/copper ions are used, but the plots are distinctly concave up. However, if you exclude the early time data, they are approximately linear. This shows that disinfection (k) rates reported in the literature could not be indicative of true performance if duration of the experiment is not long enough, and that

further studies should be done on longer term bacterial and amoeba disinfection to better understand and more accurately predict disinfection kinetics in the field.

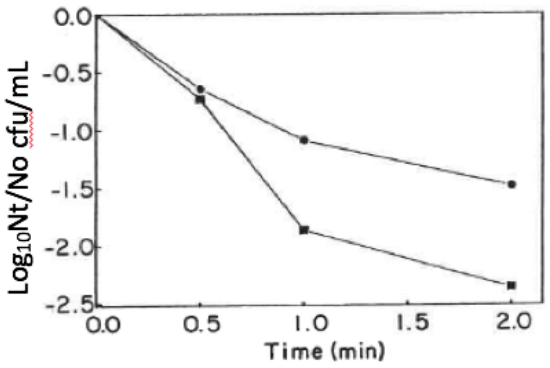

Figure 2.3a: Reduction of *Staphylococcus* sp. Numbers in water systems after exposure to ❁, Free chlorine (0.8 mg/L) ■, copper:silver (595 and 85 ug/L copper and silver respectively) and free chlorine (0.25 mg/L)[5]

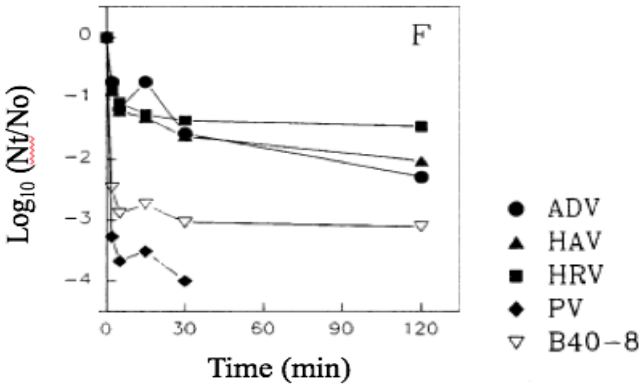

Figure 2.3b: Inactivation of human enteric viruses by free chlorine (0.2 mg/L) and copper (700 ug/L) and silver ions (70 ug/L) for adenovirus (ADV), hepatitis A virus (HAV), human rotavirus (HRV), poliovius (PV), and Bacteriophage B40-8 (B40-8)[13]

While the cause of the observed inactivation kinetics is not fully understood, virus aggregates were detected via electron microscopy in test samples treated by disinfection combinations including silver and copper ions.[13] It has been documented that viruses persist for longer periods of time when they form aggregates as opposed to their presence as individual particles and that divalent cations have been reported to induce virus aggregation.[4,18,19] Because of this, it is likely that electrolytically generated Cu^{2+} ions influenced the disinfection kinetics of the viruses in this study. Unfortunately, data for the disinfection of silver ions or copper ions in combination with chlorine was not tested in the study, so an association between silver and aggregation of these viruses was not determined.

However, the presence of Cu^{2+} alone cannot account for the bimodal kinetics observed in inactivation curves, as the inactivation kinetics observed for free chlorine alone in these experiments also did not exhibit first order behavior.[13] A likely explanation is that in the absence

of proper evidences, the reported first order disinfection kinetics reported in reality are pseudo-first order kinetics, and the data did not fit to a first order disinfection kinetic because one of the reactants was not in excess. This behavior could also be due to various environmental factors, such as temperature, light, pH, dissolved oxygen or halogen demand of the sample, which could affect microorganism susceptibility to silver and the interaction of copper and silver.[20-23] Disinfection kinetics could have also been affected by well water constituents which could have caused silver or copper ions to precipitate out of the solution.

2.4.1 DISINFECTION OF BACTERIA

Microorganisms develop charged surfaces due to the ionization of prototrophic groups such as carboxyl, amino, guanidyl, and imidazole groups, creating a net negative charge on organisms near a neutral pH.[24-25] Silver and copper are attracted to these negatively charged organisms and undergo reactions at the surface. These metal ions can also attack DNA, RNA or enzymes through combination with carriers or the presence of special channels in the cell membrane.[9] They also oxidize sulfhydryl groups, inhibiting enzymatic activity and also binding to nucleic acids.[26-29] The binding to sulfhydryl groups impairs bacterial respiration.[30] Domek et al, found that exposure of *E. coli* to copper impaired respiratory enzymes resulting in the use of fermentative processes rather than aerobic pathways.[31] Silver and copper in combination have been shown to have a synergistic effect: positively charged copper ions form electrostatic binding sites with negatively charged binding sites on the cell wall, resulting in a weakening of the cell membrane while silver binds DNA or RNA and respiratory enzymes, deactivating the cell and ultimately leading to cell lysis or cell death.[32]

However, silver and copper face specific challenges as universal disinfectants. After

binding to a sulfhydrul group, silver ions may return to solution, no longer preventing cellular respiration and providing an opportunity for the cell to recover.[30] Some bacteria have also been shown to avoid disinfection through the production of proteins that complex metal ions. For example, *Xanthomonas campestris* pv. *vesicatoria* and *Pseudomonas syringae* have been identified as having a copper resistance gene and *Citrobacter freundii, Proteus mirabilis, Enterobactor cloacae,* and *Klebsiella pneumoniae* have been indentified to be silver resistant.[33-38] Silver tolerant microorganisms taken in the proximity of a soil mine were shown to accumulate a mean of 23 g silver per dry weight gram of bacteria.[39] In addition, the effects of pH have a great influence on bacteria inactivation.[40]

2.4.2 DISINFECTION OF VIRUSES

Well over 100 different virus strains are found in wastewater and may contaminate surface waters used for recreational purposes.[41] Disinfectants must remove or destroy viruses to such an extent that successful reproduction in a cell is prevented either by immobilizing viruses on a surface, blocking or destroying host cell receptors, or inactivating the nucleus acid in the viral capsid.[42] Metal ions may inactivate viruses through various mechanisms via binding to electron donor groups on proteins or nucleic acids.[43] It is believed that the inactivation of biological macromolecules involves a modified site-specific Fenton mechanism producing hydroxide radicals, which may affect the peptide backbone of the capsid proteins of virions.[44] In order to truly be inactivated, any released nucleic acid from viruses must be inactivated, as damaged, noninfectious virions have been shown to pool genetic information in order to generate an infectious, plaque forming unit.[45]

Evidence has suggested that well-dispersed viruses may not be the predominant class of

viruses present in water.[46] Aggregation of virions will reduce the likelihood of a virion coming in contact with disinfectant, as it will be more likely to be surrounded by other virions. In addition some viuses, such as vaccina virus were completely resistant to silver specifically, while others such as the influenza virus, were relatively insensitive,[46] which could potentially be due to the fact that some viruses have a more stable molecular structure than others.[48]

2.4.3 DISINFECTION EFFICACY OF BACTERIA AND VIRUSES

The literature reports levels of reduction for a variety of pathogens or indicators of pathogens that are can be found in water and are hazardous to human health. These values are displayed in Table 2.3. However, in addition to the diversity of water chemistries employed in each experiment, the range of time to measurement disinfection of disinfection is large, which makes comparisons difficult. Also, many of the values were not reported and were instead displayed on graphs, so a range was reported instead of a specific quantity of pathogen reduction, as it could not be determined exactly from the original charts. Even with the constraints described, the trends observed in Table 2.1 are still seen. For pathogens with available data in a differentiable range, the amount of free chlorine in the disinfection system seemed to be the most influential factor in pathogen reduction. In accordance with Table 2.1, it seems that addition of copper and silver ions to lower levels of free chlorine resulted in pathogen reduction comparable to that of higher levels of free chlorine alone.

The experiment that produced low reductions of *Staphylococcus* sp. and *L. pneumophila* cannot be compared to the rest of the values pulled from the literature, as the experimental design involved continuous doses of bath water and urine as well as a constant replenishment of free chlorine, silver, and copper levels, as opposed to the other work cited that used well water

with single doses of the disinfectant combinations described in Table 2.3.[5] However, it is important to consider the drastic effect organic loads can have on potential disinfection, particularly if these combinations are employed as the sole source of water treatment. This could be the case when point-of-use water treatment is employed as the sole source of water treatment in low and middle income countries.

Table 2.3: Disinfection Efficacy of Bacteria and Viruses

Pathogen	**Source**	**Free Chlorine (ppm/ Copper (ppb)/ Silver (ppb) Dose**	**Log_{10} Reduction**	**Time to Reduction (min)**
***Staphylococcus* sp.**	(7)*	1/0/0	0.9<x<1.2	2,880
	(7)*	0/400/40	0.9<x<1.2	2,880
	(7)*	0.3/400/40	0.9<x<1.2	2,880
L. pneumophila	(7)*	0/400/40	0.05<x<0.10	2,880
	(7)*	0.3/400/40	0.15<x<0.20	2,880
	(7)*	1/0/0	0.20<x<0.25	2,880
L. pneumophila	(15)	.1/400/40	1<x<2	7
	(4)	.2/400/40	2<x<3	5
	(15)	.4/0/0	2.6	1.5
	(4)	0/400/40	3	1,440
	(4)	.3/400/40	3<x<4	3
	(15)	.4/400/40	3.7	1.5
Naegleria fowleri	(16)	0/800/80	0.58	4320
	(16)	0/400/40	0.7	4320
	(16)	.1/0/0	0.99	6
	(16)	1/400/40	2	4.4
	(16)	1/800/80	2	3.9
Hepatitis A Virus (HAV)	(9)	0.2/0/0/	1<x<2	120
	(9)	0.2/700/70	1<x<2	120
	(9)	1/0/0	2<x<3	120
	(9)	0.5/0/0	2<x<3	120
	(9)	0.5/700/70	2<x<3	120
Human Rotavirus (HRV)	(9)	1/0/0	1<x<2	120
	(9)	0.5/0/0	1<x<2	120

	(9)	0.5/700/70	1<x<2	120
	(9)	0.2/0/0/	1<x<2	120
	(9)	0.2/700/70	1<x<2	120
Adenovirus (ADV)	(9)	0.5/0/0	2<x<3	120
	(9)	0.5/700/70	2<x<3	120
	(9)	0.2/0/0/	2<x<3	120
	(9)	0.2/700/70	2<x<3	120
	(9)	1/0/0	3<x<4	120
Poliovirus (PV)	(9)	0.2/0/0/	3<x<4	120
	(9)	0.5/0/0	4	< 30
	(9)	0.5/700/70	4	< 30
	(9)	0.2/700/70	4	30
Total Coliform	(7)	1/0/0	1<x	2,880
	(7)	0/400/40	1<x	2,880
	(7)	0.3/400/40	1<x	2,880
	(5)	1/0/0	2<x<3	80
	(5)	0/600/600	4<x<5	80
	(5)	0/1200/600	4<x<5	80
	(5)	0/600/1200	4<x<5	80
	(5)	0/1200/600	4<x<5	80
	(5)	1/200/1200	6<x<7	80
E. coli	(5)	0/600/600	4<x<5	80
	(5)	0/1200/600	5<x<6	80
	(5)	1/0/0	5<x<6	80
	(5)	0/1200/600	7<x<8	80
	(5)	1/200/1200	7<x	80
	(5)	0/600/1200	7<x	80
Heterotrophic Plate Count Bacteria	(7)*	1/0/0	x<0	2,880
	(7)*	0/400/40	2<x<4	2,880
	(7)*	0.3/400/40	2<x<4	2,880

7* – Data taken from a slow hydraulic circuit added bath water and chlorine with continually adjusted free chlorine, silver, and copper ions over 28 days.

2.4.4 DISINFECTION IN HOSPITAL WATER DISTRIBUTION SYSTEMS

Disinfection of *L. pneumophila* and various kinds of fungi were tested at designated places along distribution pathways in hospital drinking water systems. Water in the electrolytic

copper and silver disinfection system resulted in a 28.8% prevalence of fungi in collected samples that contained 200-400 ppm copper and 20-40 ppb silver compared to 77.1% in non-ionized water in both hot and cold water systems.[49] The majority of the reduced fungi observed in this experiment were that in fungi that are known to cause infection in immunocompromised patients. Septate molds and yeast were significantly less prevalent in ionized water samples when compared to non-ionized samples in both cold and hot water systems, the biggest difference detected in *Cladosporium* and *Penicillium* species.[49] Similar results were found when testing for *L. pneumophilia*, where there was a 14.2% prevalence in ionized water as opposed to 67.3% in the control system, and it was later proven that the sites in ionized system where Legionella was detected was due to infrequent use.[11]

2.5 CONCLUSION

Electrolytically generated copper and silver have potential as a method for water disinfection in stagnant water such as hot tubs or swimming pools as well as continuous flowing hydraulic circuits to avoid to detrimental effects of free chlorine as a sole source of disinfection. It has been seen by a comparison of inactivation rates and pathogen reduction quantities that silver and copper do not disinfect as quickly as free chlorine alone, but they can be used in combination with low levels of free chlorine to produce disinfection comparable to higher levels of free chlorine. This is evidenced by the previous discussion of inactivation rates and pathogen reduction in different combinations of free chlorine, silver ions, and copper ions. In order to better understand disinfection kinetics, more research should be conducted on disinfection via electrolytically generated silver and copper in various water chemistries and how it effects the current efficiency and longer term inactivation of the system.

Previous work has laid a good foundation to suggest potential for application in point-of-use water treatment devices in order to provide resilient and sustainably treated water in middle and low income countries, as the benefits of both chlorine and silver/copper may assist with disinfection in a developing world setting. A person in this setting may purchase a point-of-use device that utilizes only silver and/or copper, but the water to be treated may come from the municipal tap and contain chlorine.[50] If this is the case, the copper/silver ions from the device and chlorine from the water would have a synergistic effect.

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Chapter 3: Evaluation of Electrolytic Silver and Copper Ion Release for a Potential Point-of-use Device

The work presented in this chapter resulted in a journal article in preparation.

Hill, C., Smith, J., Gaylord, A., Hatley, M., Hardcastle, L., Renneker, K., "Incorporation of Electrolytic Release of Silver and Copper Ions into a New Point-of-use Drinking Water Treatment Intervention for Disinfection in Resource Limited Settings"

3.1 ABSTRACT

Point-of-use water treatment technologies that use silver as a disinfectant have been shown to be effective by killing disease-causing bacteria and preventing potential recontamination during transport and storage in rural areas. The release of silver and copper through electrolytic generation as a new point-of-use disinfection mechanism was examined. Two voltages common to commercially available batteries, 4.5 volts and 9 volts, were applied to a point-of-use apparatus with either two silver or copper wires submerged 1 inch into 10 liters of synthetic groundwater. In addition, the effects of wire diameter, ionic strength of groundwater, and other possible POU parameters on metallic ion release were examined. Silver levels measured over time by graphite furnace atomic absorption spectroscopy established a proof of concept that this kind of technology could be practically implemented in a point-of-use water treatment device in a rural setting. It was determined that the apparatus including only silver wire should be run for only 2 minutes at 9 volts to yield the target 50 ppb concentration for water treatment. Further, this conclusion was supported when 50 ppb electrolytically generated silver from the apparatus yielded up to a 5 log reduction of E. coli bacteria in synthetic groundwater. Copper was less effective in disinfection and also required 62 minutes to release the target 500 ppb for disinfection when 9 volts were applied to the system. In tandem with analysis of silver release, disinfection experiments were conducted. These results affirm that an electrolytic apparatus is promising to serve as a novel point-of-use intervention and warrant further testing. In addition, although copper by itself is not suitable for this configuration, it still has potential to be introduced in a silver and copper alloy, as it would allow for more disinfection potential while still remaining under the EPA limit for metals in drinking water.

3.2 BACKGROUND

According to estimates by the World Health Organization, 2.2 billion people globally rely on drinking water sources that are not safely managed, and even those with improved sources sometimes travel substantial distances to reach the source.[1] Members of households without an improved water source suffer detrimental effects from water-borne diseases such as cholera, typhoid, and schistosomiasis.[2,3] These diseases are often associated with severe diarrhea, a leading cause of mortality in children under the age of five[4].

Point-of-use (POU) water treatment technologies provide an inexpensive, effective solution to reduce waterborne disease as they allow for households to treat water in the home shortly before consumption. They are also not reliant on state- or community-run water infrastructure, which in low-resource settings can be unreliable and inefficient.[4] It has long been known that ionic silver is an effective disinfectant for waterborne pathogenic bacteria,[5,6] and it is currently employed in a variety of POU water treatment technologies, including the Folia Water paper filter, the MadiDrop, pot-shaped and candle-style ceramic filters, and more expensive filtration systems sold by Brita and Aquaphor[7–11]. Incorporating silver into POU technologies has been shown to disinfect bacterial pathogens in water just as well as chlorine, which is used widely in water purification, providing a maximum of 4.2 log reduction of total coliform bacteria in drinking water[9,12]. More recently, silver has been shown to be an effective disinfectant for *Adenovirus* and *Cryptosporidium parvum*.[13,14]. Research has shown that copper can also be an effective disinfectant and that the use of both the maximum concentrations of silver and copper can have a stronger combined purification power than either ion at the EPA-set secondary drinking water standard alone.[15–17] This is primarily due to the ability to use greater numbers of metal ions in the water without exceeding each individual ionic concentration limit.[15] In addition

to high disinfection efficacy, silver and copper do not alter the taste or odor of water at concentrations used for water treatment, a common adverse side-effect of chlorination[18].

Currently, there are two emerging commercial technologies that release silver into stored water for the purpose of disinfection but do not combine treatment with filtration. One is SilverDYNE (World Health Alliance, Inc.), which is an aqueous suspension of silver nanoparticles[19]. One bottle of SilverDYNE treats 600 L of water and requires dosing a specific volume of stored water on a daily basis in a dedicated storage container[19]. The dose is designed to produce a total silver concentration of 100 μg/L, which is the USEPA secondary drinking water standard.[15] However, prior studies have shown that silver nanoparticles primarily function as a disinfectant through oxidation, with resulting oxidized ionic silver serving as a disinfectant.[20] Presumably, some of the silver added by Silverdyne is consumed in metal form by the end users and only a fraction of silver that is oxidized directly contributes to disinfection.

The second commercial technology that releases silver into stored water is called the MadiDrop (Silivhere Technologies, Inc.). The product is based on the Tshivenda South African word for water (*madi*) and was developed at the University of Virginia.[8,21] According to manufacturer specifications, the MadiDrop is a 52-g porous ceramic tablet (8 x 3 x 1.4 cm) embedded with silver by a proprietary method. The tablet is placed into a 10-20 L water volume in a dedicated storage container for 8 hours, gradually releasing ionic silver into solution for disinfection. A single MadiDrop works identically every day for up to 12 months, treating up to 7000 L of water per year.[21] It gradually releases silver into water, which therefore requires additional contact time for maximum efficacy.

To improve upon the shortcomings of SilverDYNE and the MadiDrop, it is proposed that the electrolysis of silver and copper could be incorporated into a POU water-treatment device for

low resource settings. Electrolytic water disinfection is the process of generating metal ions by inserting a negatively charged metal cathode and positively charged metal anode into water to be disinfected and applying an electric current.[6] This process causes the anode to release metal ions as the metal of interest is reduced, while the free electron is used to synthesize hydrogen gas and hydroxide ions from water at the cathode. The reactions at the anode are $Ag \rightarrow Ag^{+} + e^{-}$ and $Cu \rightarrow Cu^{2+} + 2e^{-}$. The reaction at the cathode is $H_2O + e^{-} \rightarrow \frac{1}{2}H_2 + OH^{-}$. Electrolysis has the potential to deliver a target amount of metal ions quickly to contaminated water, and the small amount of metal required for treatment allows for a single anode and cathode pair to treat water daily for a long period of time. Disinfecting water via electrolysis has been examined for a variety of water treatment applications but never in an inexpensive, POU system designed for resource limited settings.[5,22–25]

This paper seeks to establish the potential of silver and copper electrolysis as a mechanism to provide adequate disinfection to untreated water in a POU water treatment technology for low-resource settings. To address this, experiments were conducted to examine the effect of various parameters on metal ion release in a POU configuration. In addition, the disinfection efficacy of electrolytically generated silver and copper ions and the long-term potential of such a device were examined.

3.3 METHODS

For all experiments, two pieces of either silver or copper wire were submerged into synthetic groundwater. A current was applied to the configuration via a DC power supply, as depicted in Figure 3.1.

