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Evaluating the Chemical and Biological Stability of Finished Waters Blended for Direct Potable Reuse in a Simulated Distribution System

Assumption Grimaldi
University of Nevada, Las Vegas, grimaldi.assumption@gmail.com

EVALUATING THE CHEMICAL AND BIOLOGICAL STABILITY OF FINISHED

WATERS BLENDED FOR DIRECT POTABLE REUSE IN A SIMULATED DISTRIBUTION

SYSTEM

by

Assumption Grace Grimaldi

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Dave James, Ph.D.   Kathryn Hausbeck Korgan, Ph.D.
Examination Committee Chair   *Graduate College Interim Dean*

Eric Dickenson, Ph.D.
Examination Committee Member

Daniel Gerrity, Ph.D.
Examination Committee Member

Patricia Cruz, Ph.D.
Graduate College Faculty Representative

ABSTRACT

by

Assumption Grace Grimaldi

Dr. David James, Examination Committee Chair
Associate Professor, Department of Civil and Environmental Engineering and Construction
University of Nevada, Las Vegas

This work evaluated the impacts of blending several different high grade recycled waters with conventional source waters for direct potable reuse (DPR) applications. Bench-scale laboratory tests were conducted for recycled water-source water blends from four participating facilities that have either considered adopting DPR or have already implemented DPR as a feasible approach to overcome water scarcity. The chemical and biological stability of the finished waters was investigated after pipe rig incubation to simulate the quality of blended waters that had aged in a potable water distribution system. The effects of blend ratio, reclaimed water treatment, and source water quality were evaluated to understand disinfection by-product (DBP) yields, generation of metal corrosion products, and changes in bacterial densities in the effluents collected from the pipe rigs. Blending higher proportions of reverse osmosis (RO)-treated water reduced Total Organic Carbon (TOC) concentrations, which resulted in lower effluent Trihalomethane (THM) concentrations. Increased THM formation occurred in the ozone-biofiltered blends from Utility 2, resulting in concentrations exceeding the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Limit (MCL) of 0.08 mg/L. Elevated concentrations of THMs were associated with both the high concentration of organic precursors present, and the use of chlorine during secondary disinfection. Total lead concentrations exceeding the 15 μg/L EPA action level were generally measured in samples with more negative Langelier Saturation Index (LSI) values. Regression analysis showed that the

relationship between pipe rig effluent lead and LSI of the finished waters was significant at a 99% confidence level ($p<0.01$). For all utilities, pipe rig effluent for RO-treated blends typically contained higher effluent lead and copper concentrations compared to ozone-biofiltered blends; however effluent copper concentrations did not exceed the 1.3 mg/L action level. Corrosion potential of the RO-treated surface water blend from Utility 4 was presumably controlled when zinc orthophosphate was added as a corrosion inhibitor. Biological Activity Reaction Tests (BART™) results indicated that the sulfate reducing bacteria and the slime forming bacteria were the most predominant groups of microorganisms that appeared at the beginning of the reaction period (1-2 days). The results from this study can help advise drinking water facilities in selecting appropriate source waters and optimal blend ratios to augment water portfolios, while conforming to Safe Drinking Water Act regulations that safeguard public health.

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In loving memory of my father, Antonio Grimaldi, Ph.D.

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CHAPTER 1. LITERATURE REVIEW

1.1   Water Rights

Establishing water rights in the Southwest has been a historical controversy that culminated with the Colorado River Compact in 1922. The agreement allotted 7.5 million acre-feet of water per year from the Colorado River to each of the Upper and Lower Basin states. However, over the years, restrictions have been imposed on water use for the Lower Basin states when reservoir elevations dropped below specific thresholds. For Lake Mead, water restrictions are enforced when water levels drop below 1,075ft, indicating a "Tier 1 Shortage" (CAP, 2014). The distribution of water impacts existing supplies because during periods of severe drought Nevada would be entitled to significantly less water (relative to base allocations) compared to California. Due to Nevada's small population size in 1922, the established 300,000 acre-feet (370 Mm^3) annual allotments were appropriate, but today, with growing population and tourism, this amount is not sufficient. Reported water usage in 2012 for two million Clark County residents amounted to 311,910 acre-feet (384.7 Mm^3) (Hinton, 2014). Assuming the number of residents continues to increase, current water resources will be further strained. Nonetheless, the implementation of "Return Flow Credits" has allowed Nevada to take out more than the apportioned quantity of water from the Colorado River, depending on the amount of treated wastewater returned to Lake Mead (Stave, 2003). This means, that for every gallon of treated water being returned to the lake, an extra gallon can be withdrawn for consumptive use (SNR, 2009).

California receives its largest allocations from the Sacramento and San Joaquin Rivers and tributaries, 28,647,404 acre-feet (35,336 Mm^3) and 55,512,047 acre-feet (68,473 Mm^3), respectively (Grantham et al., 2014). The State Water Project exploits these sources to provide

drinking water to about two-thirds of the state's population (CA DDW, 2016). Surface water rights are contended between various private, public, state and federal entities as prescribed by riparian and appropriative rights. Precedence is typically given to riparian rights, but the State Water Resources Control Board grants water rights in the absence of land ownership when the water is put to "beneficial use". Contrary to surface water rights, the state lacks a comprehensive framework for regulating groundwater rights, which are handled on a case-by-case basis. Due to drought conditions, California's reliance on groundwater consumption significantly increased in the recent years. Groundwater use can range between 30-60% of the state's total supplies with the higher rates occurring during drier periods. During the Gold Rush-era, landowners were entitled to pump an unlimited amount of groundwater from their property, but today, legislation has enforced a more controlled approach for monitoring groundwater withdrawals. Recently, California's Water Code passed a bill that imposed limitations on groundwater withdrawals, and granted state water authorities the right to assist local and private agencies with developing sustainability plans (California Legislature, 2014). The provision grants state authorities the right to perform regular inspections, and issue fines if water meter levels are below established limits. Restrictions are consistent across high priority groundwater basins, primarily residing in the Central Valley where agricultural activities are heavily based, and counties surrounding Los Angeles (USGS Water Resources, 2017).

1.2   The Effects of Climate Change and Population Growth on Water Supplies

Severe drought conditions and climatic changes have significantly impacted water quality and reduced watershed yields in the Lower Basin states, increasing pressure on water utilities to expand water portfolios with potable reuse applications. At the turn of the 21st century, many

regions in the Southwest were affected by a widespread drought, which coincided with rising temperatures, and a decline in annual precipitation rates (MacDonald, 2010). Prolonged water shortages, resulting in lower flows in the Colorado River, have an immediate effect on water supplies and economic growth in arid regions of California and southern Nevada. Moreover, future projections of population growth indicate that conventional water sources will become even more stressed. In 1995, 12% of the nation's inhabitants lived in California, and by 2025 the U.S. Census Bureau predicts that California's population is expected to increase to 15% of the nation's total, which at the time was about the population of the state of New York (U.S. Census Bureau, 1997). Although population growth is an inevitable challenge, predictive models show that reducing municipal water use through indoor conservative efforts would help reduce per capita consumption rates (Stave, 2003). However, significant amounts of municipal and commercial water are lost from outdoor use, consisting of water more difficult to collect and recycle. Compared to Nevada the amount of land used for the agricultural sector in California is much greater due to soil fertility. Therefore, significant land in California is used for agricultural production, much of which is irrigated for crops and farms. Although some irrigation water is recovered when it percolates into underlying aquifers, or as surface water runoff, a large fraction is lost by evapotranspiration.

California's conventional drinking water sources include groundwater reservoirs, and surface water systems including streams, rivers, and lakes. While northern regions rely on more frequent rainfall events to swell water networks, regions south of Sacramento in the Central Valley count on runoff from the Sierra Nevada snowpack. Nevada's primary water supplies also depend on surface water flows from snowmelt in the Sierra Nevada Mountain Range, a large portion of which feeds into the Colorado River. Climatic variations impact current supplies

because in the absence of abundant snowmelt and precipitation events, reservoir levels drop. Moreover, the rising temperatures are resulting in increased rates of evapotranspiration, potentially reducing surface watershed yields. Climatology studies show that the temperature in the troposphere is increasing at a rate faster than at the Earth's surface as measured by the number of "hot spots" detected in the troposphere (Abraham, 2015). This condition is indicative of sustained desertification which has intensified, impacting arid and semi-arid regions. The pace at which global warming is unraveling also affects coastal cities where the occurrence of natural disasters is expected to increase, and sea levels have already begun to rise with the capping of the glaciers. As a result of the environmental changes and population growth, the need to foster more potable reuse applications has become more apparent in face of the increasing demand for water.

1.3   Direct and Indirect Potable Reuse

Water recycling techniques in California have already been implemented in the form of Indirect Potable Reuse (IPR) for surface water augmentation, and groundwater replenishment via surface spreading or subsurface injection (CA DDW, 2016). In Nevada, IPR is limited to surface water augmentation due to the limited number of groundwater aquifers, which constitute less than 10% of the state's supplies. By definition, IPR is the use of an environmental buffer (e.g., lake, river, groundwater aquifer) to dilute treated wastewater exiting the wastewater treatment plant, before it undergoes conventional drinking water treatment at the downstream drinking water facility. The environmental buffer stores contaminants that escaped treatment, and allows for dilution and possible decay reactions to occur. In addition, it provides flow equalization and response time in the event of a treatment failure at the wastewater treatment plant (SNR, 2009). A Direct Potable Reuse (DPR) system bypasses this step, either piping the recycled water

immediately upstream of the drinking water facility or directly into the distribution system (CA DDW, 2016). Since IPR criteria rely on the hydraulic retention time provided by the environmental buffer to allow for additional attenuation, the DPR approach needs to use other techniques to address the lack of detention time (usually higher levels of treatment), and establish measures to effectively respond to off-specification water that does not meet regulatory limits with the use of engineered storage.

One way the water crisis has been addressed is by blending treated wastewater effluent (recycled water) with conventional drinking water sources (e.g., groundwater, surface water) for DPR. After primary and secondary (sometimes tertiary) treatment is performed at the wastewater treatment facility, the treated water enters an advanced purification site where a high grade purified effluent is produced by advanced multibarrier treatment processes which may include microfiltration-reverse osmosis-UV disinfection/advanced oxidation processes (MF-RO-UV/AOP) or ozone-biofiltration (O_3-BAF). The recycled water is then blended at different proportions with either surface water or groundwater prior to conventional drinking water treatment.