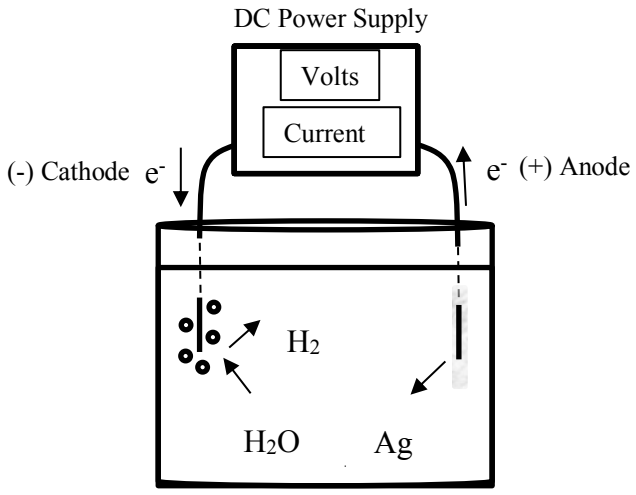

Figure 3.1: Basic configuration for experiments. A DC power source was connected to two strands of coated wire each bearing an alligator clip. The clips held wire submerged in the appropriate sized, water-filled container. A determined voltage of electricity ran through the system, converting the H_2O into H_2 gas and releasing metal ions into the water.

3.3.1 VARYING PARAMETERS AND ASSOCIATED ION RELEASE

To investigate the effect of wire diameter on metal ion release, 0.25 mm, 0.5 mm, or 1 mm thick wires were submerged 2.5 cm into 400 mL of synthetic groundwater in a 500 mL plastic container. 5 V were then applied via a DC current for 120 minutes. 4 mL water samples were taken every 20 minutes and analyzed for silver or copper concentration. Each wire thickness was tested through three trials, and this procedure was conducted for both copper and silver wire.

A second round of experiments was conducted to test the relationship between the ionic strength of the water being treated and the release of metal ions. 2.5 cm of 1-mm diameter wire was submerged in a 500-mL plastic container filled with 400 mL of either 100% synthetic groundwater, 50% synthetic groundwater and 50% deionized water, or 25% synthetic groundwater and 75% deionized water. 5 V were applied to the apparatus via a DC current for ten minutes. Water samples of 4 mL were taken at 0, 1, 5, and 10 minutes and analyzed for silver

or copper concentration. This process was completed three times for each concentration of synthetic groundwater, and experiments were conducted for both copper and silver wire. For all experiments, synthetic groundwater consisted of 1.2 g of $MgSO_4$, 1.92 g $NaHCO_3$, 0.08 g KCl, and 1.2 g of $CaSO_4$ per 20 L in a plastic container.[26]

A third set of experiments examined the relationship between the depth of wire submerged into untreated water and the release of metal ions. 1.3 cm, 2.5 cm in, or 3.8 cm of 1 mm diameter silver wire was submerged into 10 L of synthetic groundwater in a 20 L plastic container. 9 V were applied to the apparatus via a DC current for 30 minutes. Water samples of 4 mL were taken at 0, 5, 10, 20, and 30 minutes and analyzed for silver concentration. This process was completed three times for each wire depth.

Finally, the relation of the distance between the electrodes and the release of metal ions was determined. Silver electrodes were separated 6.4, 12.7, and 25.4 in apart in 10 L of synthetic groundwater in a 20 L plastic container. 4.5 V was applied to the configuration and silver concentration was measured at 5 and 10 min. This process was completed three times for each distance setting. Both these tests and those examining the depth of submerged wire examined only silver, not copper. This is because results from other experiments indicated that copper should not be used as the sole disinfection mechanism but used to supplement silver in a potential device.

Due to the linear relationship between ion release and time, the rate of release at each setting for a single parameter (diameter, ionic strength, etc.) was divided by the rate of release for the most minimum setting tested (0.25 mm, 25% synthetic groundwater, etc.). This determined the factor by which increasing a variable increased ion release rate.

3.3.2 TIME TO DESIRED ION CONCENTRATIONS

A fourth experiment was performed both to demonstrate the relation between the applied voltage and metal ion release and to establish the time required to release enough metal ions to provide adequate disinfection in a potential POU drinking water device. To create a configuration that resembled an electrolytic water treatment device in a volume of water required for treatment in a home, 2.5 cm of 1-mm diameter wire was submerged in a 20-L plastic container filled with 10 L of synthetic groundwater. The wire was attached to a DC power source set at either 4.5 or 9 V and run for 30 min. 4.5 and 9 V were chosen because these values correspond to three AAA batteries or one 9 volt battery, respectively, which could realistically be used in a POU electrolytic water treatment prototype. Water was sampled at 0, 1, 5, 10, 20, and 30 min and analyzed for silver and copper concentration. This process was conducted three times for each desired voltage for both copper and silver. The target concentration of ions determined for the prototype was 50 ug/L and 500 ug/L for silver and copper, respectively, as these values are half of the EPA secondary drinking water safety standards for these metals.[15] Using the equation for the linear trendline for each voltage, the times required to release target concentrations of 50 µg/L and 500 µg/L silver and copper, respectively, were calculated.

3.3.3 POTENTIAL FOR USE OF SILVER AND COPPER ELECTRODES

After determining the time required for a POU device with a single cathode/anode pair to release target ion concentrations, it was examined if the device could be configured so that both silver and copper were released at the same time when connected to a single power source. The configuration in Figure 3.1 was arranged so that a pair of silver and copper electrodes submerged

in water were arranged in a parallel circuit that was connected to a single DC power source. 9 V and 4.5 V were applied to the configuration, and both silver and copper were measured at 5, 10, 20, and 30 min. This process was conducted three times for each voltage.

3.3.4 DISINFECTION POTENTIAL

The disinfection efficacy of a potential device was measured by the ability of the configuration to disinfect *Escherichia coli (E. coli)* through electrolytic ion release. 2.5 cm of 1-mm diameter wires was submerged in 10 L of synthetic groundwater in a 20-L plastic container. It was determined from previous experiments that 4.5 V be applied via a DC current for 5 minutes to release 50 µg/L of silver. Similarly, it was determined that 9 V applied via a DC current for 68 minutes would release 500 µg/L copper. These times were determined best for a consumer because it would take multiple hours to generate 500 µg/L copper from 4.5 V. For silver, the longer 5 minute duration was chosen because the slower release rate of silver and slightly longer duration would allow for more user error without generated silver exceeding the EPA limit. *E. coli* bacteria was added to the 10 L of water, and 100-mL water samples were taken at 0, 2, 4, and 8 hours. The *E. coli* concentration of these samples was determined using the IDEXX Colilert Test Method for the Simultaneous Detection of Total Coliform and *E. coli* in water.[27] *E. coli* was cultured using the m-Endo broth from EMD Millipore, Billerica, MA, USA. The disinfection efficacy was measured by calculating the log reduction of *E. coli* bacteria after exposure to either 50 µg/L silver or 500 µg/L copper. This was calculated by subtracting the log of the *E. coli* bacteria in the water at each time point from the log of the *E. coli* bacteria at the beginning of the experiment. Disinfection efficacy was tested for two trials of each voltage and a control bucket with no added metal ions.

3.3.5 LONGEVITY OF USE

The potential for long-term use of an electrolytic POU water treatment device was also examined. Similar to previous experiments, 1 mm thick wires were submerged into 10 L of synthetic groundwater in a 20 L plastic container. As determined previously, 9 V were applied via a DC current for 2 minutes to release a target 50 μg/L silver. This procedure was repeated 365 times in order to simulate daily use for a year, with water being changed out before each sampled run. 4 mL samples were taken at runs 0, 10, 20, 30, and multiples of 30 and analyzed for silver concentration. The final sampling was taken at 365 runs instead of 360. This was tested in two trials. A longevity experiment was run only for silver, not copper, because results from other experiments rendered that copper should not be used as the sole disinfection mechanism but used to supplement silver in a potential device.

3.3.6 SAMPLE TESTING

All water samples tested for copper or silver analysis were prepared with trace metal grade nitric acid (Fisher Chemical, Fair Lawn, NJ, USA) and were tested on a calibrated graphite furnace (HGA 900, Perkin-Elmer, Waltham, MA, USA) atomic absorption spectrometer (AA2100, Perkin-Elmer) (GFAA).

3.4 RESULTS

3.4.1 DIAMETER EXPERIMENT

Figures 3.2 A-B shows the effect of wire diameter on the release of metal ions in a potential POU system. For both copper and silver, the wire diameter in an electrolytic system did

not influence the release rate of metal ions released in solution. When the diameter was doubled or quadrupled, the rate of release remained the same. This is supported by Table 3.3 when examining that increasing wire diameter by a factor of 2 and 4 corresponded to roughly a factor of 1 increase, or approximately no change in release rate. Throughout experiments for both silver and copper, the error bars for all three wire diameters overlapped at almost every sampling time in various combinations, indicating that the metal release of these diameters could yield an identical result.

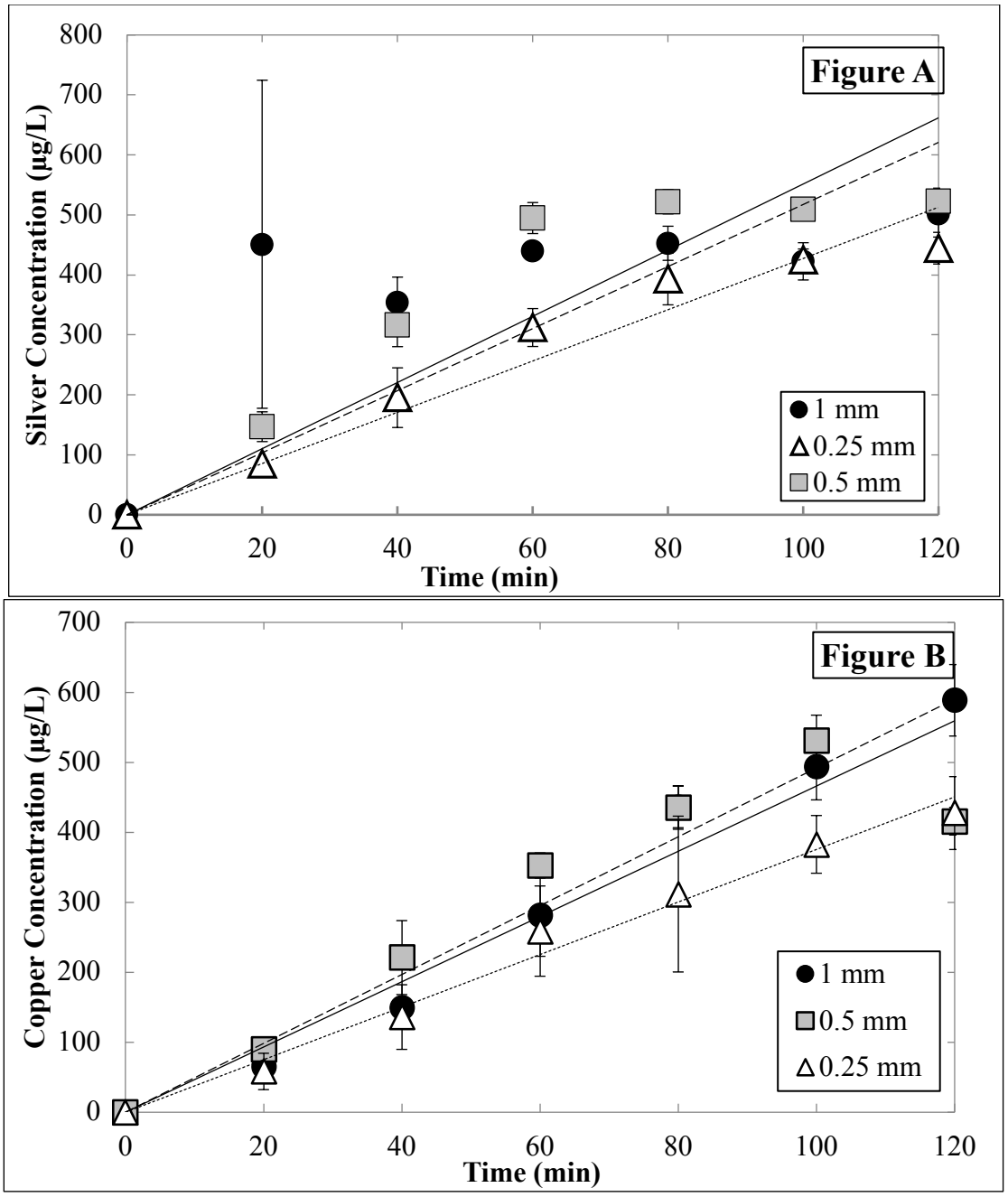

Figure 3.2: Metal ion concentration in 0.4 L synthetic groundwater as a function of time for wire diameters 0.25 mm, 0.5 mm, and 1 mm in an electrolytic apparatus. The Figure 3.2 A displays ion release for an apparatus with silver wire and Figure 3.2 B displays release for the same apparatus with copper wire. The average of three trials is shown in each graph with error bars indicating the standard error between the three trials. A trendline is included for each type of wire to depict the linear relation between metal ion release and time.

3.4.2 IONIC STRENGTH

Figures 3.3 A-B show the effect of the ionic strength of untreated water on the release of metal ions in a potential POU system. Silver and copper ion release rates increased proportionally to the ionic strength of the solution in which they are submerged. This is evidenced by the approximate 2 factor increase in release rate when doubling ionic strength from $1.15 \cdot 10^{-3}$ M to $2.29 \cdot 10^{-3}$ M and the approximately 4 factor increase in release rate when the ionic strength was quadrupled in both silver and copper. This is further supported by synthetic groundwater with an ionic strength of $4.58 \cdot 10^{-3}$ M yielding the highest average metal ion concentrations, $1.15 \cdot 10^{-3}$ M yielding the lowest metal ion concentration, and $2.29 \cdot 10^{-3}$ M consistently providing ion concentration levels between the two for all sampling times. With the exception of the first sampling at 1 minute, the metal concentration in each synthetic groundwater setting had error bars with no overlap.

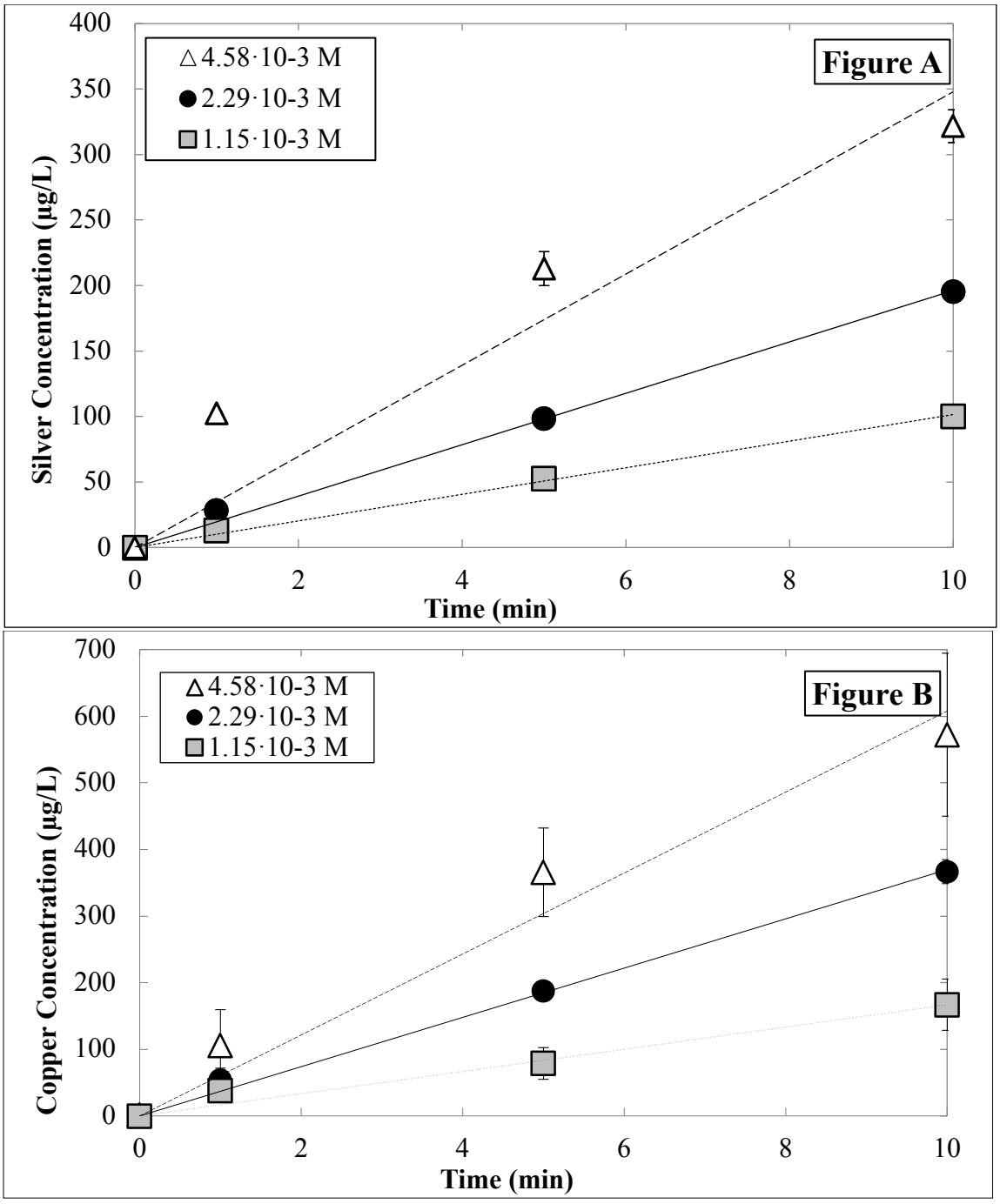

Figure 3.3: Metal ion concentration as a function of time in 0.4 L synthetic groundwater with various ionic strengths. The Figure 3.3 A displays ion release for an apparatus with 1 mm silver wire and Figure 3.3 B displays release for the same apparatus with copper wire. $4.58 \cdot 10^{-3}$ M, $2.29 \cdot 10^{-3}$ M, and $1.15 \cdot 10^{-3}$ M correspond to 100% synthetic groundwater, 50% synthetic groundwater and 50% deionized water, and 25% synthetic groundwater and 75% deionized water respectively. The average of three trials is shown in the graph with error bars indicating the standard error between the three trials. A trendline is included for each ionic strength to depict the linear relationship metal ion release and time.

3.4.3 ELECTRODE DEPTH

Figure 3.4 shows the effect of depth of wire submerged into water on the release of metal ions in a potential POU system. The amount of silver released over time increased by a factor of 0.25 due to a single factor increase in the depth of wire submerged into untreated water. In Figure 3.4, this is supported by 3.8 cm yielding the highest average silver concentrations and 0.5 V yielding the lowest for all sampling times.

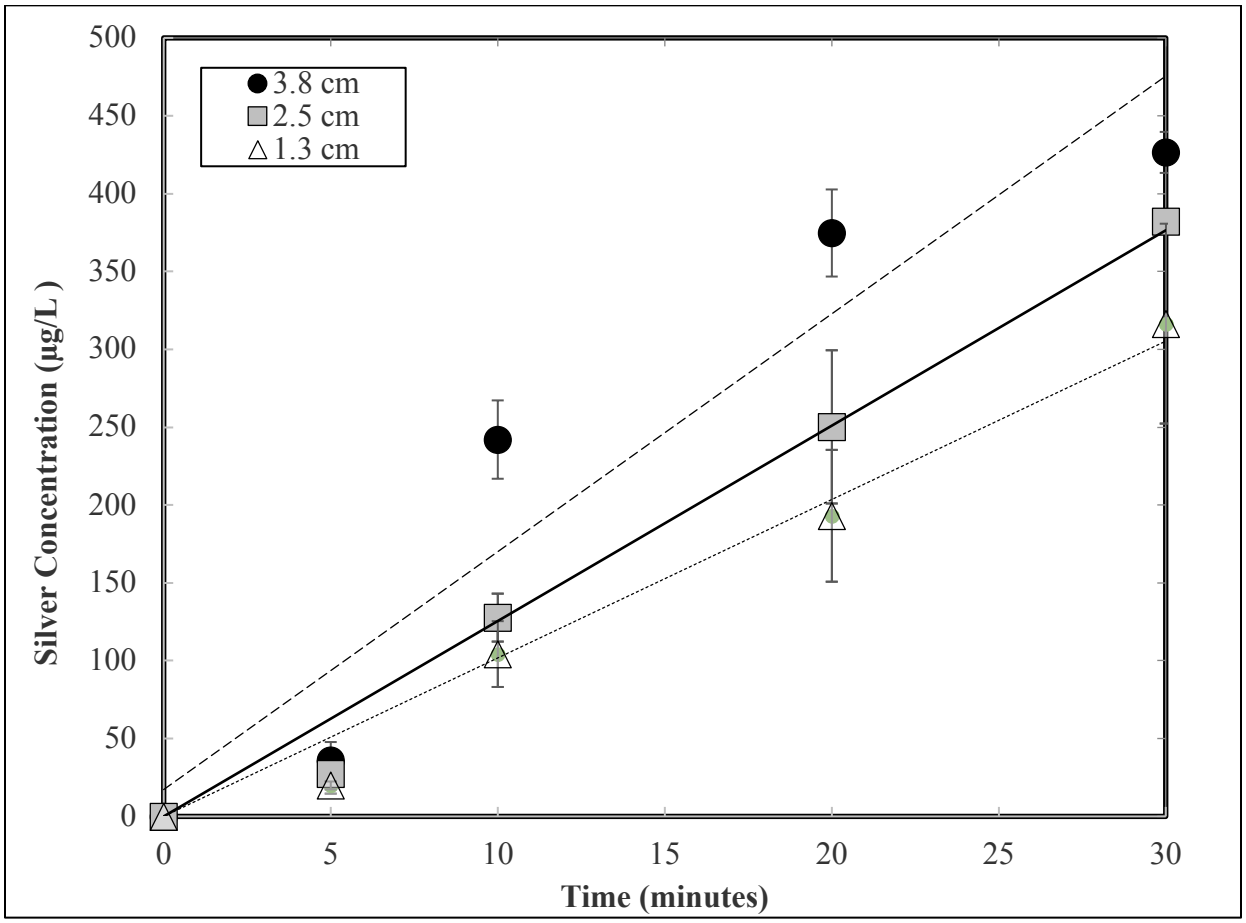

Figure 3.4: Silver ion concentration in 10 L synthetic groundwater as a function of time for 1 mm silver wires submerged 1.3 cm, 2.5 cm, and 3.8 cm in an electrolytic apparatus. The average of three trials for each depth is shown in the graph with error bars indicating the standard error between the three trials. A trendline is included for each wire depth to depict the linear relationship between metal ion release and time.

3.4.4 DISTANCE BETWEEN ELECTRODES

Figure 3.5 shows the effect of distance between electrodes in untreated water on the release of metal ions in a potential POU system. The distance between the electrodes in a POU water treatment configuration had little effect on silver release. When the distance was doubled and quadrupled, the silver release rates were very similar, with each distance releasing within 10 ug/L of each other at each time point.

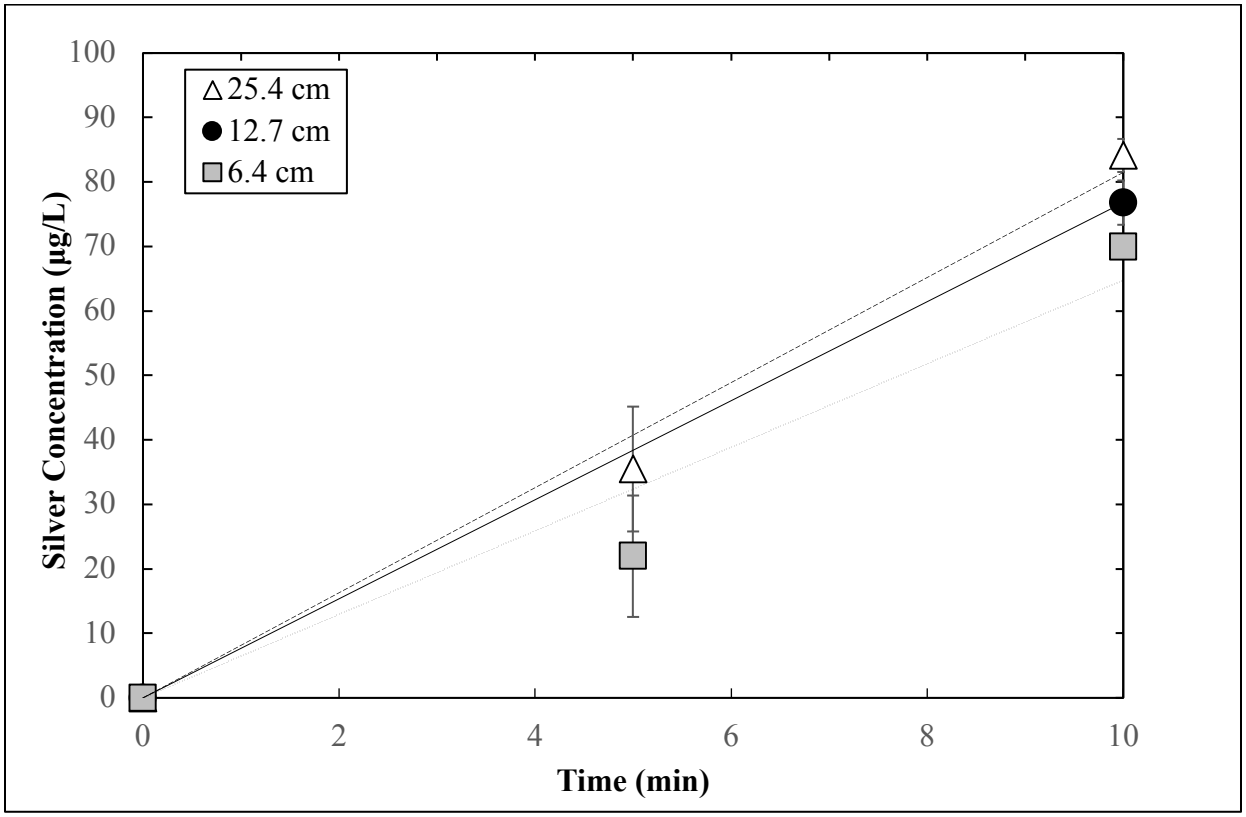

Figure 3.5: Silver ion concentration in 10 L synthetic groundwater as a function of time for 1 mm silver wires separated 6.4 cm, 12.7 cm, and 10 cm in an electrolytic apparatus. The average of three trials for each distance is shown in the graph with error bars indicating the standard error between the three trials. A trendline is included for each distance to depict the linear relationship between metal ion release and time.

3.4.5 TIME TO DESIRED CONCENTRATION

Figures 3.6 A-B show the effect of voltage on the release of metal ions in a potential POU system. The time to reach 50 µg/L of silver was determined to be 2 min with an applied

voltage of 9 V and 5 min with an applied voltage of 4.5 V. The time to reach 500 µg/L of copper was determined to be 68 min with an applied voltage of 9 V and 208 min with an applied voltage of 4.5 V. The amount of silver or copper released over time increased proportionally to an increase in voltage applied to the system. This is evidenced by the silver and copper release rate approximately doubling when increasing voltage from 4.5 V to 9 V. This is supported by 9 V yielding the highest average copper and silver concentrations and 4.5 V yielding the lowest for all sampling times. The metal concentration for each voltage setting had error bars with no overlap between the two.

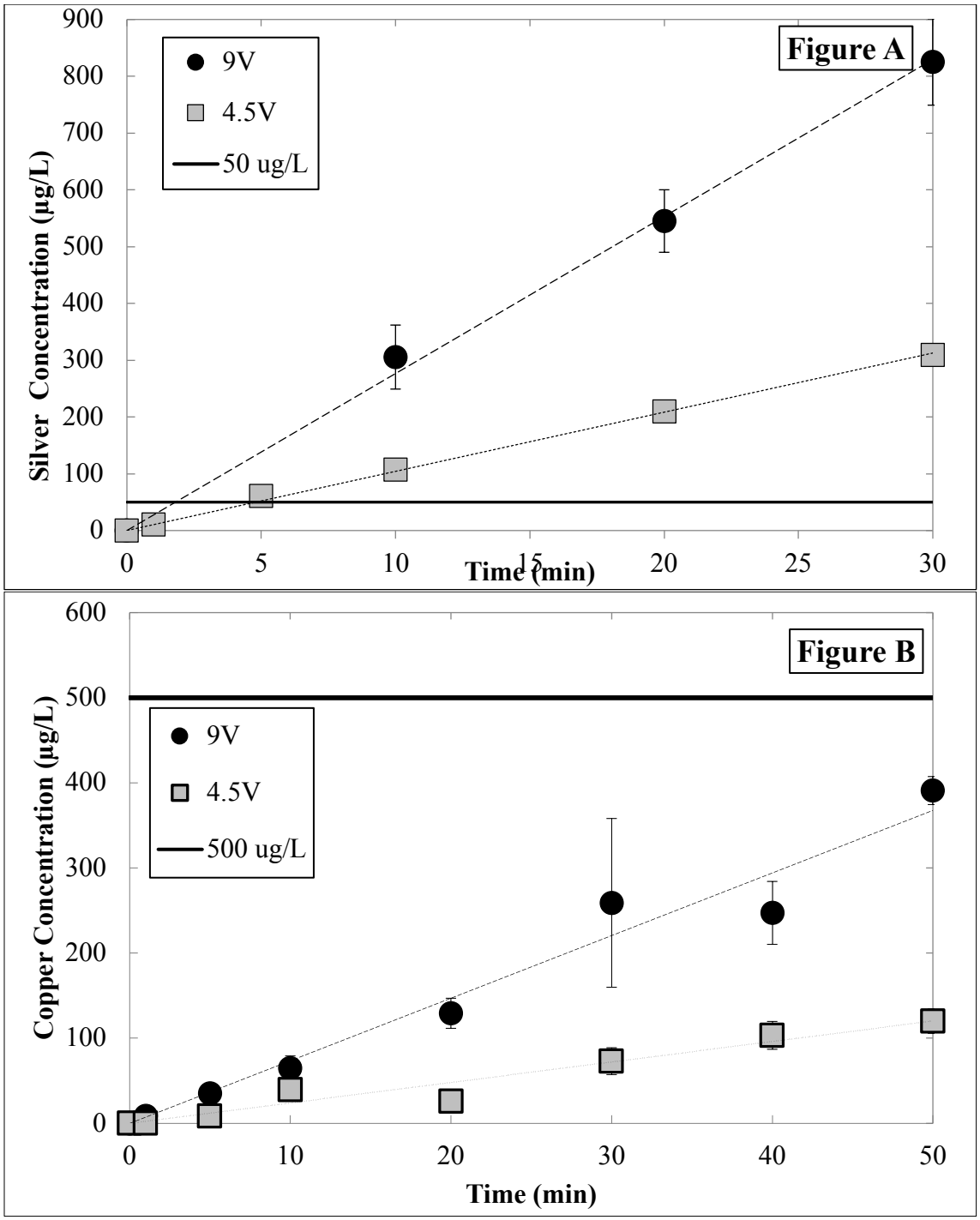

Figure 3.6: Metal ion concentration as a function of time in 10 L synthetic groundwater with applied voltages of 4.5 V and 9 V. Figure 3.6 A displays ion release for an apparatus with 1 mm silver wire and Figure 3.6 B displays release for the same apparatus with copper wire. The target concentration for silver and copper is indicated by a horizontal line in each figure. The error bars extending from each average measured concentration represent the standard error between trials. A trendline is included for each voltage to depict the linear relationship between metal ion release and time.

3.4.6 ELECTROLYTIC PARAMETERS AND METAL RELEASE SUMMARY

Table 3.1 summarizes how changing parameters in a potential electrolytic POU water treatment device affects metal ion release in untreated water.

Table 3.1: Factors of increase in Metal Ion Release with respect to Diameter, Ionic Strength, or Voltage Setting

Diameter			
Wire Diameter (mm)	Factor Increase from 0.25 mm	Silver release rate/ 0.25 mm rate	Copper release rate/ 0.25 mm rate
0.25	1	1.00	1.00
0.5	2	1.11	1.29
1	4	1.38	1.21
Ionic Strength			
Ionic Strength	Factor Increase from 25%	Silver release rate/ 25% rate	Copper release rate/ 25% rate
$1.15 \cdot 10^{-3}$ M	1	1.00	1.00
$2.29 \cdot 10^{-3}$ M	2	2.22	1.93
$4.58 \cdot 10^{-3}$ M	4	3.64	3.43
Voltage			
Applied Voltage (V)	Factor Increase from 4.5 V	Silver release rate/ 4.5 V rate	Copper release rate/ 4.5 V rate
4.5	1	1.00	1.00
9	2	3.05	2.65
Depth			
Wire Submerged (cm)	Factor Increase from 1.3 cm	Silver release rate/ 0.5 V rate	
1.3	1	1	
2.5	2	1.23	
3.8	3	1.58	
Distance Between Electrodes			
Distance (cm)	Factor Increase from 6.4 cm	Silver release rate/2.5 in	
6.4	1	1	
12.7	2	1.19	
25.4	4	1.29	

3.4.7 POTENTIAL FOR USE OF SILVER AND COPPER ELECTRODES

Figures 3.7 A-B illustrate the potential to release both copper and silver from a single power source identical to that of a commercially available battery.

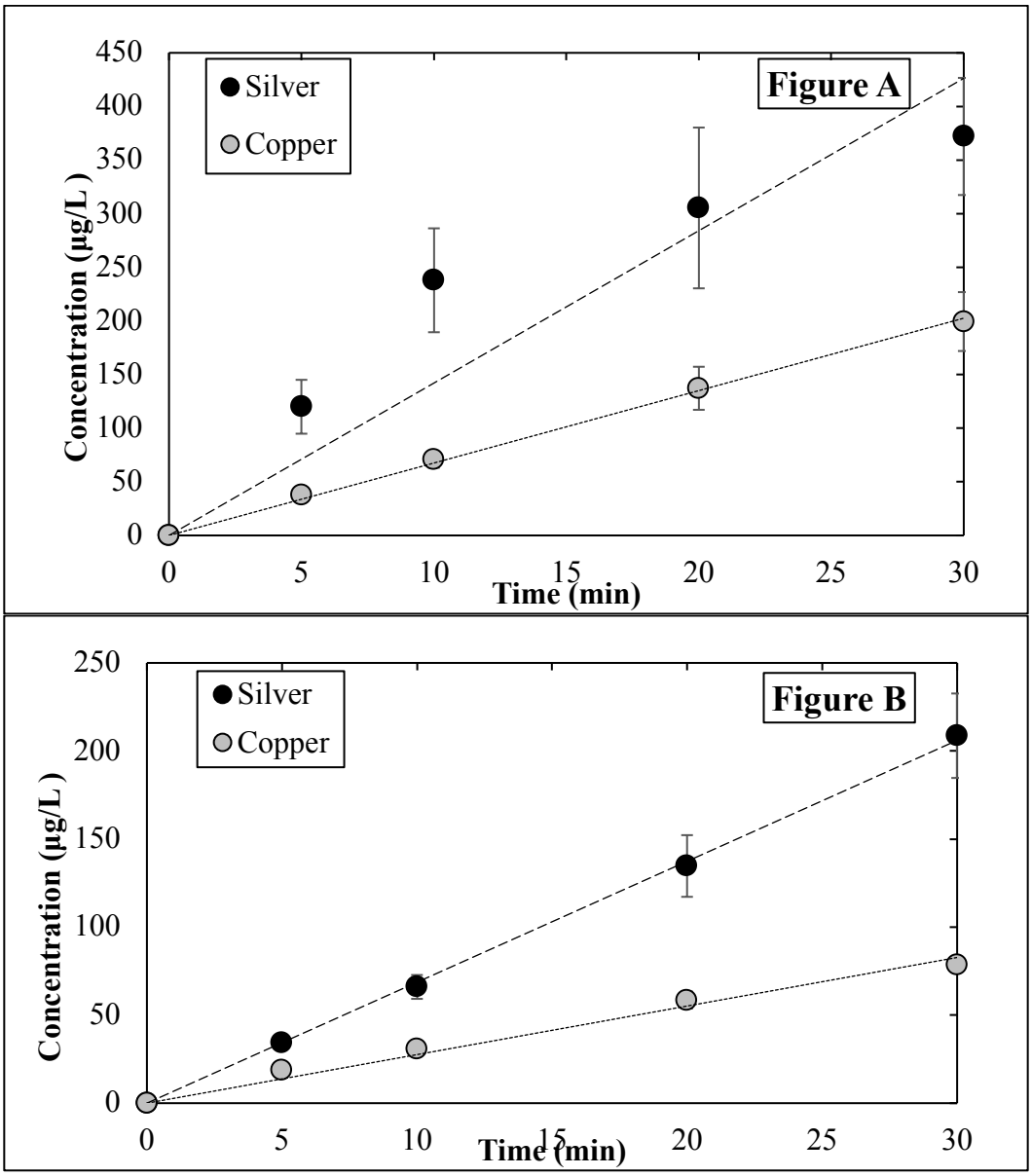

Figure 3.7: Metal ion concentration as a function of time in 10 L synthetic groundwater with 1 mm silver and copper electrodes arranged in a parallel circuit and connected to a single power source. Figure 3.7 A displays the release of silver and copper when 9 V was applied to an apparatus containing pairs of 1 mm copper and silver electrodes in a parallel circuit. Figure 3.7 B displays the release from an identical configuration when 4.5 V were applied. The average of three trials for each metal and both voltage settings is shown in the graph with error bars indicating the standard error between the three trials. A trendline is included for each metal to depict the linear relationship between metal ion release and time.

3.4.8 DISINFECTION EXPERIMENTS

Figures 3.8 A-B display the disinfection efficacy of a potential electrolytic water disinfection prototype for silver and copper with respect to time. The equivalent log reduction is included in Table 3.2. 1 log reduction of *E. coli* was observed at 2 hours after introduction of 50 µg/L electrolytically generated silver, and a 5.6 log reduction was observed after 8 hours. 0.6 log reduction of *E. coli* was observed at 2 hours after introduction of 500 µg/L electrolytically generated copper, and a 1.8 log reduction was observed after 8 hours.

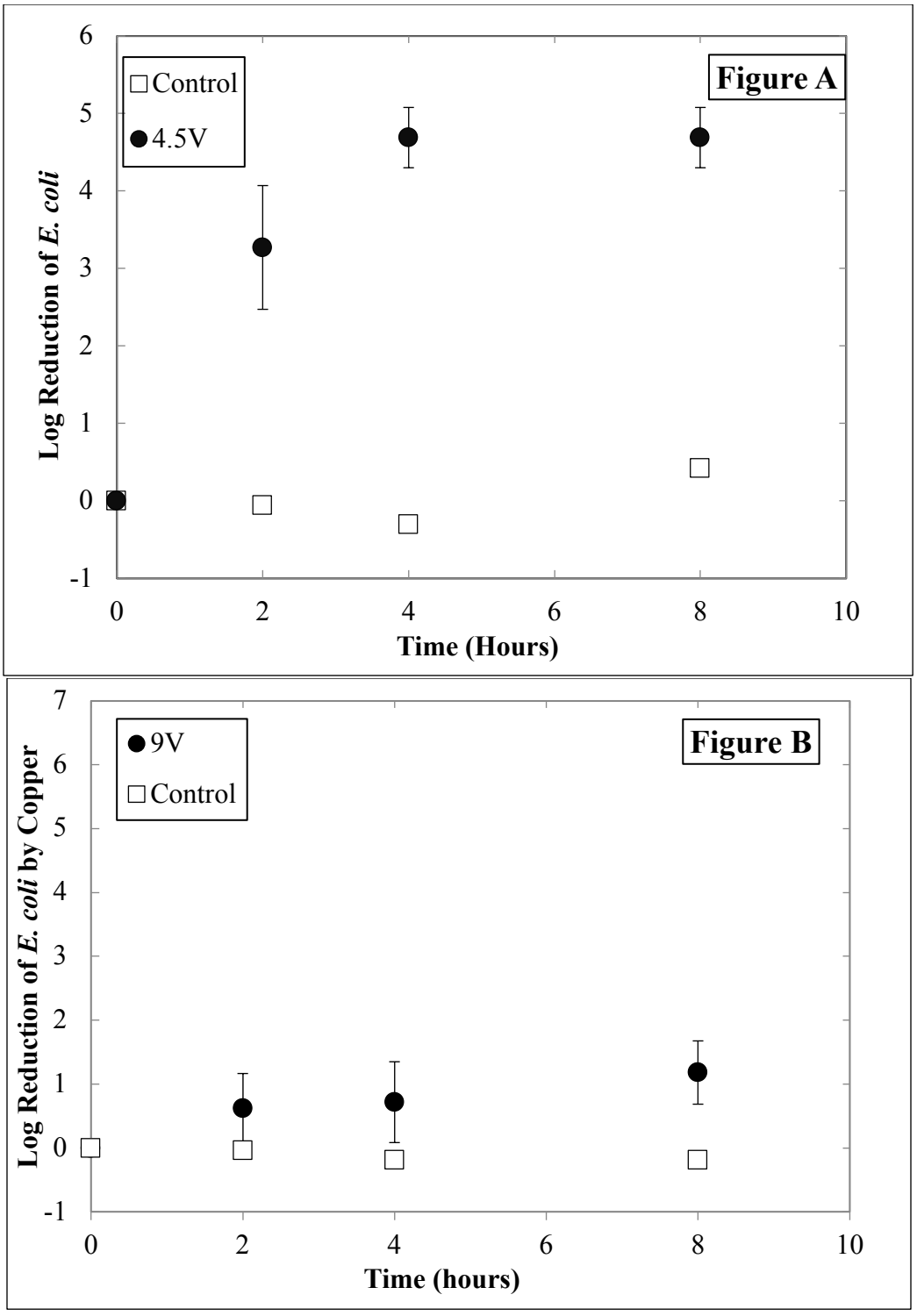

Figure 3.8: Disinfection efficacy of *E. coli* by metal ions as a function of time. Figure 3.8 A displays the disinfection of *E. coli* bacteria by 50 µg/L ionic silver generated by applying 4.5 V for 5 minutes to a 1 mm silver wire. Figure 3.8 B displays the disinfection of *E. coli* bacteria by 500 µg/L ionic copper generated by applying 9 V for 68 minutes to a 1 mm copper wire. The average of two trials is shown in the graph with error bars indicating the standard error between them.