DPR implies a point-of-use application, which assumes water is more readily available as a result of the direct connection between wastewater and drinking water. It is beneficial because it would minimize water losses from evaporation and reduce energy costs associated with pumping and transporting water (i.e. conveyance costs) from the lake or ground into the drinking water facility. Non-potable reuse would actually be less economically favorable than DPR because it requires the construction of separate pipe lines for non-potable and potable streams (Gerrity et al. 2013). Also, typically the cost to treat tertiary effluent for non-potable reuse is 0.3-1.7$/m^3, and for potable reuse the cost is 0.6-1$/m^3 (Leverenz et al. 2011). Despite the associated

benefits, DPR practices are novel requiring a more detailed understanding of treatment goals and monitoring compared to IPR. For example, blending RO-treated effluent with surface water reduces the concentration of organic and inorganic constituents; however, the alkalinity may decrease significantly affecting the coagulation process during conventional drinking water treatment (WateReuse Research Foundation, 2015). There is also to consider the potential increase of recalcitrant trace organic constituents (TOrCs) and Contaminants of Emerging Concern (CECs) in recycled waters. However, blending advanced treated water with different source waters may not only compromise treatability, but the stability of the finished water, particularly in distribution systems and storage tanks where corrosion issues can occur and disinfection by-products (DBPs) can form.

Existing DPR systems use blending as a measure to attenuate potential contaminant loads into the drinking water facility. In 2013, the drinking water utility in Big Springs, TX was the first facility in the U.S. to approve a DPR system which blended MF-RO-UV/AOP advanced treated water with raw surface water at a 20% treated water and 80% raw surface water ratio (Raucher & Tchobanoglous, 2014). The DPR utility in Wichita Falls, TX followed, but became operational only for a short period to overcome severe periods of drought using a 50/50 blend of treated water and surface water. Other utilities around the world facing water shortages have expressed interest in switching to DPR, but the lack of regulatory support has rendered the legal process more challenging than for IPR. An extreme example occurred in Australia where the opposition was so strong that the DPR project was forced to solely sustain industrial activities, and nearly shut down because of limited political and public leverage (Gerrity et al., 2013).

1.4   Regulations

For decades, non-potable reuse has been extensively practiced for agricultural irrigation,

landscape irrigation (e.g. golf courses) and industrial use. However, in face of increasing future

water scarcity, recycling strategies limited to these applications will not be sufficient to offset the

rising demand for water in the future. A regulatory framework for planned and *de facto* IPR were

developed to control "source to tap" issues by adopting more stringent goals for wastewater

treatment and storing the treated wastewater effluent in an environmental buffer between four

and six months (CA DDW, 2016). The implementation of a DPR system would reduce the

hydraulic retention time in the engineered storage significantly, increasing the risk of microbial

and chemical outbreaks in the absence of a robust and reliable system.

Presently there are no federal regulations for DPR in the US. In Nevada, existing

regulations support recycling water for direct non-potable reuse. Currently, around 22,000 acre-

feet a year (27,136,560 m^3/year) of recycled water directly leave the wastewater treatment plants

in Southern Nevada to assist power plant cooling, golf course and park irrigation (SNWA, 2017).

Under the Nevada Administrative Code, five permissible reuse categories exist with Category

"A" being the most restrictive. It includes spray irrigation for non-agricultural purposes, where

some human contact can be expected. Following Categories "B" through "D" sanction

progressively increasing levels of coliform for which correspond more limitations on the

possibility of human exposure (Harrison, 2016).

Although DPR has not been approved in Nevada at a regulatory level, the state of

California has recently reviewed its feasibility by addressing the importance of achieving

microbial inactivation and chemical contaminant removal (CA DDW, 2016). The feasibility

report's expert panel recommends that the same approach for assigning log_{10} reduction values

(LRV) for IPR can be applied for DPR applications (CA DDW, 2016). Based on the design of the DPR treatment system, LRV credits can be assigned in order to comply with the 12/10/10 rule by which 12-$\log_{10}$ reduction of enteric virus, 10-$\log_{10}$ reduction of *Giardia* cysts, and 10-$\log_{10}$ reduction of *Cryptosporidium* are required (CCR, 2015). To address the health risks associated with chemical hazards (e.g., metals, DBPs), the Safe Drinking Water Act has established a list of regulated chemical contaminants that need to be monitored by conventional drinking water treatment plants. However, non-conventional IPR facilities are subject to more stringent regulations by which an additional set of chemical contaminants are to be monitored because of their expected occurrence in recycled waters e.g., N-Nitrosodimethylamine (NDMA). This more rigorous type of monitoring approach is recommended for DPR facilities, especially for treatment trains that employ an oxidant such as ozone and/or chlorine. The addition of oxidants before or after RO treatment may increase the concentration of low molecular weight compounds formed as oxidation products or DBPs (CA DDW, 2016). Since DPR treatment trains require the use of oxidants, the State Water Board advises monitoring additional contaminants that may form during treatment and consequently pose potential health risks.

If a DPR treatment facility in California or Nevada were to be established, the expert panel's findings used to delineate California's feasibility report would need to be approved by state regulators. However, the approval process does not exclusively depend on the validation of DPR technologies rather on cultural and social acceptance. The process for approving and implementing water recycling regulations requires the support of various stakeholders and policy makers, that are often more concerned with where the water came from ("toilet to tap") rather than evaluating its final quality. Many are hesitant to support potable reuse systems because there is a general misconception surrounding the meaning of treated wastewater. Efforts to

embed a different vocabulary into our society are performed through public outreach programs, and effective communication with community leaders to enable the legitimation of potable reuse programs (Harris-Lovett et al. 2015). Another reason water reuse projects fail is due to a lack in performing thorough procedural revisions (e.g., developing standard methods, manuals for monitoring performance) of the new system (Harris-Lovett et al. 2015). For these reasons, reuse schemes proposed by the City of Los Angeles and the City of San Diego have failed, while the Orange County Groundwater Replenishment Project succeeded in building a solid and well-founded IPR framework that the public could trust. Therefore, the first step in forming a DPR facility in Nevada or California would be to emulate facilities that have been successful in establishing widespread acceptance of potable reuse technologies. This means initiating a public outreach campaign that would influence target interest groups in the community to support reuse regulatory principles (Hinton, 2014).

1.5   Corrosion and Disinfection By-Product Formation in Distribution Systems

Although DPR would help overcome water scarcity in many drought-prone regions, agencies need to consider potential unintended reactions that can occur in distribution systems from using DPR treatment processes and disinfectants. Corrosion issues can arise from using chlorine and chloramines because oxidants interact with metal ions present in pipes, depleting residual, the relative mass weight of the pipe material, and may catalyze DBP formation (Li et al., 2007).

Trihalomethanes (THMs) are one class of regulated DBPs that can form after treatment from the reaction of natural organic matter and chlorine (Eugene & Suffet, 2002). Preventing the formation of THMs is a critical problem because elevated levels of these trihalogenated compounds have been associated with cancer outbreaks of the bladder, colon-rectum and brain

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(Hsu et al. 2001). The EPA has established that the Maximum Contaminant Limit (MCL) for Total Trihalomethanes (TTHMs) in drinking water is 80 µg/L (Hong et al. 2013). TTHMs are the sum of the chlorinated and brominated THM species that form from chlorinating water, which include chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$), and dibromochloromethane ($CHClBr_2$). The formation of THMs is largely determined by the properties of the source water, and the stage at which the disinfectant is added during the treatment process (Liang & Singer, 2003). More specifically, the disinfectant dose, contact time, residual concentration, and temperature can impact the kinetics of THM formation in the presence of organic precursors (Liang & Singer, 2003). Organic precursors are hydrophobic and hydrophilic fractions of dissolved organic carbon (DOC) that react with chlorine to form THMs. These organic precursors are structurally diverse in composition, especially in recycled waters which contain more hydrophilic and low molecular weight moieties than conventional source waters (Hu et al., 2016). Blending source waters high in organic matter (e.g., surface water-impacted sources) could not only increase the potential for DBP formation, but catalyze the dissolution of heavy metals in distribution pipes (AWWA, 2005; Fu et al., 2009).

THMs are problematic to remove because they form in distribution systems as contact time increases between the natural organic matter and chlorine. By minimizing THM precursors during pre-disinfection treatment processes (e.g. coagulation/flocculation, filtration), less THMs tend to form downstream in distribution systems and storage tanks. Typically, the absorption sites in biofilters effectively remove existing THMs before disinfection, however higher THM yields result from post-chlorination and increased water age (Babi et al., 2007).

In addition to addressing the problems associated with treating blended waters to mitigate DBP formation, there are needs to both establish regulatory criteria and safe operations of

different source water blends with respect to metal corrosion in distribution systems (Choi et al., 2015). Similar challenges to minimize corrosion include predicting the impacts of changing water source on existing pipe infrastructure, especially where older service lines have not been replaced. Depending on water quality characteristics, different source waters may cause existing scale deposits on pipe surfaces to dissolve, exposing the metals in fixtures, and negatively affecting the quality of the finished water (Li et al., 2016). As witnessed in the recent tragic case of Flint, Michigan, water experts have undermined the importance of monitoring and managing the chemical stability of waters (Goovaerts, 2017). Reactivity potential with disinfectants decreases from using cementitious and plastic (e.g. PVC) pipe materials for distribution lines rather than unlined iron cast mains, suggesting that the interplay between pipe material and disinfectant affect drinking water quality (Masters et al., 2015). Also, the effects of alkalinity and pH on the dissolution of metals varies across different source water types. For example, surface waters typically have a lower alkalinity after advanced treatment compared to groundwater (unless the groundwater was treated by RO-UV/AOP), which means surface water sources tend to have a higher corrosion potential than groundwater sources. Therefore, increasing the ratio of recycled surface water blended with ground water may decrease the buffering capacity of the ground water, and subsequently result in corrosion issues within a distribution pipe (AWWA, 2005). Treatment processes adopted at the advanced purification site to treat the recycled water also impact the corrosion potential of the finished water. Particularly, blending surface water with permeate product water from RO treatment processes can produce elevated concentrations of iron in a distribution pipe which were attributed to the reduced alkalinity that causes the exposed iron to corrode (Taylor et al., 2005). Therefore, blending RO treated effluents requires

evaluation of the potential of the recycled water blend ratio to affect the release of toxic metals like lead and copper.