Table 3.2: Log Reduction of *E. coli bacteria* by electrolytically generated silver (50 µg/L) and copper (500 µg/L)

Log Reduction of *E.coli*		
Time (hr)	500 µg/L copper	50 µg/L silver
0	0	0
2	0.62	1.02
4	0.72	4.12
8	1.18	5.61

3.4.9 LONGEVITY EXPERIMENT

Figure 3.9 depicts the release of ionic silver as a function of the number of tests on the same set of wires over time. For 365 pulses of 9 V for 2 minutes, the silver electrolytic system consistently released an amount of silver that is both sufficient for disinfection and also below the EPA 100 µg/L . This is supported by the near zero slope of the trendline, near zero R squared value, and the 35.7 ug/L y intercept of the trendline in Figure 3.9.

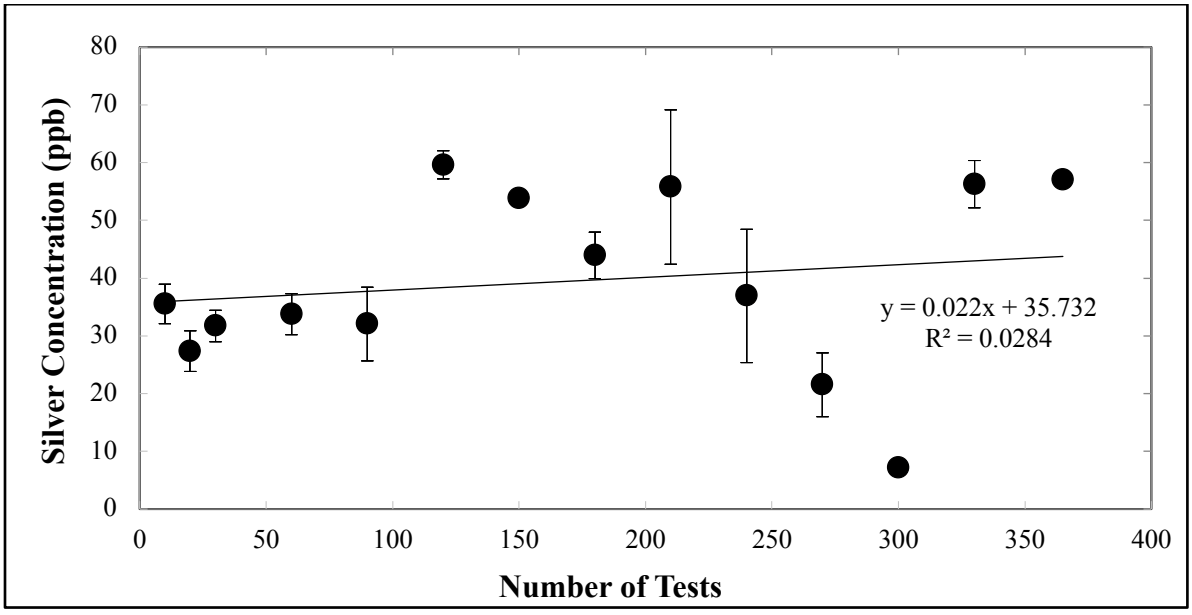

Figure 3.9: Silver release in 10 L synthetic groundwater as a function of the number of tests on the same set of wires over time. During each test, 9 V was applied for 2 minutes to 1 mm wires for a total of 365 tests. Synthetic groundwater was replaced before each sampling. The average of two trials is shown in the graph with error bars indicating the standard error between them.

3.5 DISCUSSION

This paper evaluates the viability of using silver and copper electrolysis in a POU water treatment device to deliver metal ions into stored water for disinfection. It was confirmed that silver ion concentrations sufficient for pathogenic disinfection can be electrolytically generated in 10 L using a voltage typically found in 3 AAA (4.5 V) batteries or one 9 V battery for a year. 50 ug/L of silver, an amount sufficient for disinfection but half of the EPA secondary drinking water standard, was generated in 10 L of water when 4.5 and 9 V were applied to the system for approximately 5 and 2 minutes, respectively. This is a significant improvement on current water treatment technologies that use silver ions which require much longer release rates. For example, the time required for the Madidrop to release the amount of silver required for disinfection is up to 8 hrs.[9] 50 ug/L of electrolytically generated silver ions also proved to provide more than a 5 log reduction of *E. coli* in untreated water, performing similarly to the MadiDrop.[9] Free chlorine (1 ppm) achieved a higher reduction (5-6 log),[5] but there are numerous drawbacks to using free chlorine, including a change in water, taste, and odor and dependency on temperature and pH values of the water.[24] An electrolytic system with silver also proved to reliably produce ionic silver concentrations sufficient for disinfection for 12 months, demonstrating the system's potential as a long-term POU treatment.

Electrolytically generated silver significantly disinfected contaminated drinking water, while copper was not as effective. Generating 500 ug/L of copper, an amount sufficient for disinfection but half of the EPA secondary drinking water standard, required more than an hour of electrolysis even when applying 9 V, making copper a less suitable choice for the primary disinfectant in a POU water purification technology. Copper provided less than a 2 log reduction of *E. coli* after 8 hours of exposure, further confirming it as a less suitable choice. When

investigating if copper could supplement silver in disinfection, a system that had both copper and silver electrodes in a parallel circuit yielded only 25 ug/L copper at the time that 50 ug/L silver was generated, which would not provide enough supplemental disinfectant to justify the second set of electrodes. Due to silver's relatively high ion release rate in comparison to technologies that use silver for water treatment, silver electrolysis alone could be sufficient in a POU water treatment device.

Given that diameter did not affect metal release, the biggest difference in wire thickness in a potential POU device would not be rate of metal release but the durability of the product in the home. Due to the relatively thin, fragile nature of the 0.25 mm and 0.5 mm silver and copper wires, the 1 mm wire would be best to incorporate in a POU device in a resource limited setting. Though the cost of a potential device increases as the thickness of the wire increases, the selection of a thicker, more durable wire would enable the device to be used for a greater period of time without replacement while still allowing for the potential intervention to cost less than $10. Another important consideration for a potential prototype is that the release of silver ions is proportional to the ionic strength of the untreated water in a system with constant voltage. Instead, a prototype could incorporate a constant current to allow a controlled release of ions, regardless of the untreated water's ionic strength. While the proximity of electrodes impacts resistivity and could have affected the electrolysis rate, the range of proximity of these electrodes under consideration with respect to the ionic strength of the water and applied voltage were such that this was not the case. This allows the electrodes to be placed according to what works best with a future prototype design.

The ultimate POU treatment technology based on the use of electrolytic release of silver ions into solution will be a push-button switch with a compartment that houses a conventional 9-

volt battery. To use the product, the consumer presses the button/switch to release ionic silver into untreated water. Such a device is projected to cost under $10 USD. While such an intervention is more expensive than the MadiDrop and requires periodic changing of batteries and silver wires, the device has significant advantages in that it produces silver levels sufficient for disinfection in minutes compared to the eight hours required for the MadiDrop. The technology also produces ionic silver instead of colloidal silver, which has been shown to be more effective in disinfecting pathogens, an advantage over technologies such as SilverDYNE.[28] Using silver electrolysis for water treatment in a low-resource setting has the potential to be a novel, effective way to deliver clean drinking water to those who rely on unimproved drinking water sources.

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Chapter 4: Evaluation of a Point-of-use Prototype That Utilizes Silver Electrolysis in Limpopo, South Africa

The work presented in this chapter resulted in a journal article in preparation:

Hill, C., Wasson, K., Roberts, I., You, J., Woodall, J., Turner, S., Smith, J., "Evaluation of a Point-of-use Prototype That Utilizes Silver Electrolysis in Limpopo, South Africa"

4.1 ABSTRACT

Silver electrolysis has shown to disinfect a pathogens in water in a variety of applications. However, it has never been incorporated into a point-of-use drinking water treatment device at the household level. Previously, a target amount of electrolytically silver ions, 50 ppb, was shown to provide a 4.12-log reduction of *E. coli* in four hours in a laboratory setting. Based on this work, a prototype that utilizes silver electrolysis was developed and evaluated in 20 households in Limpopo, South Africa over four weeks. The electrolysis prototype achieved a 2 log reduction in total coliform bacteria in household drinking water, which is comparable to field performance of other point-of-use devices in low-resource settings. It also consistently released enough silver sufficient for disinfection but below the WHO drinking water guideline. The use of electrolysis in a POU water treatment device is promising technology, and the field performance of the prototype suggests that such a technology could be incorporated into a low resource setting.

4.2 BACKGROUND

More than 2 billion people lack access to safe drinking water.[1] This lack of access leaves individuals vulnerable to diseases linked to contaminated water such as typhoid and cholera. These diseases are especially dangerous to children, as they can cause severe diarrhea, killing 361,000 children under 5 every year.[2] One solution in the effort to provide global access to clean water is point-of-use (POU) water treatment technologies. POU water treatment technologies are low-cost devices that allow the user to treat water in the home before it is consumed, minimizing the risk of recontamination that can happen during transport and storage if water is only treated at a centralized source.[3] These technologies have been shown to be effective in treating

household water and reducing diarrhea prevalence in vulnerable populations.[4] Previous studies have shown that POU water treatment can be more sustainable than centralized treatment in resource limited settings.[5]

Several POU devices employ ionic silver as the primary disinfecting agent.[6–8] Silver has been shown to effectively kill waterborne pathogens in untreated drinking water and has no taste or odor, a common side effect of water treated with chlorine.[9,10] Silver has been incorporated into ceramic water filters,[11–13] MadiDrops,[8,14,15] Folia Water paper filters,[6,16] and SilverDYNE[17] and has been shown to effectively treat water while maintaining effluent silver concentrations below the World Health Organization (WHO) guideline of 100 µg/L.[18]

The MadiDrop and SilverDYNE are currently the only two emerging commercial technologies that release silver into stored water for disinfection that do not include a filtration mechanism. SilverDYNE is an aqueous suspension of silver nanoparticles added to a specific volume of water for effective water treatment[17]. The MadiDrop is a porous ceramic tablet embedded with silver that releases silver ions into 10-20 L of water for disinfection[19]. While these technologies are effective in treating drinking water, both have limitations. With respect to SilverDYNE, it has been shown that silver nanoparticles disinfect primarily through oxidation, and only the fraction of SilverDYNE's introduced solution comprised of oxidized silver ions may directly contribute to disinfection.[20] For the MadiDrop, while all of the silver introduced is in ionic form, it requires an 8-hr treatment time for sufficient disinfection.[15]

Silver electrolysis has the potential to overcome the limitations of the currently available technologies, as it generates exclusively silver ions for an optimal use of silver in the system and delivers it rapidly. This method of disinfection has shown that 50 µg/L of silver can be delivered to 10 L of untreated water, which sufficient for disinfection but still below the WHO guideline.[21]

Silver electrolysis for the use of water disinfection has been used in various applications[22–24] but has never been applied to a POU system designed for a resource limited setting.

Previous work conducted at the University of Virginia explored the potential of a POU device to deliver a target amount of silver and copper to 10 L of stored drinking water. The effects of changing parameters (silver electrode thickness, distance between electrodes, water chemistry, etc.) in a POU electrolytic system was also examined.[21] Based on this work, an electrolytic POU prototype was developed at the University of Virginia to deliver a fixed amount of silver ions to 10 L of stored household water. This paper outlines the field performance of the new POU device over four weeks of use in 20 households in the Limpopo Province of South Africa.

4.3 METHODS

4.3.1 DESIGN AND PREPARATION OF ELECTROLYTIC POINT-OF-USE WATER TREATMENT DEVICE

The electrolytic point-of-use (POU) water treatment devices used in this study were developed at the University of Virginia. The devices initiated electrolysis on silver wires to release silver ions into 10 – 20 L of water with the purpose of deactivating pathogenic microorganisms. The device was developed based on previous work examining how various parameters in a potential point-of-use electrolysis system affect the release of silver ions in the electrolysis process. It was shown that electrolytically generated silver ion release rates increase proportionally to the ionic strength of the test water.[21] To account for the broad range of ionic strengths in natural waters, the device operated at a constant charge. The set amount of charge allowed for a controlled release of ions, regardless of the untreated water's ionic strength. Other

parameters such as wire diameter and distance between electrodes were not found to significantly impact silver ion release in the system due to the small range of wire thickness and distance of electrodes being considered for the system.[21]

The devices were manufactured in Charlottesville, Virginia. The 3D printed, watertight enclosure incorporated the silver wires, a power source, and the required circuitry for the system. The enclosure includes five custom parts: the housing bottom, the housing top, the O-ring clamp, the O-ring clamp insulator, and the electrode cover. The silver anode and cathode wires were designed to be on the bottom of the enclosure where water made contact with the device. A capacitive touch sensor was located in a recess on the bottom of the device where the user activated the prototype with their finger before placing the device into untreated water. The prototype was designed to float so that the handle on top of the device will not make contact with the water, allowing for the user to take the device out of the water after sufficient contact time with untreated water without the risk of recontamination. Figure 4.1 depicts photos of the device enclosure and Figure 4.2 depicts a schematic of the device's circuitry. Figure 4.3 depicts the instructions given to the user.

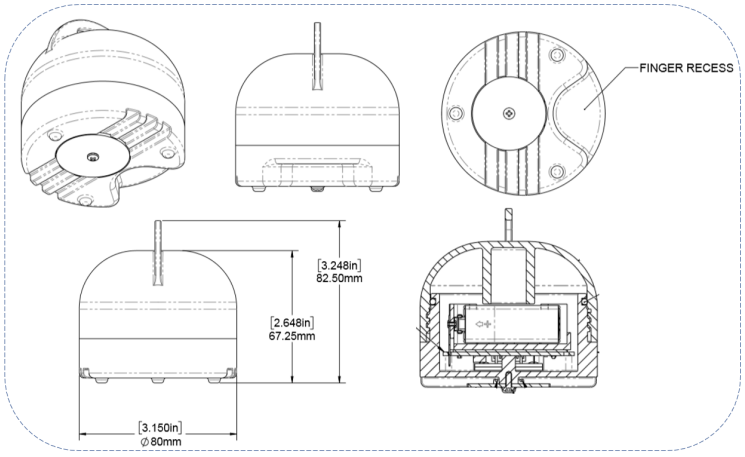

Figure 4.1. Drawing of device enclosure assembly. This includes a plastic cover with a handle and a plastic housing bottom that houses the electronics, a battery holder, and the capacitive touch sensor that activates silver release.

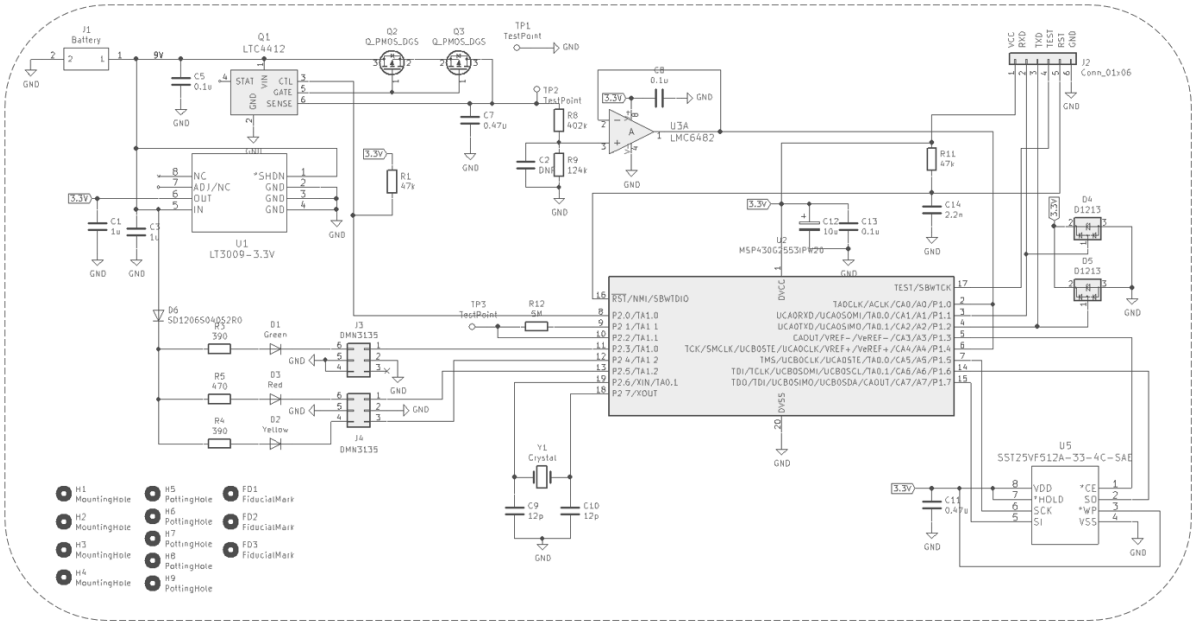

Figure 4.2: Schematic of the circuitry of the POU device. This includes the schematic for a 3.3V regulator, silver release control, comparator A+ and ADC control, capacitive touch sensor control, SPI serial falsh control, JTAG and UART control, and LED control.

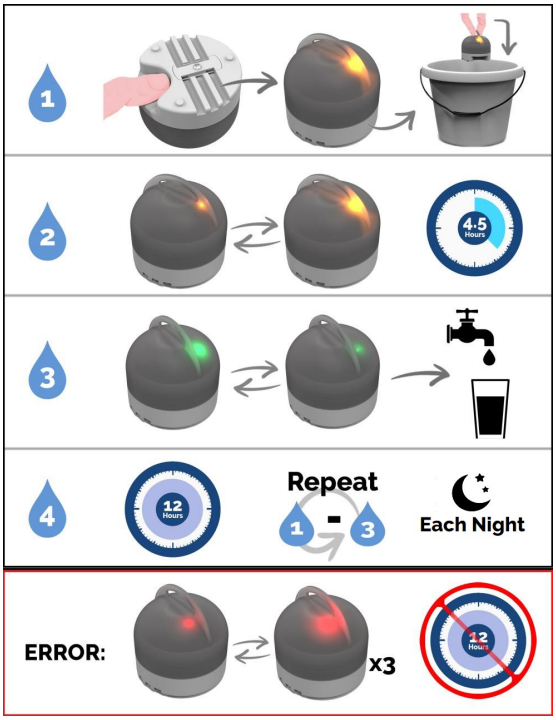

Figure 4.3: Instructions given to user that depict the device and directions guided by LED lights.

The device was powered by a single 9V battery and is controlled using the MSP430G2553 low-power microcontroller. Red, yellow, and green LED lights in the enclosure communicated to the user the different stages of the water treatment process. A solid yellow light signaled that the device was activated by the capacitive touch sensor. Once solid yellow, the user placed the device into the water container. The device then sensed the introduction of water and began to blink yellow every 8 seconds. The yellow LED blinked for the following four hours to let the user know that the device was functioning, but the water was not ready to be consumed. The target amount of electrolytically silver ions, 50 ppb, was previously shown to provide a 4.12-log reduction of *E. coli* in four hours in a laboratory setting.[21] 50 µg/L was chosen because it is half of the World Health Organization drinking water recommended guideline of 100 µg/L.[18] After four hours, the device blinked green every 8 seconds, indicating to the user that the water is safe to drink and that the device can be removed from the treated water.

In the device there was a software lock that limited silver release to once every twelve hours. This ensured that silver levels did not exceed 100 ug/L in 24 hours. If the user tried to activate the device before the software lock is lifted, the device emitted four red flashes.

After the prototypes were manufactured, each prototype was tested in the lab to ensure that a target amount of silver released that was below the WHO guideline but sufficient for disinfection. For each prototype, the capacitive touch sensor was pressed and the prototype was placed in 10 L synthetic synthetic groundwater consisting of 1.2 g of $MgSO_4$, 1.92 g $NaHCO_3$, 0.08 g KCl, and 1.2 g of $CaSO_4$ per 20 L in a plastic container. A 4 mL water sample was taken from each plastic container and analyzed for silver concentration using a PerkinElmer HGA 900 graphite furnace atomic absorption spectrometer (GFAA) with a silver cathode lamp. Water

samples analyzed for silver were acid digested using nitric acid for a final sample concentration of 2% HNO_3.

4.3.2 PARTICIPANT ENROLLMENT

The study was conducted in a village in the Dzimauli community in Limpopo, South Africa during February 2020. The site was chosen because it was previously found that only 15% of households treat their drinking water in Dzimauli.[25] 20 randomly selected households from one village in Dzimali were enrolled in the study. Community participants were eligible if the head of household was at least 18 years of age and they did not have chlorinated water piped into the home. If eligible, a translator fluent in both English and Tshivenda explained the study using a written script and answered any questions the participant had. They were then asked to participate and verbal consent was obtained. Verbal consent was considered satisfactory because this research presents no more than minimal risk of harm to subjects and involved no procedure for which written consent is normally required outside of the research context. After consent was obtained, a baseline questionnaire was conducted concerning demographics and drinking water information. At the conclusion of the study, each household was given the device to continue treating their water and an extra battery. They were instructed how to replace the battery in their water treatment device for continued use. The protocol for this study was approved by the University of Virginia Institutional Review Board for Health Sciences Research (IRB-HSR #21809) and University of Venda Research Ethics Committee (SES/19/HWR/02/0612).

4.3.3 INTERVENTION AND STUDY DESIGN

The performance of the electrolytic device was evaluated in 20 households over a 4-week period. After consent was obtained and baseline survey completed, the household received a 20 L safe-storage water container and an electrolytic water treatment device. With assistance from the translator, the participants were given a demonstration on how to use the device and were given an opportunity to practice in the presence of the researchers to ensure they could independently use their device to treat drinking water. Participants were instructed to fill the safe-storage water container with water, press a capacitive touch sensor at the bottom of the device to activate it, and place it in the water until the device flashed green which indicated that the water was sufficiently disinfected. Participants were instructed to remove the device using the handle at the top and store in a dry place until they refilled the safe-water storage container, after which they would repeat the disinfection process. Participants were instructed to continue storing water the way they were prior to receiving the device. Households were visited twice a week for four consecutive weeks.

4.3.4 SAMPLE COLLECTION

Water samples were taken twice a week from each household using Sterile Whirlpak sample bags. Two samples were taken during each visit: 500 mL of water collected from the spigot of the bucket treated with the device (effluent) and 500 mL of the untreated source water that the household used to refill their safe-storage water containers (influent). Samples were transported in coolers with ice from households to the laboratory at the University of Venda and analyzed within six hours of collection.

4.3.5 WATER QUALITY ANALYSIS

Total coliform bacteria, *Escherichia coli (E. coli)*, and total silver concentration were measured in samples collected from the study. Total silver concentration in effluent water samples was measured weekly. In the field, the Hach RapidSilver™ Visual Test Kit was used to gain approximate measurements of silver concentration in effluent water during the study to ensure that silver levels did not exceed the WHO guideline. Samples collected in South Africa were then transported back to the University of Virginia for more precise measurements of total silver concentration using a PerkinElmer HGA 900 graphite furnace atomic absorption spectrometer (GFAA) with a silver cathode lamp. Water samples analyzed for silver were acid digested using nitric acid for a final sample concentration of 2% HNO_3.

Total coliform and *E. coli* concentration were quantified twice a week using membrane filtration for both influent and effluent water samples as previously described by Ehdaie et al.[14] 100 mL of sample or diluted sample was passed through a 0.45 Millipore filter and placed in a sterile petri dish containing m-Coliblue24 growth media (Millipore) and incubated for 24 hours at 37 °C. Bacteria counts for each dish quantified bacteria concentrations for the corresponding sample. 100 mL of deionized water was passed through the membrane filtration system as a negative control for the first and last sample analyzed each day.

To quantify disinfection efficacy of the device, the absolute concentration of total coliform and *E. coli* bacteria from influent and effluent samples were used to calculate the log reduction at each household. To calculate this, the log of the total coliform bacteria concentration in the effluent was subtracted from the log of the total coliform bacteria concentration in the effluent. The disinfection efficacy of *E. coli* was also calculated this way.

4.4 RESULTS

4.4.1 SILVER CONCENTRATIONS

When prototypes were tested in the lab, the silver release by prototypes in 10L synthetic groundwater provided a mean 30 µg/L silver with a standard error of 0.8 µg/L. Throughout the study in the field, samples collected from treated water were consistently below the WHO drinking water guideline. Average silver levels measured over four weeks were 31 - 61 µg/L (Figure 4.3, Table 4.1), beginning at 61 µg/L during the first week and remaining fairly constant (31- 41 µg/L) during the second, third, and fourth week of use.

Table 4.1: Silver concentration measured in water sampled from intervention effluent over four weeks . Displayed is the average (±SEM) silver concentration.

Weeks of use of electrolysis device	Silver concentration in effluent (µg/L)
1	60 (± 12)
2	36 (± 6)
3	41 (± 8)
4	31 (± 6)

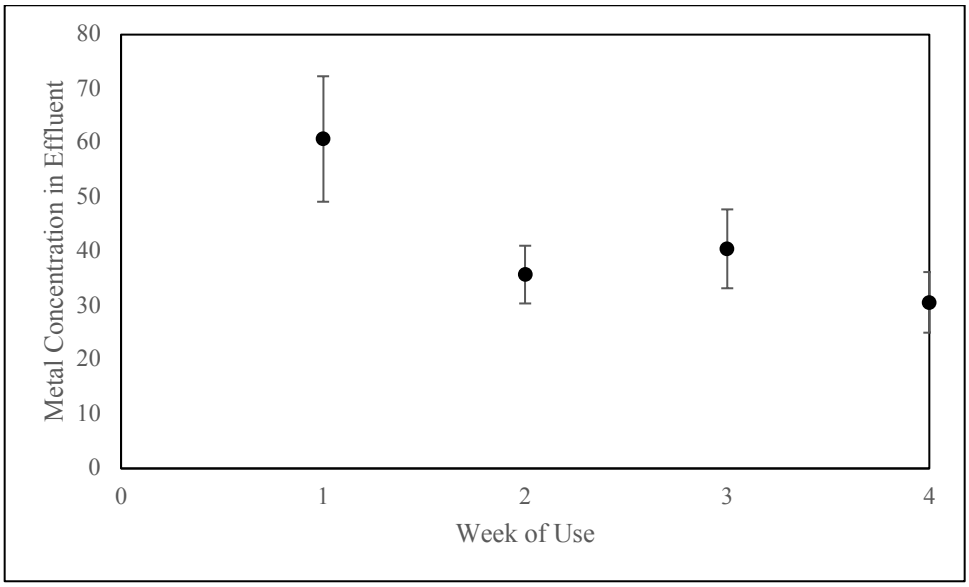

Figure 4.4: Mean values for silver concentration in effluent water from the intervention. Error bars indicate the standard error above and below the mean.

4.4.2 WATER QUALITY MEASUREMENTS

The total coliform bacteria and *E. coli* concentrations in water samples taken from households are included in Figures 4.4 and 4.5. Median total coliform concentration detected in untreated water in households over four weeks were 290-924 colony forming units per 100 mL of water. Water sampled from the effluent had a median coliform concentration of zero at weeks one and four and a median 58 and 22 total coliform bacteria at weeks two and three, respectively. This corresponded to an average 0.88 - 2.06 weekly log reduction of total coliform bacteria achieved by the device in study households (Table 4.2, Figure 4.4). *E. coli* concentrations detected in untreated household water were low, with a median of 2 *E. coli* detected during the first week and a median of 0 detected during weeks 2-4. While the initial concentration was low, *E. coli* was still reduced in outflow water, with the median and upper quartile of outflow *E. coli* concentration of zero. Table 4.3 displays the WHO risk categories for effluent samples treated by the electrolysis prototype.

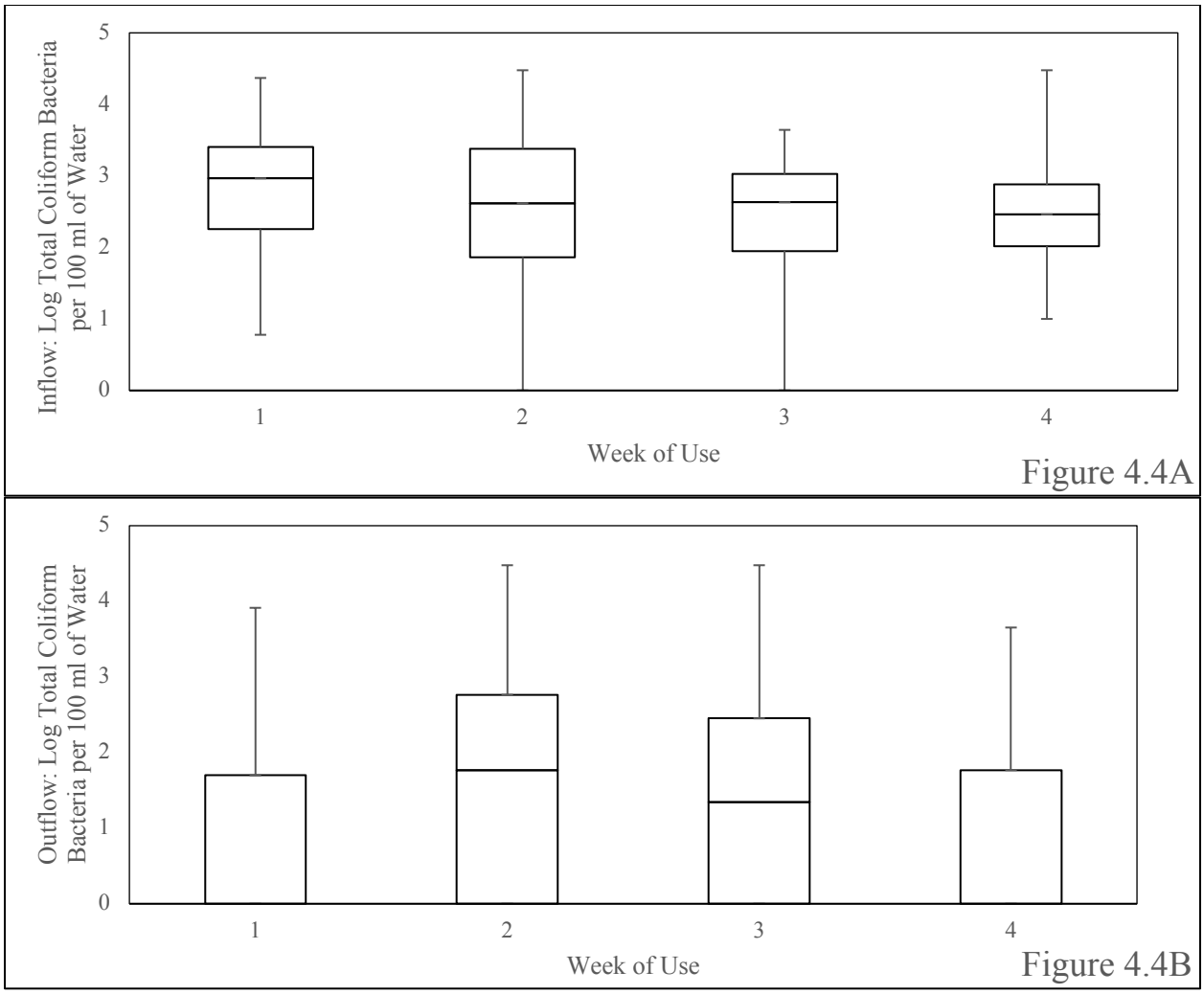

Figure 4.5: Box and whisker plot of total coliform bacteria concentration in water taken from the home and intervention spigot over four weeks. Figure 4.4A displays the log of total coliform bacteria concentration in water taken from untreated source water used by the household to fill the intervention. Figure 4.4B displays the log of total coliform bacteria concentration in treated water from the spigot. In each figure, the top and bottom boxes in each column represent the second and third quartile of the data, respectively. The line that separates them indicates the median, and the lower and upper whiskers indicate the first and fourth quartile of the data.

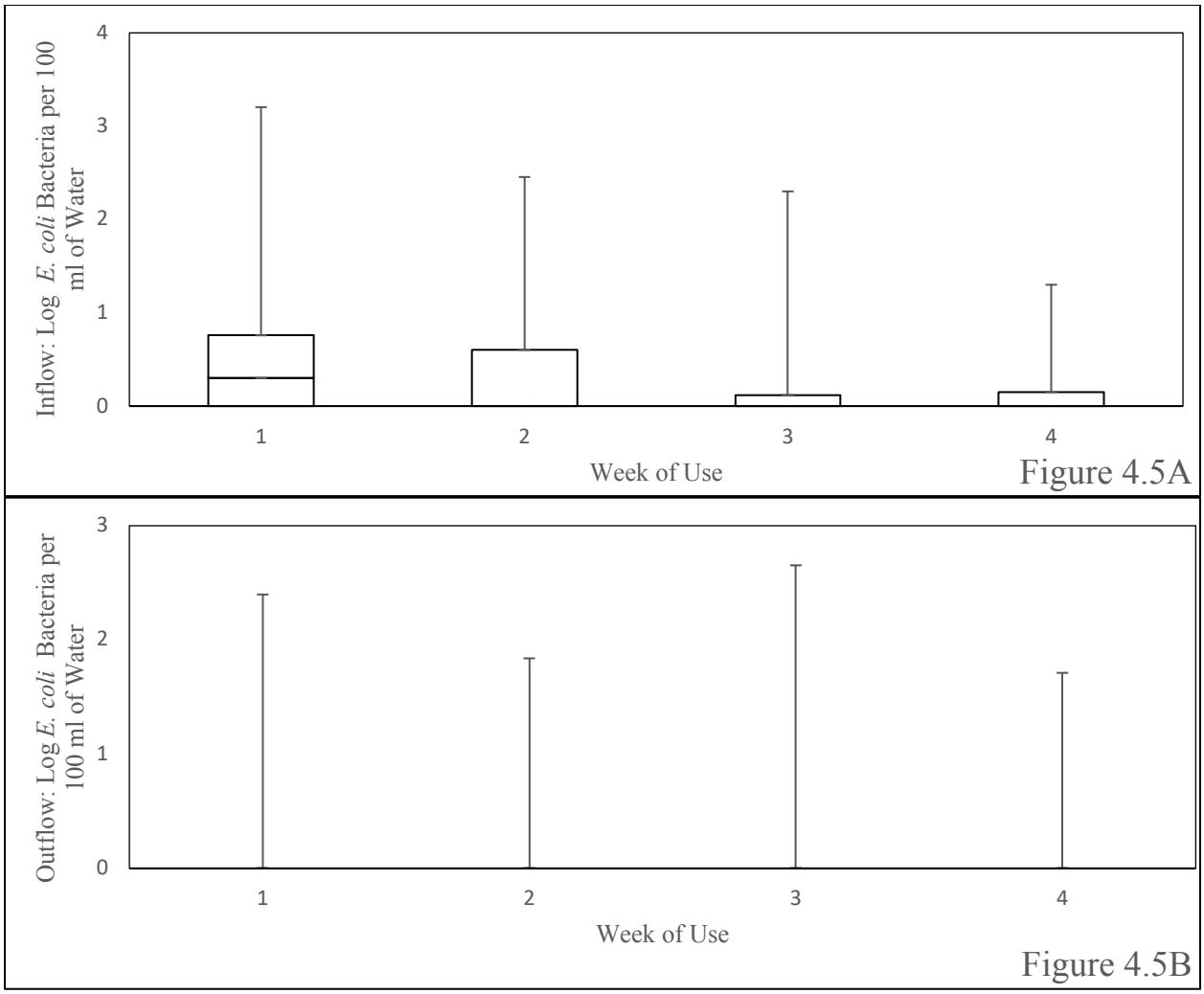

Figure 4.6: Box and whisker plot of *E. coli* bacteria concentration in water taken from the home and intervention spigot over four weeks. Figure 4.5A displays the log of *E.coli* bacteria concentration in water taken from untreated source water used by the household to fill the intervention. Figure 4.5B displays the log of *E. coli* bacteria concentration in treated water from the spigot. In each figure, the top and bottom boxes in each column represent the second and third quartile of the data, respectively. The line that separates them indicates the median, and the lower and upper whiskers indicate the first and fourth quartile of the data.

Table 4.2: Log Reduction of total coliform and *E. coli* bacteria with respect to time over the four week study. Displayed is the average (±SEM) log reduction.

Weeks of use of electrolysis device	Average log removal total coliform	Average log removal *E. coli*
1	2.06 (± 0.21)	0.29 (± 0.12)
2	0.88 (± 0.26)	0.37 (± 0.13)
3	1.07 (± 0.25)	0.09(± 0.1)
4	1.53 (±0.25)	0.04 (± 0.08)

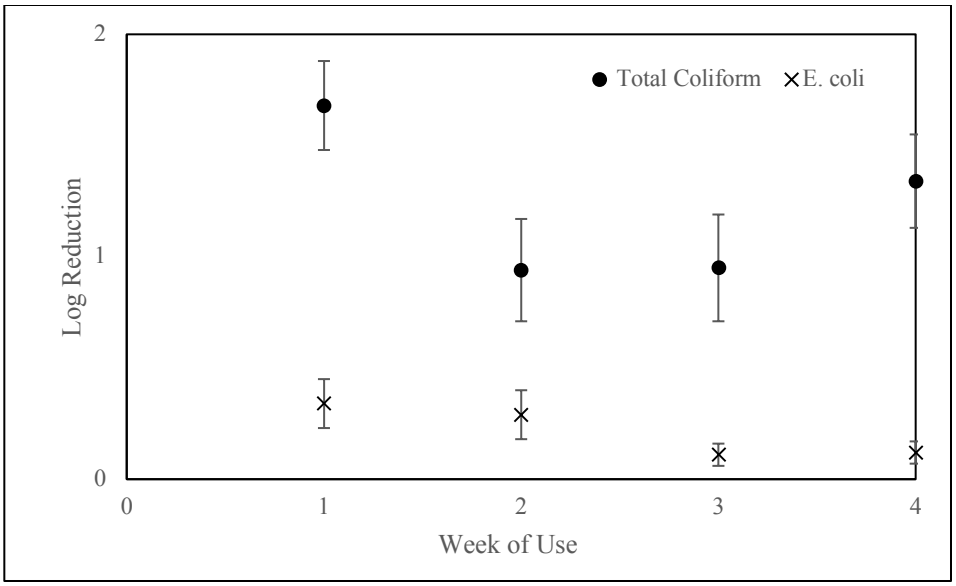

Figure 4.7: Mean values for log reduction of total coliform and *E. coli* bacteria. Error bars indicate the standard error above and below the mean.

Table 4.3: WHO risk categories for effluent samples treated by the electrolysis prototype

WHO Risk Category	Total Coliform Bacteria	Week			
	(CFU/100 mL)	1	2	3	4
No risk	<1	60.00%	30.77%	42.11%	51.43%
Low risk	1 to 10	10.00%	5.13%	5.26%	5.71%
Medium risk	11 to 100	12.50%	23.08%	18.42%	25.71%
High risk	101 to 1000	7.50%	17.95%	21.05%	8.57%
Very high risk	>1001	10.00%	23.08%	13.16%	8.57%

4.5 DISCUSSION

The results from this field study suggest that electrolysis is a promising disinfection mechanism for a POU device and that improvements should be made to make the device easier to use. Previously, 50 µg/L of electrolytically generated silver ions showed more than a 5 log reduction of *E. coli* bacteria in a laboratory setting.[21] This corresponds to the World Health Organization's top performance classification for bacteria removal, "comprehensive

protection."[26] However, when examining field results, the prototype achieved less than a 2 log reduction. This is comparable to the field performance other POU technologies: silver impregnated ceramic water filters (1.8 log reduction total coliform)[27], boiling water (1.82 log *E. coli* reduction,[28] biosand filters (2 log reduction *E.* coli)[29] and a low dose (2 mg/L) of Procter and Gamble's water purification sachet (1.9 log reduction total coliform)[30]. A high dose (3.5 mg/L) of the Procter and Gamble sachet and the MadiDrop performed better than the electrolysis prototype, achieving 3 and 3.2 log reduction of total coliform bacteria, respectively.[27,30] Silver impregnated filter paper achieved 4.2 log reduction of total coliform bacteria in a laboratory setting, lower than that achieved by electrolysis in the laboratory.[16] The performance of a water treatment device in the lab is typically better than that in the field due to the variability of human use of the device.

While the 2 log reduction of total coliform bacteria is less than the 5 log reduction observed in laboratory experiments, given the unpredictability of field use and various human factors, these results are promising for the first prototype, particularly if the design is optimized for the user. The maximum 2 log reduction achieved by the intervention is particularly impressive because the initial concentration contamination levels were lower than what would allow for a 5 log reduction in bacteria. In fact, the majority of untreated water samples would only allow for a 3 log reduction of coliform bacteria even if no coliform was detected in the effluent. This is reflected in Figure 4.4 as the median log total coliform bacteria was 3 in the influent and 0 in the effluent.

During the laboratory evaluation and during the field study, the prototype consistently released target silver levels that were below the World Health Organization guideline and safe to drink. This showed the device was able to produce enough silver sufficient for disinfection but still safe to drink. The silver concentrations detected in effluent from the electrolysis device during weeks 2-4 were comparable to mean silver levels detected in households with MadiDrops and silver impregnated ceramic filters.[27] However, the quick release of silver provided through electrolysis may be an advantage over the MadiDrop and filter that release silver over several hours, as it likely results in more rapid disinfection.