The EPA regulates lead and copper under the Lead and Copper Rule (LCR), which states that 90% of samples collected should not exceed established action limits of 0.015 mg/L for lead, and 1.3 mg/L for copper (GPO, 1991; U.S. EPA, 2007). Lead exposure in humans can result in severe mental and physical health problems, primarily affecting younger children and pregnant women. Lead uptake in high concentrations disrupts brain and central nervous system activity, leading to permanent cerebral damage, coma or death (WHO, 2016). At low concentrations, brain development in children can be impaired, and behavioral disorders can develop. Other health problems expressed in adults include anemia, hypertension and kidney damage (WHO, 2016). To address this issue, Congress recently passed a law which reduces the permissible lead content in pipe surfaces and fixtures from 8% to 0.25% weighted average lead (NDWAC, 2015). Excess copper consumption can also cause a wide range of health problems. Ingesting more than normal copper dosages (>1.3ppm) can cause nausea and vomiting, while long-term exposure is associated with adverse effects on the liver and kidneys (Water Research Foundation, 2017).

Lead can be released into water sources from industrial plant discharge of leaded-gasoline, paints, ammunition and sinkers, and from runoff of lead-based pesticides (ATSDR, 2007). Copper is typically not present naturally in source waters. However, contamination of drinking water from copper can result mainly from corrosion of brass fittings and fixtures in distribution pipes, especially in new pipes where copper levels are expected to spike due to the absence of a protective scale layer on pipe walls (Water Research Foundation, 2017).

Corrosion reactions in drinking water systems are complex due to the electro-chemical interactions that occur at the interface of the exposed metal and water. Lead has a higher

solubility in soft, acidic waters due to the effects of pH, salinity, and hardness (ATSDR, 2007).

The dissolution rate of lead can be inhibited by the presence of sulfate ions at lower pH

conditions, and by carbonate species at higher pH conditions. As a result, competing ions can

react with the dissolved lead to form stable sulfate, carbonate, hydroxyl, and chloride complexes

(Table 1).

Table 1. Relevant lead reactions in distribution systems	
Reaction type	
Lead-Ligand Complexation[1]	$Pb^{2+} + CO_3^{2-} = PbCO_3 \text{ (aq)}$ $Pb^{2+} + 2OH^- = Pb(OH)_2 \text{ (aq)}$ $Pb^{2+} + Cl^- = PbCl^+$
Dissolution of Solid Lead[2]	$PbCO_3 \text{ (s)} = Pb^{2+} + CO_3^{2-}$ $PbO_2 \text{ (s)} + H_2O = Pb^{2+} + 2OH^- + 0.5O_2$ $PbSO_4 \text{ (s)} = Pb^{2+} + SO_4^{2-}$
Lead Decomposition	$Pb(CO_3)_2 \text{ (s)} = PbO_2 \text{ (s)} + 2CO_2 \text{ (g)}$ $Pb(OH)_4 \text{ (s)} = PbO_2 \text{ (s)} + 2H_2O$ $2PbO_2 \text{ (s)} = O_2 \text{ (g)} + 2PbO$

[1]Easley & Byrne, 2011
[2]Guo et al., 2014

Lead has an oxidation state of either +2 or +4, but it is more commonly found in the +2

oxidation state. Speciation products form at different redox potentials and pH as shown in the

redox potential-pH (E_H-pH) diagram, where the carbonate species assist in hindering corrosion

by forming a scale layer on pipe surfaces (Figure 1). The lead-carbonate solubility equilibrium

resists the release of Pb^{2+} when $CaCO_3$ is present at appreciable concentrations. Despite the

buffering capacity of carbonate-rich systems, hard waters can promote elevated OH^- production,

which increases pH and lead hydroxide formation (Schock, 1980). Soluble lead ions and lead

complexes are stable at very low and very high pH values, for pH<6 and pH>11, respectively.

This means that more free lead ions, occurring as Pb^{2+} are released in water at low pH, and more

lead hydroxide complexes, present as $Pb(OH)_3^-$ are formed at elevated pH conditions. These

species are bound by the dashed lines in Figure 1, indicating they are thermodynamically stable.

The passivation zone is characterized mostly by solid phase lead oxides. In more oxidizing

conditions (higher E_H values), lead oxides form a passive layer that can more readily dissolve

(higher solubility) because they have poor scale-forming potential (Xie et al., 2010). In reducing

conditions, solid lead in its elemental state is immune to corrosion when the E_H is below -0.25

volts at pH 7.
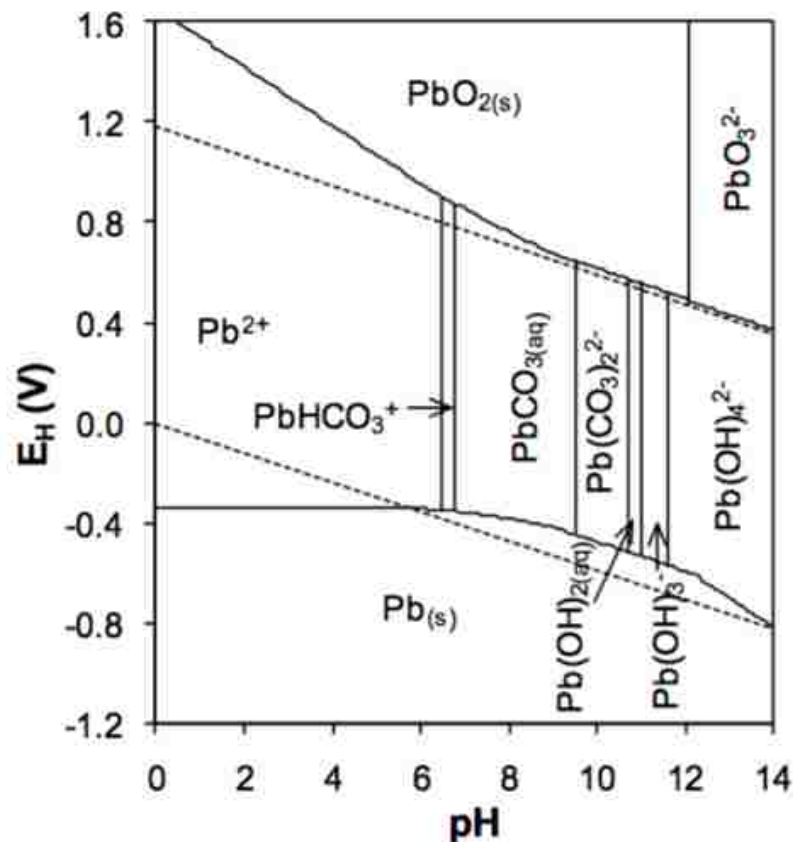
Figure 1. E_H-pH diagram of predominant lead species when the total Pb concentration is 15ppb and 30 mg-C/L of dissolved inorganic carbon are present (Xie, 2010).

Similarly, copper complexes can form with carbonate, hydroxide and oxide species in aqueous solution, and soluble copper can form from the dissociation of solid copper. Table 2 provides a list of equilibrium reactions that pertain to copper carbonate complexation and dissolution.

Table 2. Copper carbonate equilibrium reactions at 25°C (Adapted from Hong & MacAuley, 1998)

Reaction type		Rate Constant, log k
Copper-Ligand Complexation	$Cu^{2+} + CO_3^{2-} = CuCO_{3(aq)}$	6.77
	$Cu^{2+} + 2CO_3^{2-} = Cu(CO_3)_2^{2-}{}_{(aq)}$	10.2
	$Cu^{2+} + OH^- = CuOH^+{}_{(aq)}$	6.5
	$Cu^{2+} + 2OH^- = Cu(OH)_{2(aq)}$	11.8
	$Cu^{2+} + Cl^- = CuCl^+$	0.2
Dissolution of Solid Copper	$CuCO_{3(s)} = Cu^{2+} + CO_3^{2-}$	-11.5
	$Cu(OH)_2CO_{3\,(s)} = Cu^{2+} + 2OH^- + CO_3^{2-}$	-15
	$Cu_2(OH)_2(CO_3)_{(s)} = 2Cu^{2+} + 2OH^- + CO_3^{2-}$	-33.3
	$Cu(OH)_{2(s)} = Cu^{2+} + 2OH^-$	-19.32
	$CuO + H_2O = Cu^{2+} + 2OH^-$	-20.35

Copper can exhibit oxidation states of +1 or +2. Soluble forms of copper are also stable at low pH values releasing Cu^{2+}, and at high pH conditions, forming complexes such as $CuOH^+$ and $Cu(OH)_2$. This condition promotes rapid corrosion in oxidizing environments, where oxygen is consumed and E_H is gradually reduced.

Secondary disinfectants may impact the redox potential depending on the kind of oxidant used and on its residual (AWWA, 2005). Chlorine and chloramine redox potentials are compared to the redox potential at which the reduction of PbO_2 to $Pb(II)$ occurs, to determine which

oxidant will drive Pb(II) ions into solution. As the redox potential of the finished water approaches 0.7V, more soluble forms of Pb^{2+} can be produced.

$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O \qquad\qquad E_H(V)=0.7 \qquad\qquad (1)$$

Since the chloramine redox potential is closer to the lead-lead oxide redox potential, lead corrosion is likely to increase in the presence of chloramines.

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad\qquad E_H(V)=1.49 \qquad\qquad (2)$$

$$NH_2Cl + H^+ + 2e^- \rightarrow Cl^- + NH_3 \qquad\qquad E_H(V)=0.69 \qquad\qquad (3)$$

This is contrary to what would be expected because chlorine is a more potent and aggressive disinfectant, and has a higher oxidation potential compared to chloramines. Many utilities have switched from using chlorine to chloramines to comply with the Stage 2 Disinfectant/Disinfection By-Products Rule (DBPR), intended to minimize the formation of THMs and haloacetic acids (Siedel et al., 2005). However, chloramines can promote the formation of unstable metal-ligand complexes that may increase the solubility of lead species in distribution pipes (Guidotti et al., 2008; Zhang et al., 2008). Moreover, chloraminated waters can also promote the formation of *N*-nitrosamines (e.g. NDMA), which include several non-regulated DBPs.