In a future version of this prototype, it may be possible to incorporate copper so that the device releases both silver and copper ions into untreated water for disinfection. This could increase the disinfection potential as the device could not only release up to 100 µg/L silver and 1000 µg/L copper while still staying within WHO guidelines.[18] Using the maximum concentrations of silver and copper can have a stronger combined purification power than either ion at the EPA-set secondary drinking water standard alone, as it allows greater numbers of metal ions in the water without exceeding each individual ionic concentration limit.[18]

After observing user patterns in the study, several design aspects of the prototype were identified that could be changed to improve ease of use. Improving the ease of use of the device may improve device frequency of use and improve disinfection performance. During this study, the prototype floated inside of the safe-storage water container on top of the untreated water and was removed after it flashed green, indicating that the water was clean to drink. While there was a handle at the top of the device to mitigate contamination from users hands, the user still needed to open the safe storage container and reach inside to remove the device after treatment. In addition, while the safe storage containers were translucent, the green light on the prototype

might have been difficult to distinguish, causing users to uncover the bucket intermittently during treatment to check the status of the device. A more user-friendly prototype for this technology could incorporate an electrolysis device that is fixed on the outside of the safe-storage water container. This way, the LED light indicating the state of the water would be easily visible and fixing the device to the outside of the safe water storage container would minimize possible contamination as well as increasing ease of use.

In addition, it was observed that users had difficulty changing the battery inside of the device and the capacitive touch button was not intuitive as there was no physical button for the user to press on the finger recess. Because of this, improvements could be made to the battery holder to make replacement easier and to add a physical button for the user to make it clear that they've activated the device. All of the described improvements will improve the experience for the user which enhance the correct use of the device, increasing its disinfection efficacy.

The use of electrolysis in a POU water treatment device is promising technology. The disinfection of total coliform bacteria coupled with silver levels that are sufficient for disinfection by below the WHO guideline suggest that such a technology could be incorporated into a low resource setting. With the proposed adjustments to the prototype design and the addition of copper, an electrolytic POU device has the potential to provide clean water to households in low-resource settings.

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Chapter 5: Efficacy of Safe-storage Water Containers, Ceramic Water Filters, and MadiDrops: a 400-Family Randomized Trial in Rural South Africa

The work presented in this chapter resulted in a journal article in preparation:

Hill, C., McQuade, E., McCain, K., Edokpayi, J., Mzwakhe, E., Kahler, D., Taylor, D., Wright, N., Amidou, S., Guerrant, R., Dillingham, R., Bessong, P., Smith, J., "Efficacy of Safe-storage Water Containers, Ceramic Water Filters, and MadiDrops: a 400-Family Randomized Trial in Rural South Africa"

5.1 ABSTRACT

A silver-impregnated ceramic tablet (MadiDrop) disinfects water by releasing silver ions into household water-storage containers. This paper reports on the tablet's long-term field performance as part of a larger trial examining the impact of point-of-use water treatment on linear growth in children. 404 homes in Limpopo, South Africa were randomized to receive a MadiDrop, silver ceramic water filter, safe-storage water container, or no intervention. The disinfection of total coliform and *E. coli* bacteria for each intervention was measured every six months over two years. The MadiDrop's disinfection of total coliform bacteria (3.22 ± 0.27 log reduction) exceeded the performance of silver ceramic water filters (1.80 ± 0.35 log reduction) and filters without silver (1.18 ± 0.25 log reduction). Safe-storage water containers did not improve water quality (0.01 ± 0.27 log reduction). After intervention adjustments, silver concentrations in treated water were 31.8 ± 36.7 µg/L for the silver ceramic filter intervention arm and 27.4 ± 39.1 µg/L for the MadiDrop intervention arm. These mean silver concentrations were less than the 100 µg/L World Health Organization guideline for silver in drinking water. MadiDrop longevity, based on consistent silver-ion release rate, was determined to be at least 12 months of daily use.

5.2 BACKGROUND

Devastatingly, 2.2 billion people do not have safely managed drinking water sources worldwide.[1] The high levels of pathogen contamination in unsafely managed drinking water sources contribute to more than 500,000 diarrhoeal deaths per year.[2] In addition, pathogen exposure from these sources may lead to environmental enteropathy, a prevalent subclinical condition of the gut that relates to poor growth and cognitive deficits among children.[3]

Point-of-use (POU) water treatment technologies, which allow the user to treat water in their household before consumption, are one solution to reduce water-borne disease and its associated effects.[4–8] A triple bottom line sustainability assessment showed that POU water treatment can be a more sustainable and cost-effective solution in low-resource settings when compared to a central water treatment system.[9]

While POU devices have proven to be effective at removing turbidity and pathogens from drinking water, there are several challenging design criteria that must be met in order to create an effective device. They must be simple to use, socially acceptable, and inexpensive. A device called the MadiDrop, a 8 x 3 x 1.4 cm porous ceramic tablet infused with silver nanopatches,[10,11] was developed to meet these criteria. When placed in a water storage container, the MadiDrop releases ionic silver, which disinfects waterborne pathogens after 8-10 hours of contact time. The user places the MadiDrop inside a safe-storage water container, fills the container with untreated water in the evening, and, by the morning, the diffused silver from the MadiDrop has disinfected waterborne pathogens, making the water safe to drink.

The original MadiDrop prototype developed at the University of Virginia demonstrated a 3 log reduction of *Escherichia coli* while keeping the silver concentration in treated drinking water below the World Health Organization (WHO) drinking water guideline.[11] The prototype was tested in field studies in Limpopo, South Africa and Dodoma, Tanzania, achieving up to a 3.2 log reduction of total coliform bacteria.[12,13] Further research optimized the rate of ion release from the prototype and demonstrated the MadiDrop's ability to disinfect protozoa.[14,15]

While previous work on the MadiDrop showed that prototypes have been highly effective in treating water in the laboratory and short-term field studies, the commercial product has yet to

be evaluated. In addition, it was unknown if the reduction of waterborne pathogens caused by POU technologies would translate to improvements in child health.

To understand this relationship, a community-based randomized controlled trial was conducted to estimate how access to POU water treatment devices affect the linear growth of children in Limpopo, South Africa.[16] The study used both the MadiDrop and a second water treatment device, a silver ceramic water filter. This filter removes pathogens mechanically, and the silver both inactivates live pathogens moving through the filter and provides residual disinfection in the lower reservoir.[17] This type of filter is relatively well-known and widely used globally, [7,18–21] making it a useful technology to compare with the MadiDrop performance.

We investigated the impact of POU water interventions in 400 households in Limpopo, South Africa. This paper reports the first evaluation of the long-term use of the MadiDrop in the field and compares it against a conventional technology (the silver ceramic filter) and a safe water storage container. In addition, it examines the adherence to using these technologies in the field and the potential for the MadiDrop to have a longer lifespan than originally recommended.

5.3 METHODS

5.3.1 ETHICS

The protocol for this study was approved by the University of Virginia Institutional Review Board for Health Sciences Research (18662) and the University of Venda Human and Clinical Trials Research Ethics Committee (SMNS/15/MBY/27/0502). Written consent of adult caregivers in either English or Tshivenda was obtained after verbal explanation of the study in Tshivenda. Verbal assent was obtained from children age 7-15 years. Children in participating households were referred to the local clinic by fieldworkers if they were found to have

significant health concerns when study visits were made. All participants, regardless of intervention group, received a new ceramic water filter at the end of the study.

5.3.2 FIELD SITE ENROLLMENT AND ELIGIBILITY

The study was conducted in villages comprising the Dzimauli community in Limpopo, South Africa. This community was chosen because a previous study showed that only 12 percent of households reported treating their drinking water.[22] Of these households, 23% used bleach or chlorine and 5% boiled their water while the rest let their water stand and settle.[22] In addition, 35% of children were stunted at two years of age.[23] Dzimauli community members were enrolled if the household included at least one child under 3 years of age or the mother was in the third trimester of pregnancy. Households were excluded if they had chlorinated water piped into the home or routinely delivered to a permanent, engineered system that stored the water on their property, used ceramic or other commercial water treatment, planned to move outside the community in the next 6 months, the child's caregiver was under 16 years of age or unable to give consent, or the youngest child under 3 years of age was seriously ill.

5.3.3 INTERVENTIONS AND DESIGN OF STUDY

As part of the larger study, 404 households were randomized by household to one of four intervention groups to examine each intervention group's impact on early childhood linear growth. [16,24] 102 families were randomized to receive an 18-L safe-storage water container containing a silver ceramic water filter and two MadiDrops in the lower reservoir. 99 households were randomized to receive an 18-L safe-storage water container with two MadiDrops. 105 households were randomized to receive only an 18-L safe storage container, and 98 households

were randomized to receive no intervention. Two MadiDrops were chosen for the MadiDrop-only group because the MadiDrop was recommended for treatment of 10 L of water and the water storage containers provided to the participants could hold up to 18 L. For the intervention that included a silver filter and two MadiDrops, two MadiDrops in the lower reservoir were included to be consistent with the intervention that included only two MadiDrops. In this way, the interventions were identical except for the addition of the silver ceramic filter which allowed researchers to determine the additional impact of the silver ceramic filter on outcomes. The safe storage container group was chosen to determine if a safe storage container alone had an impact by preventing recontamination during storage.

Upon enrollment, participants were given instructions on how to use the given intervention and proper cleaning techniques. They were also informed that silver can disinfect waterborne pathogens and was the mechanism by which disinfection occurred in both the silver ceramic filter and the MadiDrop. Participants were instructed to use the given intervention for all drinking water consumed in the house and to only use other containers for storing and collecting untreated water. Social acceptability and adherence were measured through monthly surveys and the SmartSpout spigot. Surveys contained information regarding frequency of use and perception of the device. The SmartSpout spigot measured the household's frequency and duration of use as described in Section 2.9. In addition, monthly questionnaires were conducted to obtain sociodemographic information, water and sanitation practices, and illness surveillance for children in the home.

5.3.4 INTERVENTION CHANGES

Over the first four months of the study, silver concentrations in the treated water samples within the MadiDrop-only group and MadiDrop-plus-silver filter group were above the World Health Organization's (WHO) drinking water guideline for silver (100 μg/L) as discussed in section 3.2).[25] Based on these results, the interventions were modified several times under the guidance of an external Data Safety and Monitoring Committee (DSMC) with the aim of providing effective water treatment with mean silver concentrations below the WHO drinking water guideline. Households that originally had two MadiDrops and a silver ceramic filter were reduced to only a silver ceramic filter, and households with two MadiDrops (and no filter) were reduced to only 1 MadiDrop in the safe-storage water container after three months. At eleven months, in collaboration with its manufacturer, the MadiDrop was redesigned using 50% of the original amount of silver and these replaced the original MadiDrops. Because the 50% silver MadiDrop still resulted in a small number of households having silver levels in the treated water above the WHO drinking water guideline, all households with MadiDrops were then replaced with silver ceramic water filters at 13 months. A subsequent sampling of households with these filters showed a small number of households with silver levels in the treated water that were above the WHO guideline and the silver ceramic filters were then replaced with filters that did not contain silver at 18 months. At each change, researchers removed the intervention, drained the storage container, and replaced the intervention.

5.3.5 PREPARATION OF INTERVENTIONS

The silver ceramic water filters were produced locally in a filter production facility in Limpopo Province through the University of Virginia non-profit organization PureMadi. The

silver ceramic water filters and all safe storage containers were prepared as previously described.[12] Filters without silver were prepared in the same way, but the last step of silver application was omitted. The MadiDrops were manufactured and donated by MadiDrop Public Benefit Company in Charlottesville, Virginia; prototypes of this device have been described previously.[11,13] Details of the manufacturing process for the MadiDrop are proprietary and were not disclosed by the manufacturer.

5.3.6 WATER QUALITY SAMPLE COLLECTION

Every six months, water samples from 100 randomly selected households distributed evenly across intervention group were sampled for *Escherichia coli (E. Coli)* and total coliform bacteria (Table 1). Two 500 mL samples were collected from each household in sterile Whirlpak bags and transported in coolers with ice for analyses at the University of Venda. One sample was taken from the source of the water that was used to fill the intervention (influent), and the other was from the spigot on the safe-storage water container in households that had an intervention (effluent). Only one sample from their drinking water source was collected from households without an intervention. All samples were processed via membrane filtration within 6 hours of collection. To determine the disinfection efficacy of each intervention, the concentrations of bacteria from influent and effluent samples were used to calculate the log reduction of *E. coli* and total coliform bacteria at each household. Reasonably, this assumes that the influent is the same water quality as the effluent before treatment, this was calculated by subtracting the log of the total coliform bacteria concentration in the effluent from the log of the total coliform bacteria concentration in the influent. In households with MadiDrops and silver ceramic filters, a second disinfection efficacy calculation was done excluding households with an effluent of 0 total

coliform bacteria to capture the full disinfection potential of each intervention. The disinfection efficacy was then compared using t-tests for pairwise comparisons between the mean log reduction of total coliform bacteria among intervention groups at each sampling (0.05 significance level and two tailed test). The no control group was assumed to have an mean log reduction of zero. Water quality data at enrollment was previously reported as part of a water quality and water use practices case study and is therefore not evaluated in this manuscript.[24]

5.3.7 SILVER SAMPLE COLLECTION

To ensure that interventions did not exceed silver concentration guidelines set forth by the WHO, effluent water from interventions in randomly selected households that had a silver ceramic filter and/or a MadiDrop were originally intended to be sampled every six months. Due to intervention changes, these groups were sampled four times over the first eighteen months: (i) one month after enrollment from households that had interventions initially planned in the study (ii) six months after enrollment from households that had either a silver ceramic filter or a MadiDrop, (iii) thirteen months after enrollment from households that had either a silver ceramic filter or a MadiDrop with 50% of the original silver, or (iv) seventeen months after enrollment from households with a silver ceramic filter.

5.3.8 WATER QUALITY TESTING

Water samples were analyzed for total coliform bacteria and *E. coli* using the total coliform U.S. Environmental Protection Agency method 10023 with m-ColiBlue24 or m-Endo broth from EMD Millipore, Billerica, MA, USA. Samples tested for silver concentration were prepared with trace metal grade nitric acid (Fisher Chemical, Fair Lawn, NJ, USA) and tested on

a calibrated graphite furnace (HGA 900, Perkin-Elmer, Waltham, MA, USA) atomic absorption spectrometer (AA2100, Perkin-Elmer) (GFAAS).

5.3.9 SMARTSPOUT ADHERANCE MONITORING

To measure patterns in use of the water treatment and safe storage devices, SmartSpouts were installed at households with MadiDrops, filters, or safe-storage water containers after 12 months of follow-up. A SmartSpout is a standard Tomlinson spigot with a handle modified to include an accelerometer, microcontroller, and battery. The accelerometer measures the inclination of the handle in order to detect when the spigot is open. The microcontroller records the time and duration of each opening of the handle. Data were stored locally until read wirelessly by a fieldworker with a smartphone using near field communication.

A household was classified as having used a given intervention on a given day to retrieve water if the spigot was held open for a total of five seconds or greater. Five seconds corresponds to the amount of time required to release approximately 300 mL of drinking water. While multi-person households would be expected to consume more than 300mL of drinking water per day, data on occupancy each day were not available and this threshold was taken to represent an absolute minimum amount of use.

5.3.10 CYCLING EXPERIMENT

In response to silver concentrations observed above 100 µg/L, it was hypothesized that silver levels could rise over time due to the consumer drinking only a portion of the treated water in the safe storage container and adding untreated water to the storage container (i.e., topping off). This hypothesis was tested in the laboratory using both the MadiDrop with the original

amount of silver and 50% silver. Eight MadiDrops comprised of the original amount of silver and eight comprised of 50% of the original amount of silver were placed in a safe-storage water container and were filled with 20 L of *moderately hard* synthetic groundwater in the morning.[26] Over a span of 14 hours, either 0 L, 4 L, 10 L, or 16 L were removed in 4 equal increments every 3.5 hours to simulate consumption during the day. This was repeated for 10 days. After the fourteen-hour period, the safe storage containers were refilled with synthetic groundwater to 20 L and sat for 10 hours to simulate a participant filling the container before bed. Silver samples were taken at the end of the 14 hour period before refilling the bucket with synthetic groundwater and at the end of the 10 hour period before the first increment of water was taken from the container each day. Total silver concentrations were analyzed by GFAA as previously described.

5.3.11 LABORATORY ANALYSIS OF MADIDROPS

The manufacturer guaranteed the MadiDrop for six months, but suggested that the product would release enough silver for disinfection beyond the guaranteed period. To assess this, 100% silver MadiDrops used in households for the first 6 consecutive months during the study were transported back to the laboratory at the University of Virginia and analyzed for long-term silver release. Four 18-L safe storage containers were filled with 10 L of synthetic groundwater and replaced with new synthetic groundwater every day for an additional 6 months. Water samples were taken bi-weekly and analyzed for silver using GFAA analysis as previously described.

5.3.12 SOCIAL ACCEPTABILITY

A survey was administered to households that received either a MadiDrop with 50% of the original silver, a filter, or safe-storage water container to assess social acceptability of each intervention. Surveys were administered in two rounds: first to households with 50% silver MadiDrops before they were replaced with silver ceramic water filters and then to all households with ceramic filters without silver at the end of the study.

5.4 RESULTS

5.4.1 WATER QUALITY MEASUREMENTS

The number of households sampled for water quality in each intervention group over time is included in Table 5.1. In households with silver ceramic filters and/or MadiDrops, a median of zero total coliform bacteria was detected in treated water. The one exception to this was a median of 2 total coliform bacteria detected in the silver ceramic filter group at 12 months. At all of these samplings, the median total coliform bacteria in untreated water was as high as 8500 (Figure 5.1). In the one exception, a median of 4 total coliform bacteria was detected at six months in effluent water in households with a silver ceramic filter compared to a median 500 total coliform bacteria detected in untreated water in those households. Households with various configurations of MadiDrops and/or silver ceramic water filters corresponded to 1.56 - 3.51 mean log reductions of total coliform bacteria (Table 5.2). When compared to the safe-storage water container, the mean log reduction of total coliform bacteria by MadiDrops was 2.49 log and 2.83 log higher, at six and twelve months, respectively ($p<0.001$). The mean log reduction of total coliform bacteria by silver ceramic filters was 1.57 log and 2.16 log higher than the safe-storage water container at six and twelve months, respectively ($p<0.001$).

Households that had MadiDrops achieved higher log reduction of total coliform bacteria than households with a silver ceramic filter. This was true when comparing the performance of the original MadiDrop (2.5 log reduction) to that of a silver ceramic filter (1.56 log reduction) ($p=0.03$). When excluding households that had an effluent of 0 total coliform bacteria, the mean log reduction of total coliform bacteria was 3.22. While the 50% silver MadiDrop (2.47 log reduction) also achieved a higher log reduction of total coliform bacteria than the silver ceramic filter (1.80 log reduction), the difference was not significant ($p=0.1$). MadiDrops with 50% of the original silver disinfected just as well as MadiDrops that contained the original amount of silver, both achieving approximately an mean 2.5 log reduction of total coliform bacteria ($p=0.9$).

Ceramic water filters without silver provided 1.18 log reduction in total coliform bacteria at the beginning of use (18 months). This was 1.28 log more than the negative log reduction of total coliform bacteria provided by the safe-storage water container ($p<0.001$). The difference in the mean log reduction achieved by filters without silver at 18 months compared to no intervention was also statistically significant ($p=0.002$). Water taken from recently installed ceramic filters with no silver had a median of 300 total coliform bacteria detected in effluent water compared to a median 3250 total coliform bacteria detected in untreated water in those households. After six months of use at 24 months, the capacity of ceramic water filters without silver to remove total coliform bacteria declined with treated water containing a median of 421 total coliform bacteria in treated water and 708 total coliform bacteria in untreated water. This corresponded to an equivalent 0.13 mean log reduction of total coliform bacteria, 1 log less than the total coliform bacteria removal capacity of the intervention when it was installed in the home ($p<0.001$). The performance of the no silver filter at 24 months was 0.7 log more than the

reduction of total coliform bacteria provided by the safe-storage water container (p=0.04). However the log removal between filters at 24 months and no treatment was similar (p=0.6).