When lead and copper levels exceed action limits, utilities practice corrosion control by adding a corrosion inhibitor in the final treatment step before discharge into distribution systems. The inhibitor is typically a phosphate-based compound (e.g., zinc orthophosphate) that prevents the release of metals by forming a hydroxyl-phosphate scale on wetted surfaces from the precipitation of lead or copper phosphate. The corrosion potential of the blended waters is typically determined using one of the several stability indices, one of which is the Langelier Saturation Index (LSI).

Biological corrosion in distribution systems can deteriorate the aesthetic quality of the finished water, leading to potential impacts on human health if not addressed. Some issues caused by nuisance bacteria include cloudiness, discoloration, odor and infectious outbreaks (Droycon Bioconcepts Inc., 2004). The Bacterial Activity Reactivity Tests (BART™) provide more specialized testing compared to analytical methods limited to detecting surrogate parameters (e.g. ATP). The bacteria are cultivated in sterile vials to determine for the presence of Sulfate Reducing Bacteria (SRB), Heterotrophic Aerobic Bacteria (HAB), Slime Forming Bacteria, Denitrifying Bacteria (DNB), Nitrifying Bacteria, and Acid Producing Bacteria (APB). The biodetectors are designed to qualitatively and semi-quantitatively estimate the activity or "aggressivity" of bacterial populations based on a time-lag correlation. Rather than counting colonies on agar plates, the bacteria are quantified in relation to the number of days it takes for the turbidity, color-change or foaming reactions to occur. As the time lag to the detection of a reaction increases, the smaller the aggressive population of the microbial consortium being measured. The reaction is confirmed by monitoring for several visual indicators that will be later discussed to determine corrosion and/or biofouling potential of the target microbial species.

1.6   Research Questions and Objectives

The overall goal of this study was to investigate the final quality and stability of finished blended waters in distribution systems. Raw lake water and treated groundwater were blended with recycled waters at different ratios (0%, 5%, 10% 50%) from four anonymous facilities in Nevada and California. The blended and non-blended waters were subjected to bench-scale treatments to simulate full scale drinking water treatment processes. Pipe rig incubation tests were performed to mimic detentions in a house-hold premise plumbing system. The following

research questions were addressed by analyzing a suite of water quality parameters of the blended treated water after uniform holding times:

- What are the impacts of blending surface and groundwater with treated wastewater effluent on the simulated-treated water quality as measured by ambient THMs, THM precursors, and Dissolved Organic Carbon (DOC)?

- How does blending impact water quality for THMs, trace metals, and bacterial activity in simulated/incubated distribution tests?

- What statistical correlations can be made in regards to effluent lead and copper concentrations with disinfectant residual, LSI and other water quality parameters?

- Are there variations in effluent THM and metal concentrations within each utility to indicate impacts of treatment and/or blend ratio?

The above questions were used to define the following research objectives:

(1) investigate the impact of blending ratio, source water type, and recycled water treatment on the finished water quality exiting a drinking water facility, and

(2) examine the stability of several water quality parameters, THMs and metals after pipe rig incubation as blended water ages in a simulated distribution system.

Stabilities of the test waters were determined by calculating the LSI, and for one of the RO-treated surface water blends, the effects of adding a corrosion inhibitor were evaluated to determine the lead and copper concentrations in the effluent from the pipe rigs.

I hypothesize that blending recycled water effluents with conventional source waters can help improve drinking water quality for DPR operations by reducing THM precurors, THM concentrations, and mitigating chemical and bacterial corrosion issues. My hypothesis was tested through laboratory testing at the Southern Nevada Water Authority (SNWA) by measuring THM

concentrations at different stages of treatment, and determining changes in lead and copper concentrations in the influent and effluent to and from incubated pipe rigs/loops for different blends of source and recycled waters.

Further pipe rig analysis using Environmental Scanning Electron Microscope (ESEM) with an attached X-ray Energy Dispersive System (EDS) was performed by project collaborators at Virginia Tech, including Marc Edwards, Amy Pruden and Jeff Parks.

1.7   Knowledge Gaps in the Literature Related to the Stability of Blended Waters in Direct Potable Reuse Applications

Water quality may deteriorate significantly in distribution systems where lead and copper can leach, disinfection by-products can form, and biofilm growth can consume disinfectant residual, affecting the aesthetic quality of the water. With the exception of a few states, to date, a framework of DPR guidelines has yet to be accepted for the operation of recycled water blends with regards to reducing corrosion issues in distribution pipe systems. The Lead and Copper Rule (LCR) provisions have helped to clarify the requirements for appropriate sampling, and define action plans (e.g., corrosion control practices, replacement of lead pipe lines) for conventional source waters. However, there is still limited research surrounding the applicability of LCR for blended waters in DPR applications. Numerous studies on the formation of disinfection by-products have been conducted to understand the impacts of using chlorine and chloramines for the disinfection of surface waters and groundwaters. However, the impacts of disinfecting recycled water blends for DPR using chlorine-based oxidants are still a topic of research, especially recycled waters treated by O_3-biofiltration, which removes less TOC and Total Dissolved Solids (TDS) compared to RO-processes and increase the level of DBP

precursors. The results of this study will help to build confidence in DPR technologies to bolster

water supplies, and lead to future implementation of more reuse treatment facilities.

CHAPTER 2. MATERIALS AND METHODS

2.1   Blending Protocol

Source water samples (20 – 25 gallons) and treated wastewater samples (~12.5 gallons)

were collected in 5-gallon Cubitainers®, and shipped from the four participating utilities in

California and Nevada to SNWA's Applied Research and Development pilot plant. Upon arrival,

different proportions of the treated wastewater effluents were blended with collected source

water (surface water and/or groundwater) samples to generate varying ranges of input water

quality parameters (subsequently defined as chemical matrices) that were measured before and

after bench-scale simulated treatment and pipe rig incubation. Figure 2 shows a general flow

chart of the experimental plan describing the order in which the waters were blended, treated,

stored and incubated in duplicate pipe rigs.
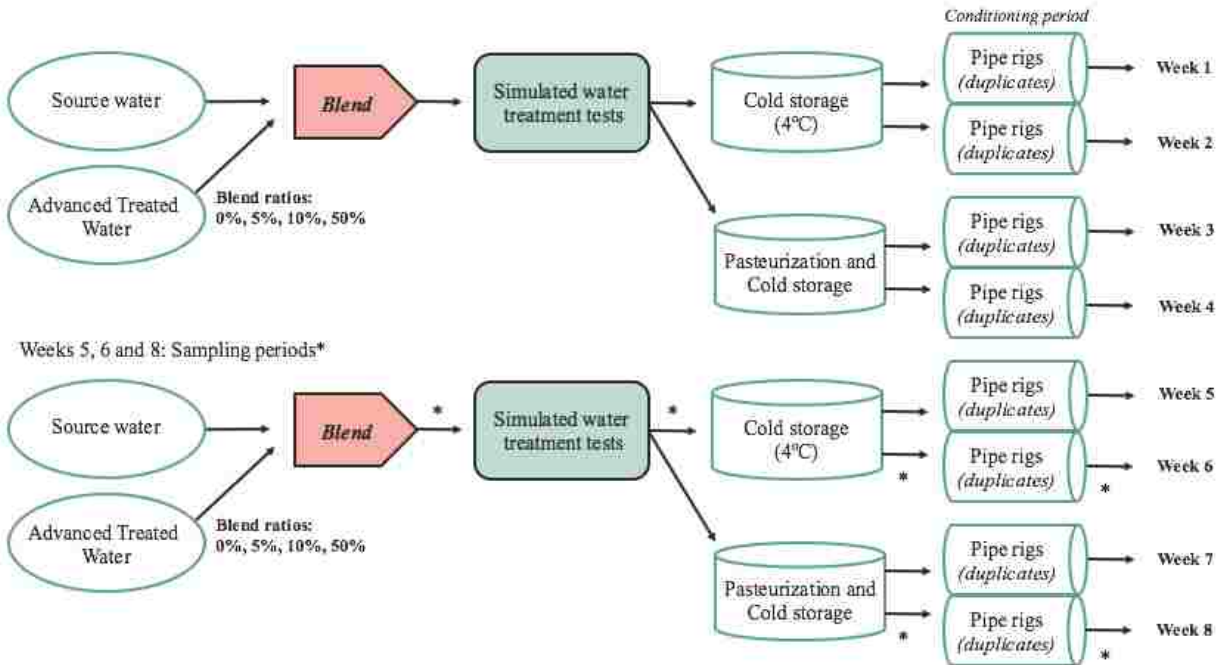
Figure 2. Flow chart summarizing the 8-week experimental protocol
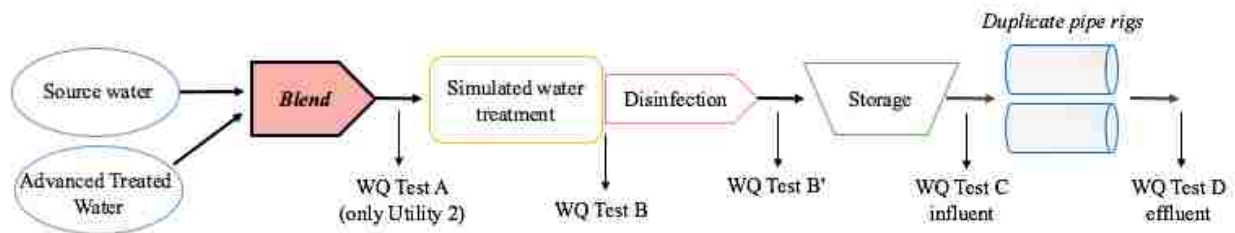
Water Quality Tests	Parameters
WQ Tests A	Ambient THMs, THM-Formation Potential (Utility 2)
WQ Test B (before disinfection)	THM-Formation Potential
WQ Test B'(post disinfection)	THMs, TOC, DOC, pH, UV_{254}, alkalinity, ATP, electrical conductivity, Langelier's Saturation Index (LSI)
WQ Test C Influent	THMs, nutrients, disinfectant residual, trace metals
WQ Test D Effluent	THMs, nutrients, disinfectant residual, trace metals, biological corrosion

Figure 3. Sampling and analytical protocol. Water Quality Tests A, B and B' were performed on week 5, and Water Quality Tests C and D were performed on weeks 6 and 8.

During each 8-week test period, fresh water samples were received and treated twice at the beginning of weeks 1 and 5. The first batch was processed for weeks 1 – 4 and the second batch was processed for weeks 5 – 8. A 30-gallon Uline® stainless steel container was used for blending and storing samples before bench-scale treatment. Simulated water treatment processes were the bench-scale drinking water treatment processes performed to simulate existing or potential full-scale Direct Potable Reuse (DPR) systems at the respective utilities. Bench-scale treatment of the blended and non-blended waters entailed one or more of the following processes: ozonation, coagulation/sedimentation/flocculation, filtration, and chlorine and/or chloramine disinfection. In Figure 3, water quality tests (A, B, B', C, D) were performed for specific analytes to monitor their influence on THM formation and potential corrosion. Results from the A tests were used to evaluate the background analytes appearing in the blended and unblended waters from Utility 2 prior to simulated water treatment (i.e. THM precursors, DOC). The B tests evaluated the formation potential of THMs (surrogate measurement for THM

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precursors) after simulated treatment, but prior to chlorine disinfection. B' tests were performed after simulated water treatment and after disinfection. Then, tests C and D compared the water quality before and after pipe rig incubation with respect to concentrations of metals and THMs. Pipe rig tests were performed for each blend in duplicates. On weeks 6 and 8, the aged water samples from the pipe rigs were tested approximately after a 48-hour incubation period, while on the remaining weeks effluent samples were discarded.

For Utility 1, the drinking water source was raw surface water (S_1) collected from the South Bay Aqueduct in California, which was blended with purified reuse water produced from two separate advanced purification sites. In the first scenario, raw surface water was blended with recycled water (Wb_1) treated from an ozone-biologically active (O_3-BAF) pilot filter at blend ratios of 0% (0% Wb_1/100% S_1) and 10% (10% Wb_1/90% S_1). The raw surface water in the second scenario was blended with recycled water (Wm_1) from a MF-RO-UV/AOP (hypochlorite or hydrogen peroxide) pilot treatment train at blend ratios of 10% (10% Wm_1/90% S_1) and 50% (50% Wm_1/50% S_1). The blended and non-blended test waters were then subjected to bench-scale treatment simulating conventional drinking water treatment processes. A comprehensive summary of the acronyms, blending scenarios and simulated bench-scale experiments is shown in Tables 3a and 3b, where subscripts 1, 2, 3, and 4 have been used to denote blending conditions for Utilities 1, 2, 3, and 4, respectively.

Table 3a. List of acronyms

Acronym	Description of Acronym	Reclaim Process train
Wm	Wm means microfiltration	Microfiltration (MF), Reverse Osmosis (RO), Ultraviolet/Advanced Oxidative Processes (UV/AOP)
Wb	Wb means biofiltration	Ozone (O_3), Biofiltration (BAF)
Wt	Wt means tertiary effluent	Secondary treatment by nitrification/partial denitrification, Bio-P removal, followed by tertiary treatment by dual media anthracite-sand filtration
Wu	Wu means ultrafiltration	Ultrafiltration (UF), Reverse Osmosis (RO), Ultraviolet/Advanced Oxidative Processes (UV/AOP)
Wp	Wp means pasteurization	Pasteurization, Ultrafiltration (UF), Reverse Osmosis (RO), Ultraviolet/Advanced Oxidative Processes (UV/AOP)
Wab	Wab means reclaimed industrial wastewater	Microfiltration (MF), Reverse Osmosis (RO), Ultraviolet/Advanced Oxidative Processes (UV/AOP)

Table 3b. Blending scenarios and simulated bench-scale treatment of the blended and non-blended test waters

| Water Utilities | Source Water and Blend ratio | | Treatment at Utility | | Simulated bench-scale tests |
	Symbol	Description	Scale	Reclaim Process train	
Utility 1	S_1 (100%)	Raw surface water	None	None	O_3, coagulation, filtration, disinfection (Cl_2/CLM[1])
	Wm_1 (100%)	Reclaimed wastewater	Pilot	MF, RO, UV/AOP	None
	Wb_1 (100%)	Reclaimed wastewater	Pilot	O_3, BAF	None
	Wm_1/S_1 (10/90%)	Blended Wm_1 and S_1	None	None	O_3, coagulation, filtration, disinfection (Cl_2/CLM)
	Wm_1/S_1 (50/50%)	Blended Wm_1 and S_1	None	None	O_3, coagulation, filtration, disinfection (Cl_2/CLM)
	Wb_1/S_1 (10/90%)	Blended Wb_1 and S_1	None	None	O_3, coagulation, filtration, disinfection (Cl_2/CLM)
Utility 2	S_2 (100%)	Raw surface water	None	None	Coagulation, filtration, disinfection (Cl_2/CLM)
	Wb_2 (100%)	Reclaimed wastewater	Pilot	O_3, BAF	None
	Wt_2 (100%)	Reclaimed wastewater	Full	Sec. treatment, dual-media tertiary filtration	None
	Wb_2/S_2 (50/50%)	Blended Wb_2 and S_2	None	None	Coagulation, filtration, disinfection (Cl_2)
	Wb_2/S_2 (10/90%)	Blended Wb_2 and S_2	None	None	Coagulation, filtration, disinfection (Cl_2)
	Wt_2/S_2 (5/95%)	Blended Wt_2 and S_2	None	None	Coagulation, filtration, disinfection (Cl_2)
	Wt_2/S_2 (10/90%)	Blended Wt_2 and S_2	None	None	Coagulation, filtration, disinfection (Cl_2)
Utility 3	G_3 (100%)	Treated ground water	Full	Fe/Mn removal, chlorination	Disinfection (CLM[2])
	Wu_3 (100%)	Reclaimed wastewater	Pilot	UF, RO, UV/AOP	None
	Wp_3 (100%)	Reclaimed wastewater	Full	Pasteurization, UF, RO, UV/AOP	None
	Wu_3/G_3 (10/90%)	Blended Wu_3 and G_3	None	None	Disinfection (CLM)
	Wu_3/G_3 (50/50%)	Blended Wu_3 and G_3	None	None	Disinfection (CLM)
	Wp_3/G_3 (10/90%)	Blended Wp_3 and G_3	None	None	Disinfection (CLM)
	Wp_3/G_3 (50/50%)	Blended Wp_3 and G_3	None	None	Disinfection (CLM)
Utility 4	G_4 (100%)	Treated ground water	Full	Chloramination	Disinfection (CLM)

| Water Utilities | Source Water and Blend ratio | | Treatment at Utility | | Simulated bench-scale tests |
	Symbol	Description	Scale	Reclaim Process train	
	S_4 (100%)	Raw surface water	None	Drinking water reservoir	None
	Sf_4 (100%)	Finished surface water	Full	O_3, coagulation, filtration, chloramination	Disinfection (CLM)
	Wm_4 (100%)	Reclaimed wastewater	Pilot	MF, RO, UV/AOP	None
	Wab_4 (100%)	Reclaimed industrial wastewater	Pilot	MF, RO, UV/AOP	None
	Wm_4 (10/90%)	Blended Wm_4 and G_4	None	None	Disinfection (CLM)
	Wm_4 (10/90%)	Blended Wm_4 and S_4	None	None	O_3, coagulation, filtration, disinfection (Cl_2/CLM), $Zn(PO_4)$
	Wab_4 (10/90%)	Blended Wab_4 and Sf_4	None	None	Disinfection (CLM)

[1]Cl_2/CLM: chloramines formed after chlorination from the addition of aqua ammonia
[2]CLM: samples were dosed with preformed chloramines

For Utility 2, raw surface water (S_2) from Lake Mead was blended with two types of recycled water sampled after tertiary treatment by dual media (anthracite-sand) filtration (Wt_2), and after advanced treatment from a pilot O_3-BAF unit (Wb_2). The O_3-BAF treated effluent was blended with raw surface water using 10% (10% Wb_2/90% S_2) and 50% (50% Wb_2/50% S_2) ratios to determine the effects of added treatment post tertiary treatment. The tertiary filtered water was blended with raw surface water at 0% (0% Wb_2/100% S_2), 5% (5% Wt_2/95% S_2) and 10% (10% Wt_2/90% S_2) ratios.

The drinking water source for Utility 3 was finished groundwater (G_3) treated for iron and manganese, and chlorinated from a full-scale facility. G_3 samples were blended with treated wastewater (Wu_3) produced from an ultrafiltration (UF)-RO-UV/AOP pilot treatment train at 10% (10% Wu_3/90% G_3) and 50% (50% Wu_3/50% G_3) blend ratios. The finished groundwater was also blended with treated wastewater (Wp_3) from a pasteurization-UF-RO-UV/AOP pilot system at blend ratios of 0% (0% Wp_3/100% G_3), 10% (10% Wp_3/90% G_3), and 50% (50% Wp_3/50% G_3).

The RO-treated effluents from Utility 4 were stabilized prior to blending by boosting the pH to 8 with NaOH, and adding $50 - 70$ mg/L of $CaCl_2$. This pre-treatment measure was performed to reduce corrosion potential by shifting the Langelier Saturation Index (LSI) closer to equilibrium in the $-0.5 - 0.5$ range. The online Lenntech LSI calculator was used to input known pH, temperature and conductivity values to determine the amount of Ca^{2+} needed based on the calculated LSI. In the first scenario, treated wastewater (Wm_4) sampled from a pilot MF-RO-UV/AOP treatment train was blended with finished ground water (10% Wm_4/90% G_{F4}) produced at the full-scale plant. From Utility 4, raw surface water (S_4) was also sampled and blended with Wm_4 water at a 10% (10% Wm_4/90% S_4) blend ratio. In another scenario, MF-RO-UV/AOP product water (Wab_4) from a full-scale industrial plant was blended with filtered surface water (Sf_4) by applying a 10% recycled water ratio (10%Wab_4/90% Sf_4).

The effects of blend ratio and/or treatment of the recycled waters on metal and THM concentrations were evaluated among each utility using statistical methods. Analysis of variance (ANOVA) calculations were performed to determine if there were significant differences among treatments. If significance ($p < 0.05$) was indicated from the ANOVA, Duncan's Multiple Range test calculations were performed to determine for which blends there were significant differences among concentration means. The Student's t-test was used to determine the significance of the coefficient of determination for regressions of concentrations on blend ratios. When the p-value, calculated from the t-test was below the designated significance level ($p < 0.05$), the null hypothesis of no correlation of parameter values with blend ratio was rejected. Results were generated using statistical equations published in Alder & Roessler (1964).