Median total coliform bacteria concentration in households with only a safe-storage water container were comparable to or more contaminated than untreated water found in households with no intervention. Households with only a safe storage container had a median total coliform bacteria concentration ranging from 908 to 6800 cfu/100 mL in untreated water and 1050 to 7350 cfu/100 mL coming from the safe storage container's spigot. At 6, 12, and 18 months, the 0.01, -0.36, and -0.26 mean log reduction of total coliform bacteria, respectively, were similar to those of households with no intervention (p=1.0, p=0.3, p=0.2, respectively). In some cases, there was an increase in total coliform bacteria in water coming from the spigot. At 24 months, the mean 0.57 log increase in total coliform bacteria was statistically significant compared to no treatment (p=0.04). The total coliform bacteria levels detected in homes with no intervention was similar to that of untreated water in homes with interventions. *E. coli* concentrations in influent and effluent water samples are included in Figure 5.2. *E. coli* and total coliform reductions for each group over time are reported Table 5.2 and Table 5.3. The WHO risk category for effluent samples in households with MadiDrops, ceramic water filters, and/or safe water storage containers is included in Table 5.4

Table 5.1: Number of households samples from each intervention group for water quality analysis over the duration of the study. SWS = Safe-storage water container

	Number of Households Sampled (% of Available Households)			
Months	Filter	MadiDrop	SWS	No Intervention
6	28 (27.5%)	28 (28.2%)	22 (20.9%)	26 (26.5%)
	Filter	50% Ag MadiDrop	SWS	No Intervention
12	23 (22.5%)	24 (24.3%)	24 (22.9%)	23 (23.5%)
	No Ag Filter		SWS	No Intervention
18	48 (23.9%)		21(20%)	25 (25.5%)

	No Ag Filter	SWS	No Intervention
24	46 (22.9%)	23 (21.9%)	23 (23.5%)

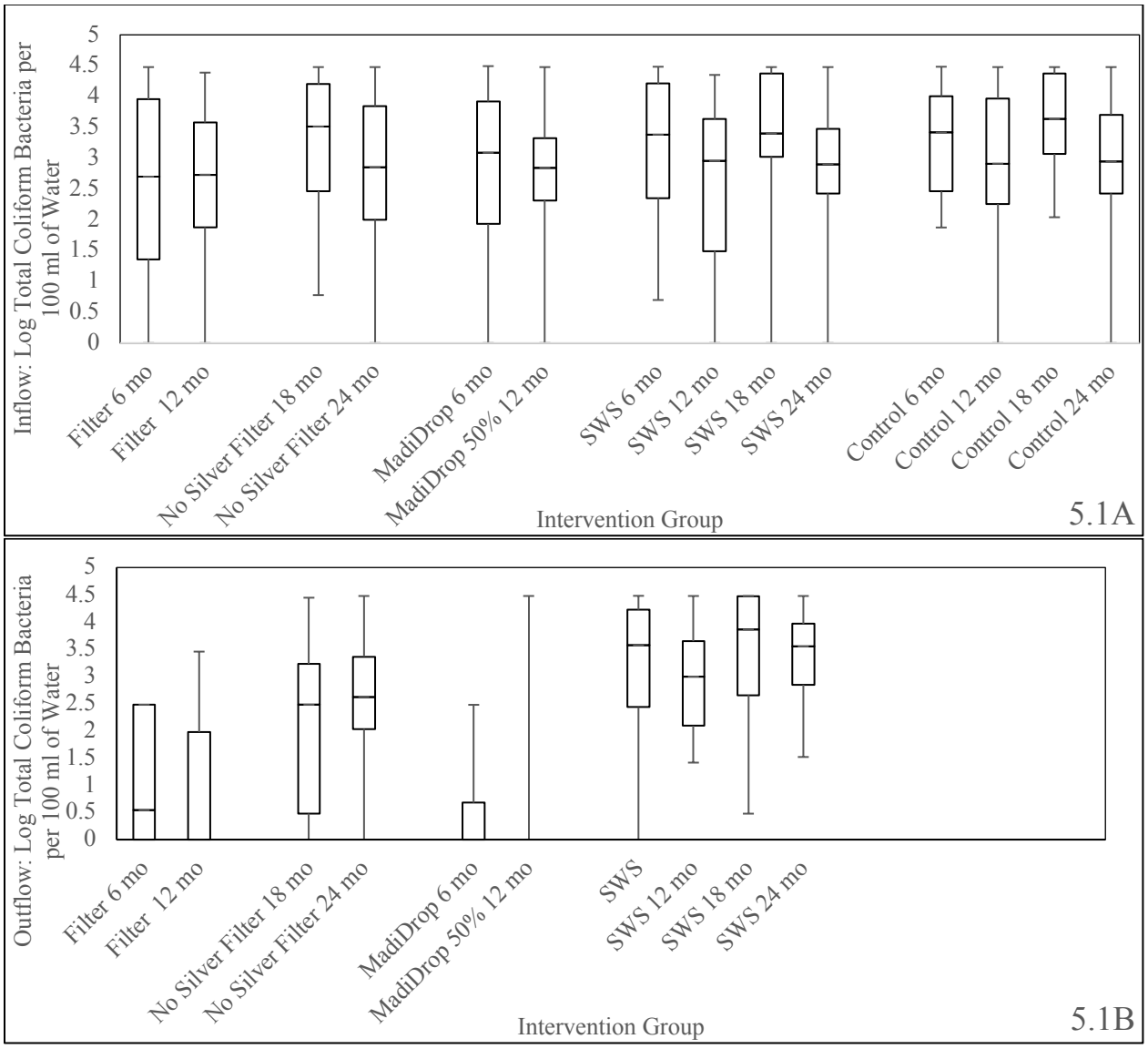

Figure 5.1: Total coliform bacteria concentration in water taken from the households and intervention spigot at six month intervals over two years. Figure 5.1A displays the log of total coliform bacteria concentration in influent water taken from untreated source water used by the household to fill the intervention. Figure 5.1B displays the log of total coliform bacteria concentration in effluent treated water from the spigot. Filter represents households that had a silver ceramic filter in a safe-storage water container, No Silver Filter represents households that had a filter with no silver applied to the ceramic in safe-storage water container, MadiDrop represents households with a MadiDrop in a safe-storage water container that contained the original amount of silver, MadiDrop 50% group represents households with a MadiDrop made with 50% of the original amount of silver in a safe-storage water container, SWS represents households with only a safe storage container, and the control group represents households that

had no intervention. The minimum and maximum detection limits for this analysis was 0 and 4.5 log total coliform bacteria, respectively.

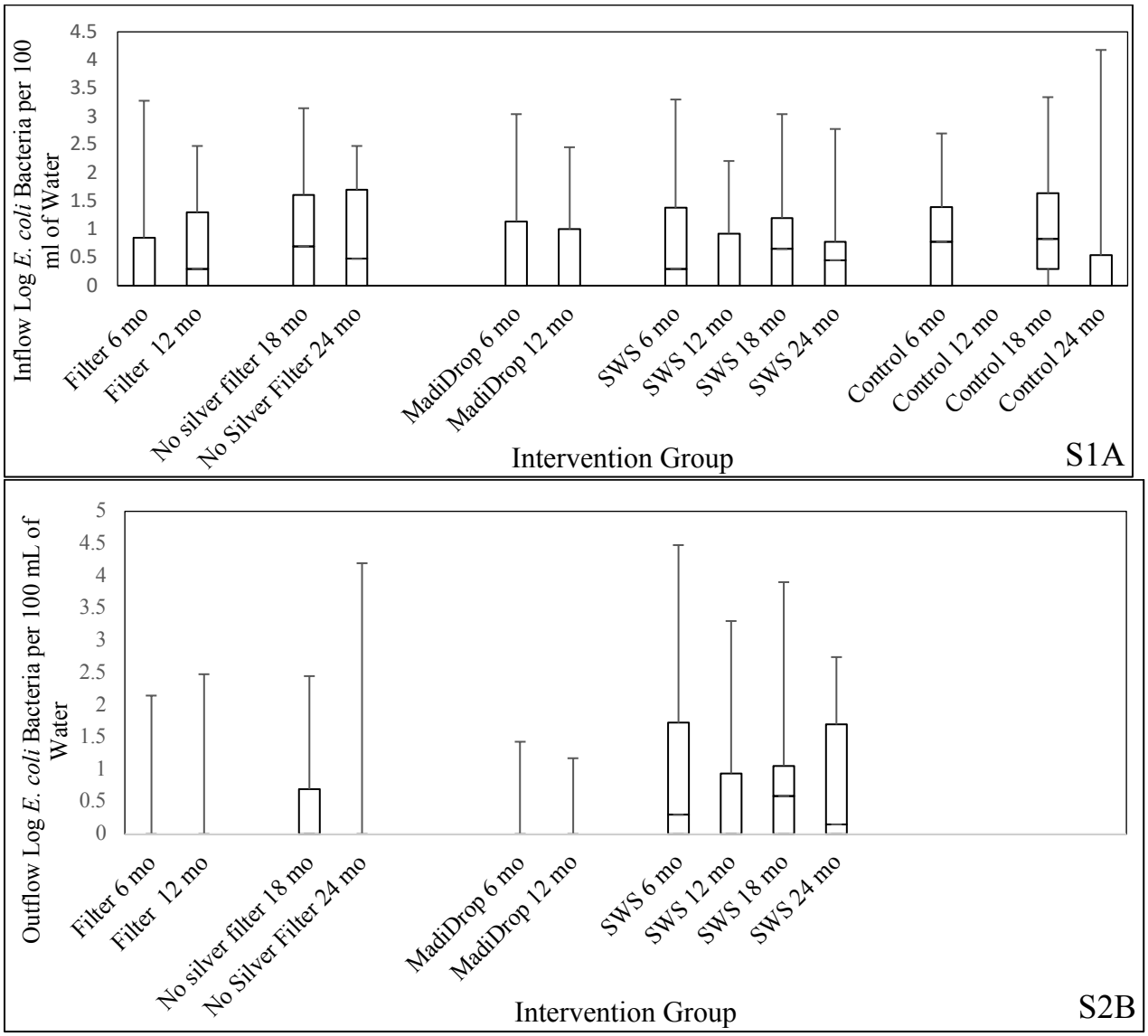

Figure 5.2: *E. coli* bacteria concentration in water taken from the home and intervention spigot at six month intervals over two years. Figure 5.2A displays the log of *E. coli* bacteria concentration in water taken from untreated source water used by the household to fill the intervention. Figure 5.2B displays the log of *E. coli* bacteria concentration in treated water from the spigot. Filter represents households that had a filter in a safe-storage water container, No Silver Filter represents households that had a filter with no silver solution painted onto the ceramic in safe-storage water container, MadiDrop represents households with a MadiDrop in a safe-storage water container that contained the original amount of silver, MadiDrop 50% group represents households with a MadiDrop made with 50% of the original amount of silver in a safe-storage water container, SWS represents households with only a safe storage container, and the control group represents households that had no intervention.

Table 5.2: Log Reduction of total coliform bacteria with respect to intervention group over the duration of the study. Displayed is the average (±SEM) log reduction. SWS = Safe-storage water container. Values marked with * indicate the average log reduction of total coliform bacteria excluding households that had 0 total coliform bacteria in effluent water.

Months	Log Reduction of Total Coliform Bacteria					
	Filter + 2 MadiDrops		2 MadiDrops		SWS	No Intervention
0	3.51 ± 0.26		3.47 ± 0.23		0.00 ± 0.31	-
	Filter		MadiDrop		SWS	No Intervention
6	1.56 ± 0.34	0.94 ± 0.38*	2.50 ± 0.24	3.22 ± 0.27*	0.01 ± 0.27	-
	Filter		50% Ag MadiDrop		SWS	No Intervention
12	1.80 ± 0.35	1.52 ± 0.59*	2.47 ± 0.24	2.35 ± 0.85*	-0.36 ± 0.33	-
	No Ag Filter				SWS	No Intervention
18	1.18 ± 0.25				-0.26 ± 0.18	-
	No Ag Filter				SWS	No Intervention
24	0.13 ± 0.19				-0.57 ± 0.27	-

Table 5.3: Log Reduction of *Escherichia coli* with respect to intervention group. Displayed is the average (±SEM) log reduction. SWS = Safe-storage water container

Months	Log Reduction of *Escherichia coli* Bacteria			
	Filter + 2 MadiDrops	2 MadiDrops	SWS	No Intervention
0	Not measured	Not measured	Not measured	-
	Filter	MadiDrop	SWS	No Intervention
6	0.35 ± 0.20	0.63 ± 0.16	-0.19 ± 0.21	-
	Filter	50% Ag MadiDrop	SWS	No Intervention
12	0.47 ± 0.22	0.51 ± 0.16	-0.08 ± 0.25	-
	No Ag Filter		SWS	No Intervention
18	0.48 ± 0.12		-0.10 ± 0.23	-
	No Ag Filter		SWS	No Intervention
24	0.27 ± 0.18		-0.57 ± 0.27	-

Table 5.4: WHO risk category of samples from households with respect to intervention group

WHO Risk Category	Total Coliform Bacteria	Month				
	(CFU/100 mL)	0	6	12	18	24
		Filter + 2 MadiDrops	Filter	Filter	No Silver Filter	No Silver Filter
No risk	<1	96.15%	35.71%	54.17%	13.73%	6.38%
Low risk	1 to 10	0.00%	21.43%	20.83%	17.65%	4.26%
Medium risk	11 to 100	0.00%	14.29%	0.00%	9.80%	10.64%
High risk	101 to 1000	3.85%	28.57%	16.67%	31.37%	46.81%
Very high risk	>1001	0.00%	0.00%	8.33%	27.45%	31.91%
		2 MadiDrops	MadiDrop	50% Ag MadiDrop	-	-
No risk	<1	100.00%	71.43%	80.00%	-	-
Low risk	1 to 10	0.00%	10.71%	12.00%	-	-
Medium risk	11 to 100	0.00%	14.29%	4.00%	-	-
High risk	101 to 1000	0.00%	3.57%	0.00%	-	-
Very high risk	>1001	0	0	0.04	-	-
		SWS				
No risk	<1	3.85%	4.55%	0.00%	0.00%	0.00%
Low risk	1 to 10	3.85%	9.09%	0.00%	4.55%	0.00%
Medium risk	11 to 100	0.00%	4.55%	13.04%	4.55%	8.70%
High risk	101 to 1000	19.23%	18.18%	39.13%	18.18%	21.74%
Very high risk	>1001	73.08%	63.64%	47.83%	72.73%	69.57%

5.4.2 SILVER CONCENTRATIONS FROM HOUSEHOLDS

The number of households sampled per intervention group for silver testing is reported in Table 5.4. At six months, eleven samples (41%) from randomly sampled households with one full strength MadiDrop had silver concentrations greater than the WHO guideline of 100 µg/L,

and these values were 103 -306 µg/L. No randomly sampled households in the silver ceramic filter group had silver concentrations above this WHO guideline. At 13 months, a comprehensive sampling of all homes using MadiDrops with 50% the original silver resulted in a mean silver concentration of 27.4 ± 39.1 µg/L. Six samples (7%) had silver concentrations greater than 100 µg/L, and these values were : 223, 181, 165, 135, 127, and 102. A random sampling of silver ceramic water filters conducted at the same time showed a mean silver concentration of 10.1 ± 0.46 µg/L with no silver concentrations above 100 µg/L. At 17 months, a random sampling of households with silver ceramic filters yielded a mean silver concentration of 31.8 ± 36.7 µg/L. Three samples (3%) had silver levels greater than 100 µg/L and these values were: 274, 130, and 112.

Table 5.5: Number of households sampled from each intervention group collected for silver concentration measurement over the duration of the study. SWS = Safe-storage water container

	Number of Households Sampled (% of Available Households)			
Months	Filter + 2 MadiDrops	2 MadiDrops	SWS	No Intervention
1	23 (22.5%)	21 (21.2%)	X	X
	Filter	MadiDrop	SWS	No Intervention
6	27 (26.5%)	27 (27.3%)	X	X
	Filter	50% Ag MadiDrop	SWS	No Intervention
13	22 (21.5%)	87 (100%)	X	X
	Filter		SWS	No Intervention
17	93 (100%)		X	X

5.4.3 SMARTSPOUT ADHERANCE DATA

Households with a MadiDrop or a safe-storage water container had a similar prevalence of intervention use with a mean of 81% of households using their intervention for at least 5 seconds on a given day in each group (Figure 5.3). In comparison, a mean of 71% of households with a silver ceramic water filter used their intervention for at least 5 seconds on a given day.

During the week of August 13th, the Smartspout captured the change of intervention when households with MadiDrops had their MadiDrops replaced with silver ceramic filters. As displayed in Figure 5.3, when this change occurred, the mean percent households using the intervention for at least 5 seconds on a given day dropped from 81% to 68%, comparable to that of the households who already had a silver ceramic filter.

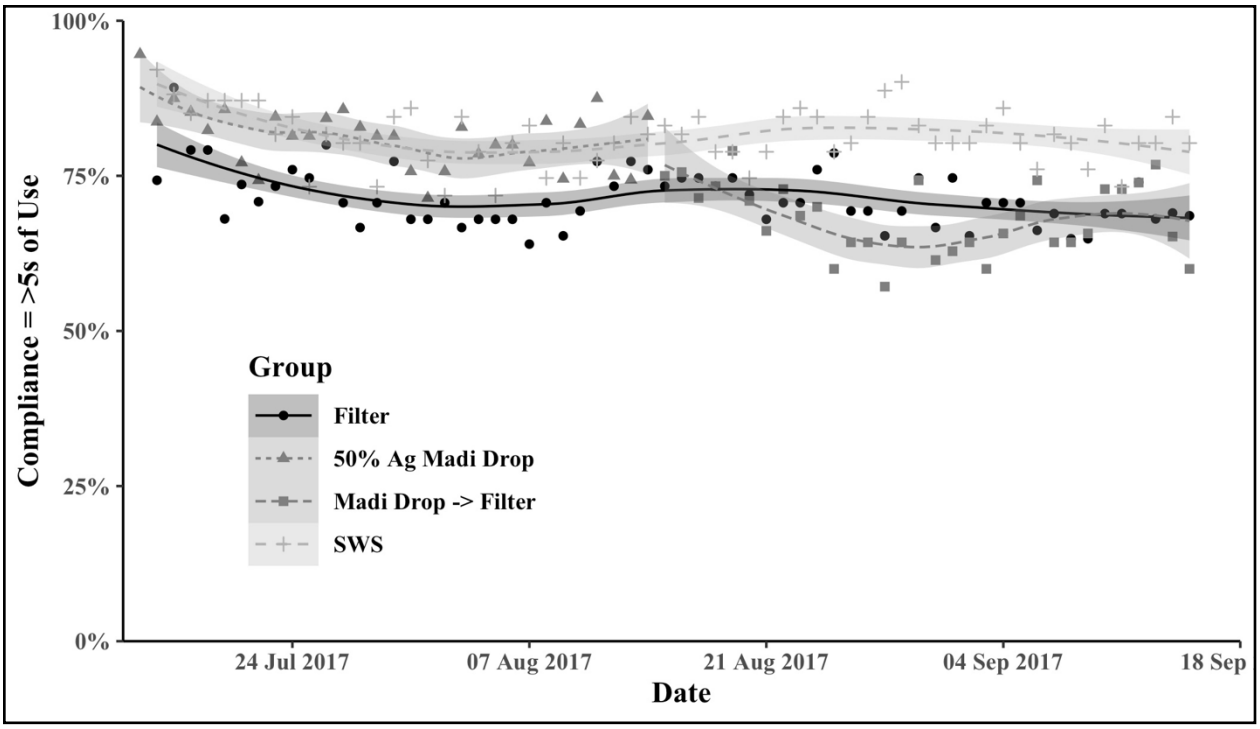

Figure 5.3: Percent of households using their intervention five or more seconds on a given day over a two month period. Data for households with a silver ceramic filter, 50% silver MadiDrop, or a safe-storage water container is displayed with a trendline for each intervention group. The solid black line represents households with a silver ceramic filter. The solid gray line represents households with a safe-storage water container. The dashed gray line represents households that had 50% MadiDrops but were switched to silver ceramic filters during the week of August 13, 2017.

5.4.4 CYCLING EXPERIMENT

For all scenarios with 50% or 100% Ag MadiDrops, silver levels rose gradually over time if all water was repeatedly not replaced by the end of the day (Figure 5.4). In scenarios where water remained in the safe-storage water container at the end of the day and was "topped off" with untreated water, replacing 4 liters each day with new water resulted in the fastest increase of

silver concentration over time while replacing 16 liters daily with new water resulted in the slowest increase for the 50% and 100% MadiDrop. It was observed that if the water was not completely replaced, silver levels could rise above the 100 µg/L silver guideline within a few days for both types of MadiDrop.