2.2   Simulated Treatment Tests

Blended and non-blended waters stored at 4°C in stainless steel drums were transferred to 1-gallon amber glass bottles (VWR International, PA), which had been previously washed with soap (Equinox non-residue detergent) and tap water, then washed in 10% HNO_3/10% HCl acid baths to remove trace metals, and rinsed three times with Ultrapure Milli-Q water (Millipore, MA). The samples from the bottles were subjected to bench-scale water treatment performed to mimic current or future drinking water treatment processes adopted for the full-scale operation of the respective utilities. Depending on the quality of the blend, some samples only required disinfection with no additional simulated treatment, achieved by augmenting the combined chlorine residual. With the exclusion of the surface water blend from Utility 4 (10% Wm_4/90% S_4), water samples from Utility 3 and 4 required only disinfection to attain a target chloramine residuals similar to the residuals maintained at the corresponding utilities. This type of treatment condition would simulate a scenario where the blended water can be directly piped into a distribution system rather than transferred upstream to a drinking water facility (blending location).

For Utility 1, all blended samples, and the non-blended surface water samples (S_1) were treated at bench-scale by ozonation, coagulation/flocculation/sedimentation, vacuum filtration and chlorine/chloramine disinfection. For Utility 2, treatment of all blended samples and non-blended surface water (S_2) was performed by coagulation/flocculation/sedimentation, vacuum filtration, and chlorine disinfection. The raw surface water blend from Utility 4 (10% Wm_4/90% S_4) was treated by ozone disinfection, coagulation/flocculation/sedimentation, vacuum filtration, chlorine/chloramine disinfection, and zinc orthophosphate addition (~1 mg/L).

2.2.1   Ozone

Bench-top ozone experiments were carried out in a 4 L batch reactor according to previously published procedure by Wert et al. (2011) using an oxygen-fed ozone generator (CFS-1A, Ozonia North America, Inc., NJ). The stock O_3 concentration in the reactor was measured using potassium indigotrisulfonate (APHA, 1998), prepared from methylene blue crystals (ACROS Organics, Thermo Fisher Scientific). The dissolved ozone residual is determined in relation to the bleaching of the indigo solution, which is measured as the absorbance using a Hach DR 5000 Spectrophotometer. The concentration of the stock solution was consistently around 60 mg/L dissolved O_3. All blended samples, and the non-blended surface water (S_1) samples from Utility 1 were dosed with 2 mg/L O_3 by dispensing a pre-determined volume of the stock O_3 solution into the 1-gallon sample bottle to achieve the source Utility's target dose. For Utility 4, only the surface water blend (10% Wm_4/90% S_4) was ozonated to achieve that Utility's target dose of 0.5 mg/L. After ozonation, water samples were stored in a refrigerator for subsequent treatment.

2.2.2   Enhanced Coagulation and Filtration

Enhanced coagulation was simulated using a six-paddle programmable jar test apparatus (PB-900 Phipps and Bird, Richmond, VA). Samples were transferred from cold storage into 2 L acrylic jars ($BKER^2$ Phipps and Bird, Richmond, VA), and the required dosages of coagulants and flocculants needed were established by the Utility's protocol. For Utility 1, ozonated samples were transferred into the 2 L acrylic jars, and dosed with 38 mg/L of alum (44% aqueous) coagulant and 1.5 mg/L of 20% cationic polymer. For the rapid-mix phase, samples were agitated at 100 rpm ($G = 170$ s^{-1}) for 2 minutes to promote coagulation. Then, flocculation was induced by adding 0.18 mg/L of 10% non-ionic polymer at a slow mixing rate of 30 rpm (G

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= 51 s^{-1}) for 26 min. For Utility 2, blended (Wb$_2$10%/ S$_2$ 90%), (Wb$_2$50%/ S$_2$50%), (Wt$_2$5%/ S$_2$95%), (Wt$_2$10%/ S$_2$90%), and non-blended samples (S$_2$) were transferred from the stainless steel drum into the 2 L acrylic jars, and each jar was dosed with 0.6 mg/L of 40% FeCl$_3$. Coagulation was promoted through rapid mixing at 100 rpm for 2 min, followed by slow mixing at 30 rpm for 26 min to enhance flocculation (Wert et al., 2011). The ozonated test water from Utility 4 (10% Wm$_4$/ 90% S$_4$) was dosed with 1.5 mg/L of 40% FeCl$_3$ and 1.2 mg/L of 20% cationic polymer. The apparatus was timed to rapidly mix the samples at 100 rpm for 2 min to promote coagulation, and then slow mixing was set at 30 rpm for 30 min to enhance floc formation. All samples were allowed to settle in the jars for 0.5 – 24 h before proceeding to filtration. After sedimentation, paddles were removed and samples were filtered through a 1.5 µm Whatman Glass Microfiber Filter (Type 934-AH, VWR International) to remove floc particles. Filtered samples were transferred to clean 1-gallon amber glass bottles prior to disinfection.

2.2.3   Disinfection

Blended and non-blended test waters from the simulated bench-scale tests were disinfected to simulate the disinfection protocol at the respective Utility by targeting pre-established disinfectant residuals. The chlorine stock solutions were prepared from commercial grade sodium hypochlorite (5.65-6% NaOCl, Fisher Chemicals), and diluted using de-ionized water from a Milli-Q-Gradient purification system. Filtered water samples from Utility 1 [(10% Wb$_1$/ 90% S$_1$), (10% Wm$_1$/ 90% S$_1$), (50% Wm$_1$/ 50% S$_1$), and (S$_1$)] were dosed with ~2.6 mg/L of stock sodium hypochlorite (NaOCl) solution as free Cl$_2$, and mixed for 11 minute contact time to yield 1.8 – 2.2 mg/L Cl$_2$ residual. Chloramines were formed by adding ammonium hydroxide

(NH$_4$OH) to the chlorinated water at a Cl$_2$:NH$_3$ ratio of 4.5:1 mass ratio to yield target residual of 1.6 – 1.8 mg/L as combined Cl$_2$. Utility 2 test waters [(10% Wb$_2$/90% S$_2$), (50% Wb$_2$/50% S$_2$), (5% Wt$_2$/95% S$_2$), (10% Wt$_2$/ 90% S$_2$), and (S$_2$)] were disinfected with chlorine (~2 – 2.4 mg/L dose) to achieve a chlorine residual of 1.5 mg/L as free Cl$_2$. The required dose was determined by performing chlorine decay kinetic tests such that the free chlorine residual was 1.5 mg/L after 2-hour contact time on the shaker. For Utility 3, test waters [(10% Wu$_3$/90% G$_3$), (50% Wu$_3$/50% G$_3$), (50% Wp$_3$/50% G$_3$), and (G$_3$)] were dosed with preformed chloramine stock solution (1.4 g/L as free Cl$_2$) to yield a target combined Cl$_2$ residual of 3.8 mg/L. The surface water blend from Utility 4 (10% Wm$_4$/90% S$_4$) was disinfected with a 3.1 mg/L dose of stock sodium hypochlorite (NaOCl) solution as free Cl$_2$. The samples were mixed for 16.5 minutes to yield a 2.5 mg/L free Cl$_2$ residual, then ammonium hydroxide (NH$_4$OH) was added immediately after to quench free chlorine and form chloramines at a 5:1 Cl$_2$:NH$_3$ ratio. The blended and non-blended groundwater samples [(10% Wm$_4$/90% G$_4$) and (G$_4$)] were disinfected with preformed chloramines from a stock chloramine solution (1.4 g/L as free Cl$_2$) to achieve the Utility's target combined Cl$_2$ residual of 2.5 mg/L. In the second scenario of Utility 4, samples [(10% Wab$_4$/90% Sf$_4$) and Sf$_4$] were dosed with preformed chloramines (Cl$_2$:NH$_3$ 3.5:1) to obtain a 2.6 mg/L combined chlorine residual. The preformed chloramine stock solutions were prepared by combining Cl$_2$ and ammonia from ammonium chloride (NH$_4$Cl) at the established Cl$_2$:NH$_3$ ratios provided by the Utility. Stock chlorine and chloramine concentrations were verified using the Iodometric titration method (SM 4500-Cl B).

2.3   Pasteurization and Storage

In addition to the simulated bench scale tests, half (~12 gallons) of the finished water samples from each batch were pasteurized to minimize microbial activity during cold storage (4°C), i.e., prior to filling the pipe rigs. The pasteurization protocol was conducted following a previously reported method by Escobar & Randall (2000). Blended and non-blended finished water samples were pasteurized in water baths heated to 70°C. Each 1-gallon water sample was incubated in a water bath for 3 – 4 hours, and monitored until the temperature of the test waters reached 72°C. Once the water temperature reached 72°C, samples were further incubated at 72°C for an additional 30 minutes. After 30 minutes, samples were removed from the water bath and allowed to cool down at room temperature, and then placed in ice baths for 30 minutes. After 30 minutes, samples were stored in the refrigerator and, prior to filling the pipe rigs, disinfected to boost the residual that was partially lost during the heating process. Gambarini et al. (1998) experimentally determined that chlorine decay during pasteurization is likely due to thermal decomposition of sodium hypochlorite which remains stable at 50°C. Moreover, the chlorine residual is further reduced at elevated temperatures from the increased rate of reaction with organic constituents present in the matrix, causing a higher conversion of free chlorine to total chlorine (Liu & Reckhow, 2015).

2.4   Pipe Rig Loop Tests

Eight-week pipe rig tests were conducted using 5 feet (1.5 m) long pipes constructed from polyvinyl chloride (PVC) (Fig. S1, Supplementary information). Each pipe contained two 14-inch (36 cm) long CDA (Copper Development Association) round brass bars (½ inch, 1.27 cm diameter) lodged on opposite sides of the pipe to simulate a household premise plumbing

located past the main distribution pipe. The CDA brass material was nominally composed of 60% copper, 35% zinc, and 3% lead. Two pipe rigs per test water (a total of ~26 pipe rigs) were constructed at the Virginia Polytechnic Institute, and pre-tested for lead and copper leaching using the National Science Foundation (NSF) Standard 61 Section 9 extraction water-wash protocol (NSF, 2007) before the pipe rigs were shipped to SNWA.

Finished blended and non-blended water samples from the four Utilities were each distributed into duplicate pipe rigs "as received" for an eight-week conditioning period. During this conditioning period, water in the pipe rigs was changed out twice or three times a week (for the weeks requiring sample collection) a week by dumping out aged water samples and refilling the pipe rigs with fresh test water samples retrieved from the refrigerator. Ideally, recirculating water through the pipe loops would have emulated actual hydraulic conditions in a distribution system. However, in this case, test waters were not recirculated and water quality analyses were performed on stagnant water to simulate scenarios of low flow conditions and longer storage periods. Before filling the pipe rigs, refrigerated samples were allowed to stand at room temperature for approximately 2-3 hours. Non-pasteurized samples were used to fill the pipe rigs on weeks 1, 2, 5 and 6. Pasteurized samples were disinfected, and used to fill the pipe rigs on weeks 3, 4, 7 and 8 to minimize bacterial activity as the water aged in storage, and ensure stability of the water samples after treatment and during storage prior to pipe rig incubation.

2.5   Water Quality Analysis

The water quality parameters monitored before and after treatment and pipe loop tests, standard analytical methods, and their method reporting limits are summarized in Table 4.

Table 4. Measured analytes, standard methods and their method reporting limits

Bulk parameter	Water quality test	Specific analyte	Method	Reporting limit
Bulk water quality	B', C, D	pH	SM 4500H+ B	N/A
	B', C, D	TOC	SM5310 B	0.5 mg/L
	A, B', C, D	DOC	SM5310 B	0.5 mg/L
	B', C	Electrical conductivity	SM 2510 B	
	A, B', C	UV$_{254}$	SM 5910 B	0.002 cm^{-1}
	B', C, D	Alkalinity	SM 2320 B	2 mg/L
	B', C, D	ATP	LUMINULTRA test kit	0.1 pg/mL
Disinfection by-product formation potential	B	THM-FP	SM 5710B	0.0005 mg/L
Disinfection by-products	A, B', C, D	THM$_4$ and HAA$_5$	EPA 524.3 and EPA 552.2	0.001 mg/L
Disinfectant residual	B', C, D	Free and total Cl$_2$	SM 4500-Cl G	0.01 mg/L
Biological corrosion	D	Acid producing bacteria	Biological reactivity (BART) test kit	Presence/ Absence
		Denitrifying bacteria		
		Heterotrophic aerobic bacteria		
		Nitrifying bacteria		
		Slime producing bacteria		
		Sulfur reducing bacteria		
Nutrients	C, D	NH$_3$	SM 4500-NH G	0.02 mg/L
	C, D	NO$_3$	SM 4500-NO$_3^-$	0.05 mg/L
Trace metals	C, D	Calcium	SM 3500-Ca B	2.5 mg/L
	C, D	Lead	EPA 200.9	0.001mg/L
	C, D	Copper	EPA 200.8	0.0005 mg/L

Test waters were collected at five different sampling points specified by water quality tests A, B, B', C, and D. The bulk water quality parameters included pH, TOC, DOC, electrical conductivity, UV 254, alkalinity, and ATP. All pH measurements were recorded directly in the pilot plant using a portable Accumet AP115 pH/ORP meter (Fisher Scientific). Samples were prepared for aqueous ATP analyses following LuminUltra® Quench-Gone™ Aqueous (QGA) test kit instructions. After sample preparation, ATP results were generated using the LumiCalc™ Data Analysis Software integrated to a USB-operated luminometer (PhotonMaster™ Luminometer, LuminUltra). For TOC, DOC, conductivity, UV 254, and

alkalinity analyses, samples were transferred into vials and analyzed in the laboratory, where Standard Method procedures were followed (Table 4). Free and total chlorine were also measured directly in the pilot plant using the *N,N*-diethyl-*p*-phenylendiamine (DPD) colorimetric method with a pocket colorimeter (HACH DR 800).

The Trihalomethane Formation Potential (THM-FP) test (Test B) was performed to determine the concentration of THM precursors in the samples collected after blending and simulated treatment, but before disinfection. Following Standard Method 5710B, the samples were spiked with sodium hypochlorite to hit a target free chlorine residual of 3 – 5 mg/L after 7 days. The experiment required a minimum of three 250 mL bottles per sample, to which was added 10 mM of phosphate buffer at pH 7. Each bottle was dosed with different concentrations of sodium hypochlorite starting from lowest to highest dose. Bottles were filled completely with sample water leaving no headspace, and stored in the dark for 7 days. At the end of the 7-day period, the free chlorine concentrations were measured. The sample closest to the 3 – 5 mg/L range was transferred into two separate vials for chlorine quenching before being analyzed for THMs. The 40ml vial contained 30μl of 10% w/w sodium thiosulfate, and the 60ml vial contained 3mg of ammonium chloride. In accordance with USEPA Method 524.3, a total of four THM species were quantified, which included chloroform, chlorodibromomethane, bromoform, and bromodichloromethane. THMs were also measured for water quality tests A, B', C and D to identify ambient THMs after blending, and track THM formation after simulated treatment, storage and pipe rig incubation.

Microbial activity was measured using six Biological Activity Reaction Tests (BART™) specific for detecting Sulfate Reducing Bacteria (SRB), Heterotrophic Aerobic Bacteria (HAB), Slime Forming Bacteria, Denitrifying Bacteria (DNB), Nitrifying Bacteria (NB), and Acid

Producing Bacteria (APB). Each biodetector was filled with 15 mL of effluent sample (Test D) from the duplicate pipe rigs, and monitored for the number of days indicated by a reaction day chart provided in the BART™ kit. The vials contained a nutrient-rich medium selective to maximize growth of the target bacteria, and "activate" otherwise potentially dorment bacteria. The biodetector also contained a ball that functioned as a barrier against oxygen diffusion, which allowed a redox gradient to form within the column. Aerobic growth was induced at sites around the ball and anaerobic growth occurred at the base of the vial. The presence or absent of a specific bacterial group was determined by identifying visual changes (e.g. cloudiness, foam bubbles, discoloration) occuring in the column, and matching the reaction pattern to the microbial consortia. The approximate population size of the microbial community was estimated in relation to the number of days needed for the reaction to occur. The more aggressive bacteria were identified at the beginning of the test, while less aggressive bacteria were quantified as the time lag increased to the detection of the reaction. Results were obtained by relating the reaction day to an approximate population size using a reference chart provided by the BART™ manufacturer (Table 5). The number of reaction days were different for each test because different bacterial genera have different growth curves. For example, a three-day reaction for SRB was indicative of aggressive bacteria, but a three-day reaction for denitrifying bacteria indicated a more moderate growth rate. Due to an initial misinterpretation of the BART™ quantification method, Utility 1 was exclusively analyzed based on a negative or positive test result (absent or present) at the end of the reaction period (after 4 – 10 days).

Table 5. Sample reference chart for determining approximate population size of SRB

Days to reaction	Population size (cfu/mL[1])	Growth rate
1	2,200,000	Aggressive
2	500,000	Aggressive
3	115,000	Aggressive
4	27,000	Aggressive
5	6,000	Aggressive
6	1,400	Moderate
7	325	Moderate
8	75	Moderate
9	20	Not aggressive
10	5	Not aggressive

[1]cfu/mL are the units of measurement in colony forming units per mL

Metals concentrations were measured before (Test C) and after (Test D) pipe rig incubation to determine the potential effect of the blends on the water quality after exposure to the brass fittings. Influent and effluent samples to and from the pipe rigs were collected in vials, and tested for copper and lead using EPA 200.8 and 200.9 procedural methods.

All influent data from Test C were evaluated based on the average of two sampling points collected on weeks 6 and 8. Whereas effluent data were analyzed in duplicates from Test D average concentrations, evaluated based on four values measured on weeks 6 and 8.

2.6   Langelier Saturation Index

The Langelier Saturation Index (LSI) was used to estimate the tendency of the finished waters incubated in the pipe rigs to be either corrosive (negative LSI) or scale-forming (positive LSI). The indices were calculated according to the previously published method by Faust and Aly (1998) using equation (1):

$$LSI = pH - pH_s \qquad\qquad (1)$$

Where pH$_S$ is the pH at saturation with calcium carbonate, which can be calculated using the following equation:

$$pH_s = (9.3 + A + B) - (C + D) \tag{2}$$

Where A, B, C and D values correlated to the following expressions:

$$A = (Log_{10} \text{[TDS]} - 1)/10$$

$$B = -13.12 \times Log_{10} (^oC + 273) + 34.55$$

$$C = Log10 [Ca^{2+} \text{ as } CaCO_3] - 0.4$$

$$D = Log_{10} [alkalinity \text{ as } CaCO_3]$$

[Ca^{2+}] and [HCO_3^-] concentrations were expressed in mg/L as $CaCO_3$. The total dissolved solids (TDS) concentration was calculated using electrical conductivity (EC) from the following linear relationship TDS = k (EC), where k is a constant that varies between 0.5 and 0.9 (0.67 was used) (Shammas & Wang, 2015). Parameters (e.g., alkalinity, pH) measured after simulated treatment (Test B') at 21°C were used to calculate equations (1) and (2). The indices derived from utilizing this method were verified using the Lenntech online calculator (Lenntech, 2017). The LSI values of the RO-treated effluents from Utility 4 were calculated before blending and simulated treatment using the same online calculator to determine if stabilization was required, which was achieved adjusting the pH and increasing the calcium concentration. The LSI was measured to predict the solution's ability to dissolve calcium carbonate scales, but more specifically to estimate the corrosion potential of the treated samples.