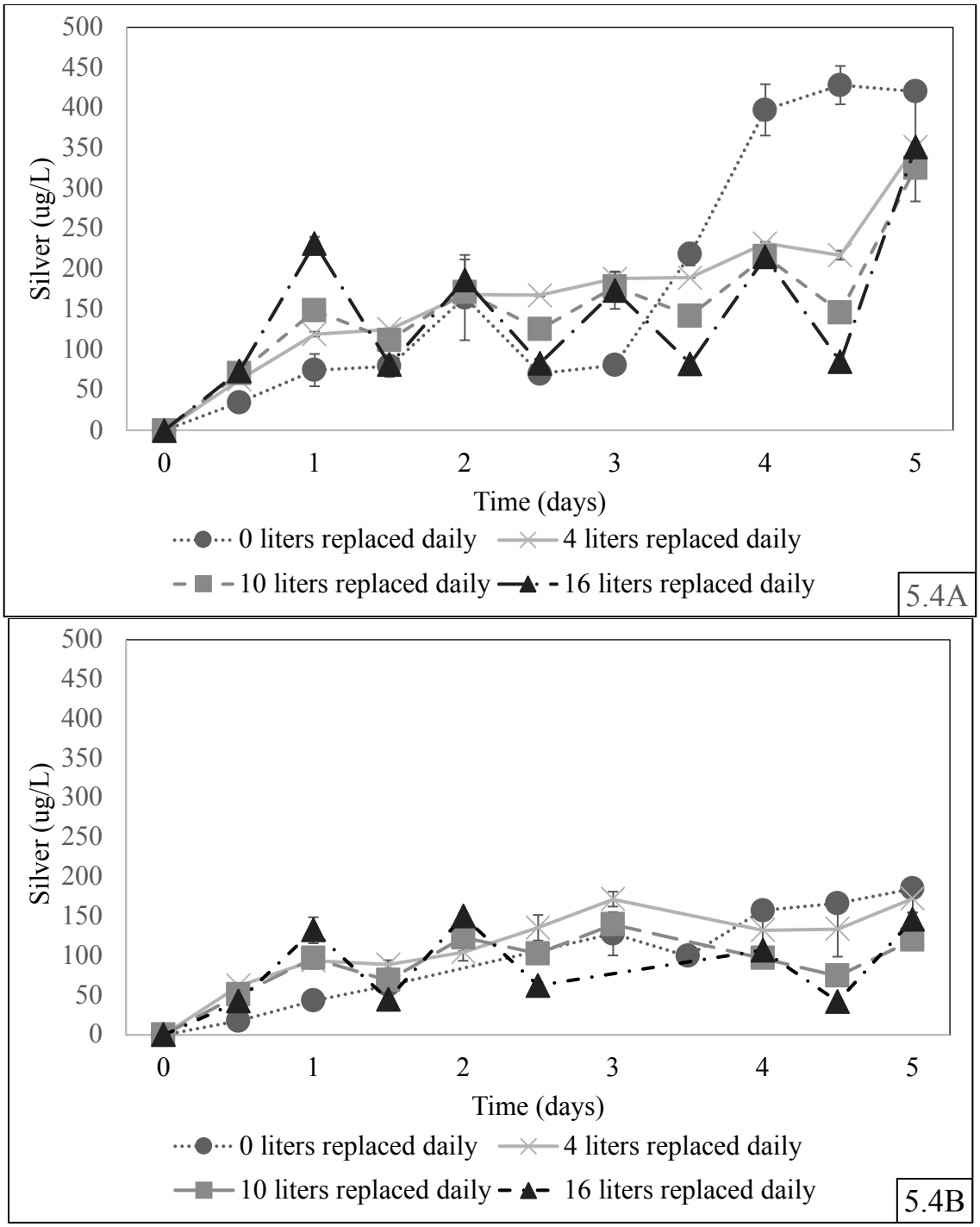

Figure 5.4: Silver concentrations in safe-storage water containers with MadiDrops in which different volumes of water were replaced each day in laboratory experiments. Figure 5.4A displays silver release of original MadiDrops in 20 L of synthetic groundwater over time. Figure 5.4B displays silver release of a MadiDrops containing 50% of the original silver in 20 L of synthetic groundwater over time. Each series represents the silver concentrations over time for a bucket filled with 20 L synthetic groundwater in which 0, 4, 10, or 14 L was removed throughout the day and then replaced with new synthetic groundwater. Error bars in both figures represent the standard error between two identical trials

5.4.5 LABORATORY ANALYSIS OF MADIDROPS

Figure 5.5 shows the release of silver from a MadiDrop with 100% of the original silver in a laboratory setting after it was used in South Africa for the recommended six months. After six months of use in the field, MadiDrops released a mean 27.4 ± 4.3 µg/L for an additional six months, which is sufficient for disinfection but below the WHO guideline. During this experiment, sampled water did not exceed the WHO guideline.

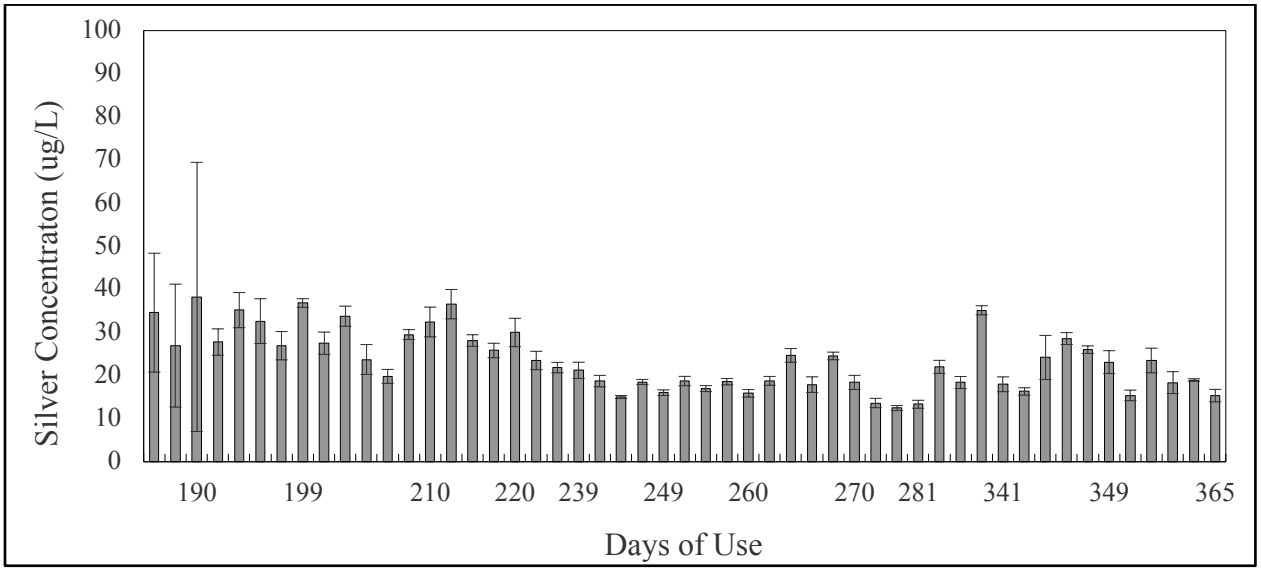

Figure 5.5: Silver release of a MadiDrop with 100% of the original silver in 10 L synthetic groundwater between six months and 1 year of use in a laboratory setting after six months of use in a field setting. Days of use indicated on the x axis is inclusive of the six months that the MadiDrop was used in South Africa. The errors bars indicate the standard error between four trials.

5.4.6 SOCIAL ACCEPTABILITY

Results from the survey administered to assess social acceptability is described in Table 5.5. Households reported that they were very happy or happy with their inventions in 95% (n=142) of homes with filters, 100% of homes with MadiDrops (n=79), and 98.7% (n=77) of homes with safe-storage water containers. 97.9% of households with filters (n=142), 100% (n=79) of households with MadiDrops, and 98.7% (n=77) of households with safe-storage water containers said they would continue using the interventions after the study. 66.2% of households who had

either the ceramic filter (n=142) or the safe-storage water container (n=77) said that they would have bought the intervention if it was not provided for free, while 88.6% (n=79) of households with the MadiDrop said that they would have bought the intervention. The MadiDrop was more positively received in every question of the survey except when households were asked if they thought the intervention prevented diarrhea in children. 71.1% of households with filters (n=142) thought it could reduce diarrhea, while only 64.9% (77) and 55.7% (n=79) of those with safe-storage water containers and MadiDrops thought their intervention could reduce diarrhea in children, respectively.

Table 5.6: Social Acceptability survey of households with 50% Silver MadiDrops, filters with no silver, and safe-storage water containers

	Filter	MadiDrop	Safe storage
	(n=142)	(n=79)	(n=77)
Overall, how happy/satisfied are you with the intervention?, n (%)			
Very happy/satisfied	67.61%	75.95%	67.53%
Happy/satisfied	27.46%	24.05%	31.17%
Neutral	1.41%	0.00%	0.00%
Unhappy	2.82%	0.00%	0.00%
Dissatisfied	0.70%	0.00%	1.30%
Very unhappy/dissatisfied	0.00%	0.00%	0.00%
If you are not happy/satisfied, why not?, n (%)			
intervention did not treat enough water	0.00%	0.00%	0.00%
intervention was too slow at treating the water	1.41%	0.00%	0.00%
intervention was difficult to use	0.00%	0.00%	0.00%
intervention was difficult to use	0.00%	0.00%	0.00%
The intervention broke or did not function properly	1.41%	0.00%	0.00%
filter left a taste or smell in the water	1.41%	0.00%	0.00%
Other	0.00%	0.00%	1.30%
Do you think use of the intervention helped prevent diarrhea in your children?, n (%)			
Yes	71.13%	55.70%	64.94%
No	28.87%	44.30%	35.06%
If yes, when did you notice reductions in diarrhea in your children?, n (%)			
Immediately after using it	26.06%	31.65%	20.78%
1 week	6.34%	5.06%	7.79%
2 weeks	2.11%	3.80%	5.19%
1 month	16.20%	11.39%	14.29%
greater than 1 month	20.42%	3.80%	16.88%
Would you say this intervention is better or worse at cleaning the water than other cleaning methods you use/have used (e.g. boiling water, chlorination, etc.)?, n (%)			

much worse	0.00%	0.00%	1.30%
worse	1.41%	0.00%	1.30%
about the same	2.11%	6.33%	10.39%
better	44.37%	50.63%	58.44%
much better	52.11%	43.04%	28.57%
Will you continue to use the intervention?			
yes	97.89%	100.00%	98.70%
no	2.11%	0.00%	1.30%
Would you have bought the intervention if it were not provided for free?, n (%)			
yes	66.20%	88.61%	66.23%
no	33.80%	11.39%	33.77%
Would you recommend this intervention to your family, friends or neighbors?, n (%)			
yes	97.18%	97.47%	97.40%
no	2.82%	2.53%	2.60%
Have you had any problems with the intervention?, n (%)			
yes	4.23%	2.53%	3.90%
no	95.77%	97.47%	96.10%
Do you think the intervention can be improved?, n (%)			
yes	13.38%	3.80%	15.58%
no	85.92%	96.20%	84.42%
Do you think you have enough financial resources to keep the intervention running for your household?, n (%)			
yes	44.37%	not asked	49.35%
no	54.93%	not asked	50.65%
If the intervention broke or stopped working properly, would you buy a new one?, n (%)			
yes	61.27%	not asked	68.83%
no	38.73%	not asked	31.17%

5.5 DISCUSSION

This paper evaluates the disinfection efficacy of a safe-storage water container and two point-of-use water-treatment technologies: a ceramic water filter with and without silver and a silver impregnated ceramic disk, the MadiDrop. Although the MadiDrop technology has been evaluated at various stages of its university-development history, [12,11,13–15] this is the first study to evaluate the field and long-term performance of the commercial technology.

Silver ceramic filters and/or MadiDrops consistently exhibited high reductions in bacteria compared to a safe-storage water container and no intervention when implemented over 17 months. At each water sampling, the MadiDrops removed more total coliform bacteria than the

silver ceramic filter. In addition, the laboratory experiment examining silver release over an additional six months suggests that the MadiDrop could be used up to one year instead of the originally recommended six months, effectively halving the cost of the intervention.

When ceramic water filters without silver were introduced into households at 18 months, they showed a reduced capacity for removing total coliform bacteria in comparison to MadiDrops or silver ceramic filters. These results are consistent with results found in a laboratory setting[17] and are the first documentation of the impact of silver on ceramic filters in a field setting. Our data, there, indicate that silver improves the performance of porous ceramic water filters with respect to total coliform bacteria reduction.

The SmartSpout spigots showed that more households with a MadiDrop or safe-storage water container used their intervention compared to households with a silver ceramic water filter. The similarity in prevalence of use in the MadiDrop and safe-storage water container households is likely because the user fills a safe-storage water container the same way regardless of whether or not it contains a MadiDrop. Users appear, therefore, to prefer POU devices, like the MadiDrop, which can be used like a safe-storage water container. The higher frequency of use seen in households with MadiDrops coincides with MadiDrop users being happier with their interventions, more likely to continue to use the interventions, and more likely to have bought the interventions in the social acceptability surveys. While users reported less satisfaction with the filters, it is possible that being able to see water flow through the filter makes them more confident that it could prevent diarrhea in children when compared to the MadiDrop.

The small number of households where silver levels were above the WHO guideline observed in the field is a potential limitation for both the MadiDrop and the silver ceramic filter and an important insight from the study. It should be noted that this result, to our knowledge, has

not been previously reported for the silver ceramic filter, which is widely used. The cycling laboratory experiments with the MadiDrop suggest that high silver levels were likely due to the partial refilling of a safe water storage containers that already contained treated water. Furthermore, using the improved MadiDrops, the mean silver level was 27.4 ± 39.1 μg/L, which is approximately 25% of the WHO silver guideline for drinking water. In the case of the silver ceramic filters, while no laboratory experiments were conducted to investigate the cause of the excess silver levels, it is likely in these three cases that the households did not use the intervention frequently, allowing for water to be in prolonged contact with the filter, which continued to release silver.

The accumulation of a disinfectant in a storage container could occur with other daily disinfectant additions, including chlorine tablets or sachets (e.g. Aquatabs). This may in part explain the poor social acceptability of chlorine dosing. If the chlorine concentration increases due to incomplete daily water usage and daily addition of the disinfectant tablet/sachet, the taste of the water may quickly become unacceptable for many users. However, there is a distinction between the passive release of silver by MadiDrop and the active addition of chlorine by the user in this scenario. Prior studies of chlorine dosing have demonstrated a relatively low rate of continued intervention usage after 1-year periods.[27,28]

Two recent studies have documented a potential solution to silver leaching from silver ceramic water filters.[29,30] These studies present a new method of silver application that results in significantly lower effluent silver concentrations from silver ceramic water filters without sacrificing performance. The method uses silver nitrate as a precursor ingredient, lowering the material costs for manufacturing. By keeping more silver in the filter, the filter lifespan may be increased. Furthermore, this new method eliminates the need for workers to handle powdered

colloidal silver, which potentially represents an inhalation hazard. In light of the results of this study, this new silver application methodology could be an important new finding that further improves the safety and efficacy of silver ceramic water filters.

In 2018, MadiDrop Public Benefit Company was acquired by Silivhere Technologies, Inc. Based in part on the results of this study, Silivhere Technologies has made small but important design changes to the MadiDrop technology to reduce silver release. The current commercial product treats 10-20 L/day for 12 months, or over 7000 L per year. The technology has recently received NSF 42 certification for water treatment, which includes certification for silver concentrations below the WHO guideline. Instructions for use have changed. Prior to initial use, the MadiDrop must be rinsed for 3 min in a stream of flowing water. Users are also instructed to fully empty the water storage container at least once per week. This extra water can be used for other purposes such as irrigation or cleaning.

While the MadiDrop and silver ceramic filter technologies significantly improve microbiological water quality, the technologies also have weaknesses. Silver ceramic filters have a relatively high capital cost (about $40 in 2020 in South Africa, $0.0046 per liter of treated water at full retail price). They are also relatively difficult to manufacture, are heavy, fragile, and difficult to transport (packaging and shipping costs can often match the retail price of the filter unit itself). Virus removal by the silver ceramic filters may not be significant,[31] as the pore sizes prevent physical filtration and silver is only modestly effective at virus disinfection. By contrast, silver ceramic filters effectively remove turbidity and bacterial and protozoan pathogens.[32] Furthermore, they are manufactured locally in low-resource settings, providing an economic stimulus to developing economies. They are ideal for local production and local sales

and distribution, particularly if the large capital cost is supplemented for users by local non-profit or government organizations.

Unlike silver ceramic filter technologies, the MadiDrop does not remove turbidity. Because it gradually releases silver, it requires a contact time of 8 hours to be effective. However, if some water from the previous day's treatment remains in the water storage container, disinfection will be significantly faster because there will be ionic silver in the water immediately after refilling. Silver concentrations may exceed WHO guidelines if the storage container is not completely emptied before refilling for several consecutive days. Silver ions are highly effective disinfectants for bacterial pathogens, but are less effective for viruses than chlorination.

The MadiDrop meets most of the critical design criteria for point-of-use water treatment. It is technologically effective, low cost (about $15 in 2020, $0.002 per liter of treated water at full retail price), simple to use, and socially acceptable based on survey results.[12,13] According to the manufacturer, it is durable, easy to transport, and has a perpetual shelf life. Furthermore, recent data indicate that ionic silver can be effective for protozoa disinfection.[15,32] By contrast, chlorine-based technologies have no significant disinfection effects against protozoan pathogens.[33] As per any water treatment technology, there is wide variability in use by individuals. It is important to use these technologies as directed to maximum efficacy and safety. Given its efficacy in disinfecting total coliform and *E. coli* bacteria, low cost, and socially acceptable, overall the MadiDrop is a promising technology for point-of-use water treatment when used according to its current label instructions.

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Chapter 6: Conclusions and Future Work

The research presented in this dissertation explores the potential for silver and copper electrolysis to be incorporated into a novel point-of-use treatment device and the performance of a prototype that uses this technology. It also evaluates the long term performance of comparable technologies, the MadiDrop and silver ceramic filters, in a field setting. The results suggest that POU technologies are effective in treating drinking water at the household level. Both the proof-of-concept experiments and the electrolysis field study suggest that silver electrolysis is a promising new technology that overcomes some of the disadvantages of current commercial available POU technologies that use silver.

When considering POU water treatment the employs electrolysis as the disinfection mechanism, future work on this subject should further explore the use of copper and silver in a prototype. Preliminary experiments with copper and silver electrodes showed that a direct current system would not provide enough supplemental disinfectant to justify the second set of electrodes in a direct current system. However, in a future version of this prototype, it may be possible to incorporate copper so that the device releases silver and copper ions into untreated water through an alternating current with one silver and one copper electrode. This could allow one current to be applied when generating silver ions and a greater current be applied to the copper ions to increase the rate of copper release. Using the maximum concentrations of silver and copper can have a stronger combined purification power than either ion at the EPA-set secondary drinking water standard alone, as it allows greater numbers of metal ions in the water

without exceeding each individual ionic concentration limit. In addition to increasing the concentration limit, silver and copper may produce a more complete bactericidal effect against mixed bacterial populations that could be common in a low-resource setting.

While an electrolysis POU device has shown promising disinfection potential, the work in this dissertation only examined the functionality of the device and did not consider cost effectiveness for the target population. More work should be done in regards to a cost analysis of the device and efforts to make the device affordable for a low-resource setting. Ultimately, the device would need to be within the range of $15-$40 to be comparable to commercially available POU technologies.

The work presented in this dissertation highlights the challenges of ensuring that a water treatment technology performs well in the field after what can be years of testing in a laboratory setting. In the case of the electrolysis device, this is captured when comparing the more than 5 log reduction of *E. coli* bacteria achieved by electrolysis in the lab and only a maximum 2 log reduction in the field. In the case of the MadiDrops and silver ceramic filters, while these technologies were excellent at disinfecting bacteria in a field setting, an additional challenge was presented when some of the households had effluent silver levels above the WHO standard. Both of these results highlight that the variety in human use of these technologies is both the most important consideration and challenge in designing an effective water treatment technology, as it is the most unpredictable. This work also highlights the importance of field research, as the performance of a technology in a laboratory setting is not sufficient to ensure that it will be effective when it is used by the consumer.

Researchers who work on POU devices must be in tune with how the devices are being used and utilize this understanding when balancing disinfection efficacy and safety. Both field

studies suggested that behavior change is an important challenge for any POU technology, as the SmartSpout detected that no more than 80 percent of households with MadiDrops or ceramic filters were using their device on a given day. As previously discussed, the high silver levels detected in the small number of households after intervention modifications were made may be due to these households not using their interventions, even with a local fieldworker checking up with them monthly about their device. During the electrolysis field study, while the prototype was received with enthusiasm, several houses admitting to forgetting to treat their water with the device when researchers arrived, emphasizing that behavior change is very difficult, even if the device is provided for the household and participants approve of the intervention.

While POU devices are effective in treating household water in low-resource settings, it is important to understand that these devices are a solution to a greater underlying economic problem barring citizens from access to clean water in the first place. While we should be working to improve these technologies, hopefully, governments are also working towards the justice of ensuring that their citizens have reliable, continuous access to treated water, particularly in densely populated communities where piped access is possible or already exists. It is also important to note that while drinking water carries pathogens that cause devastating health outcomes, people may still be exposed to pathogens through other pathways. For example, children are exposed to enteric pathogens through a variety of transmission pathways including contaminated food and exposure to soil contaminated with animal feces. Preventing transmission only through pathways involving drinking water allows for children to still be exposed through these alternate pathways. Comprehensive approaches with multiple interventions are likely needed to ensure the health of members in low-resource communities.