CHAPTER 3. ASSESSMENT OF THE TRIHALOMETHANE FORMATION IN BLENDED WATERS

3.1   Introduction

The stability of the blended waters can be impacted by the formation of disinfection by-products (DBPs) downstream of drinking water treatment plants in storage tanks and distribution systems. Trihalomethanes (THMs) are one category of DBPs that form predominantly from the reaction of chlorine and/or bromine with natural organic matter (NOM). The consumption of chlorinated drinking water has been linked to the increased occurrence of bladder cancer due to the formation of trihalogenated DBPs post chlorine disinfection practices (Villanueva et al., 2004). The carcinogenic effects of THMs may affect the brain, and severely hinder reproductive functionality as reported in cases of spontaneous abortion (Hsu et al., 2001). Due to the associated health risks, THMs are federally regulated by the United States Environmental Protection Agency. The Maximum Contaminant Limit (MCL) of 0.08 mg/L was established for the Total THMs (TTHMs), which is the sum of the four regulated THMs. Haloacetic acids (HAAs) are another class of DBPs that can form from the chlorination of drinking water. Compared to THMs, HAAs have a more conservative regulatory limit which is set at a MCL of 0.06 mg/L. The total sum of HAAs include bromoacetic acid (BrAA), chloroacetic acid (ClAA), dibromoacetic acid (Br_2AA), dichloroacetic acid (Cl_2AA), and trichloroacetic acid (Cl_3AA).

Generally, chlorinated systems exhibit a high yield for THMs in the presence of NOM which may include humic compounds and elevated levels of bromide (Rodriguez et al., 2004). The properties of the NOM can be used to predict precursor reactivity in forming THMs by measuring nonspecific parameters such as the total organic carbon (TOC) and specific ultraviolet

absorption (SUVA). A high fraction of hydrophobic compounds (e.g., humic and fulvic acids) result in an increased ability to absorb light, leading to more elevated SUVA values compared to the hydrophilic counterpart (Musikavong et al., 2005). As a result, the water matrix has an increased tendency to form THMs in the presence of elevated hydrophobic compounds. Other factors that may affect the formation potential of THMs are source water type, treatment efficiency, pH, temperature, chlorine dose, and contact time.

Removal of THMs is challenging in distribution systems where chlorine residuals must be maintained to prevent biological regrowth. Some utilities have adopted aeration technologies in storage tanks to remove THMs by inducing volatilization with scouring (e.g., PAX Water Technologies). However, this process brings out of solution the more volatile chlorinated THM species, and less effectively removes the more toxic brominated species. One strategy for mitigating THM formation can be to install re-chlorination stations along the distribution system at sites located further away from the treatment plant. This approach would reduce the chlorine dose applied at the treatment facility and provide protection against THM formation, and potential biological regrowth downstream.

The objective of this part of the research was to investigate the impact of blending different ratios of high purity recycled water on the formation of THMs in chlorinated and chloraminated systems. The objective was achieved by measuring THMs at various sampling points after treatment, storage and pipe rig incubation to simulate the conditions of testing aged water as contact time with the disinfectant increases. THM concentrations were tracked more rigorously for Utility 2, where additional analyses were performed on the untreated test waters.

3.2   Methods and Materials

For all utilities, THMs were measured in blended and unblended waters after treatment (Test B'), after storage and before pipe rig incubation (Test C), and after pipe rig incubation (Test D). The Trihalomethane Formation Potential (THM-FP) test (Test B) was performed after treatment prior to disinfection by dosing the samples with high concentrations of chlorine to determine the maximum yield of THMs that would form after 7 days. Test waters from Utility 2 were further analyzed for ambient THMs (Test A) before treatment and disinfection, and for their THM-FP (Test B) after treatment but before disinfection.

In accordance with EPA method 524.3, samples were analyzed for THMs using Purge and Trap Gas Chromatography/Mass Spectrometry (GC/MS). Test waters were collected in headspace-free amber glass vials to prevent volatile species from evaporating. Samples were then submitted to the compliance lab for analysis, and tested according to the following reworded standard method procedure. The free chlorine concentration of the samples was quenched with ascorbic acid, and maleic acid was used to adjust the pH to ~2. A 5 mL volume of sample was transferred to a glass sparging vessel where the organic compounds were purged from water using helium, and trapped to a sorbent surface. Then, the trapped analytes were heated and flushed into a capillary GC column. The temperature inside the GC column was optimized to improve separation of the compounds, which subsequently travelled to a mass spectrometer for analysis. The peaks generated by the mass spectrometer were identified by referencing peaks obtained from running the calibration standards under the same established conditions. Quantification of the peaks was performed using the internal standard technique, by which the concentration of the analyte was calculated (USEPA, 2009).

3.3   Results

3.3.1   Impact of blending, source water and treatment on DBPs in distribution systems

The Total THMs (TTHMs) measured for the Trihalomethane Formation Potential (THM-FP) test (Test B) included the four regulated species of THMs, which were Chloroform, Dichlorobromomethane, Bromoform and Chlorodibromomethane. For Utility 1, the effects of blending reduced THM yields as observed in the decreased THM concentration in the 10% Wb_1/ S_1 blended water compared to the non-blended S_1 sample (Figure 4). Although the non-blended water and the 10% ozone-biofiltered blend had nearly the same DOC concentrations, the TTHM concentration was higher in the non-blended water. The ozone-biofiltered effluents were collected from the pilot plant at different dates, resulting in a variable quality of effluent, so the batch used to produce the 10% ozone-biofiltered blend generated fewer THMs than expected when observing THM concentrations measured in the 100% ozone-biofiltered (Wb_1) water sample. Similar TTHM concentrations were observed comparing the 10% Wb_1/ S_1 (0.21 mg/L) blend with the 10% Wm_1/ S_1 (0.18 mg/L) blend, however a higher fraction of the brominated species was present in the 10% RO-treated blend. Increasing the blend ratio of RO-treated water from 10% to 50% further decreased overall TTHM concentration. As expected, the DOC concentration also decreased as the recycled blend ratio of RO-treated water increased.
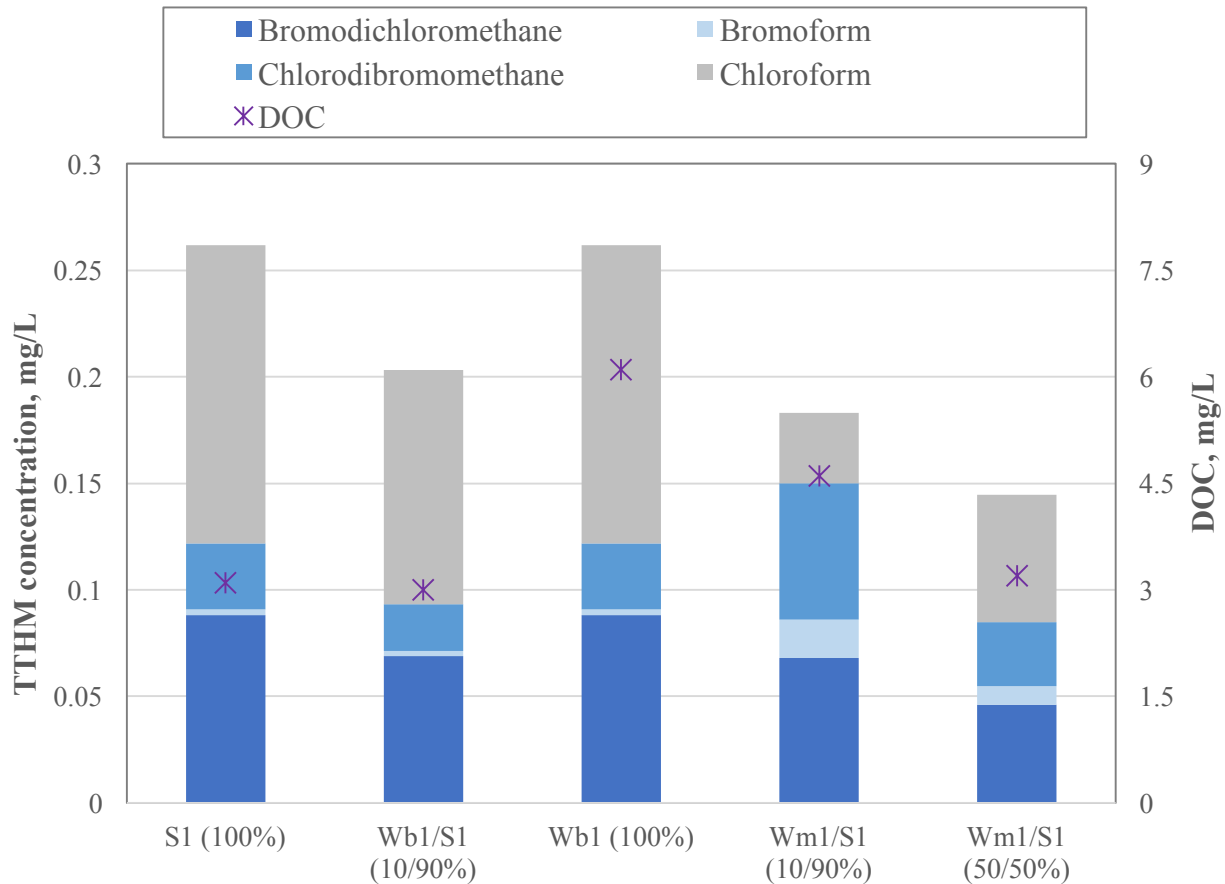
Figure 4. Trihalomethane Formation Potential Test results across Utility 1

Blending recycled water with surface water from Utility 2 had the opposite effect, in the sense that THM concentrations increased in both scenarios when the recycled water ratio increased. As the blend ratio of tertiary treated water increased from 5% (5% Wt_2/ 95% S_2) to 10% (10% Wt_2/ 90% S_2), THM concentrations slightly increased from 0.118 to 0.129 mg/L (Figure 5). Similarly, in the second scenario increasing the blend ratio of ozone-biofiltered water from 10% to 50% also increased THM concentrations. But, compared to the tertiary treated blends and the non-blended surface water sample, added treatment by ozone and biofiltration increased the portion of chlorinated THM species as observed in the higher concentrations of chloroform relative to the chlorodibromomethane species. Also, compared to the 10% ozone-biofiltered blend, the more elevated DOC concentration measured in the 50% ozone-biofiltered

blend corresponded to a higher TTHM concentration. The results confirmed an underlying link between DOC and THMs, suggesting that DOC can be a potential surrogate parameter used to predict THM yields. As shown in Figure 5, results show that the effects of added treatment by ozone and biofiltration had a minimal effect on reducing TTHM concentrations. Test B was performed also on the untreated waters to determine the formation potential of ambient THMs. The decrease in THM yields between treated and untreated samples also correlated to a decrease in SUVA values, validating the efficiency of the applied bench-scale treatment processes in removing reactive organic precursors.
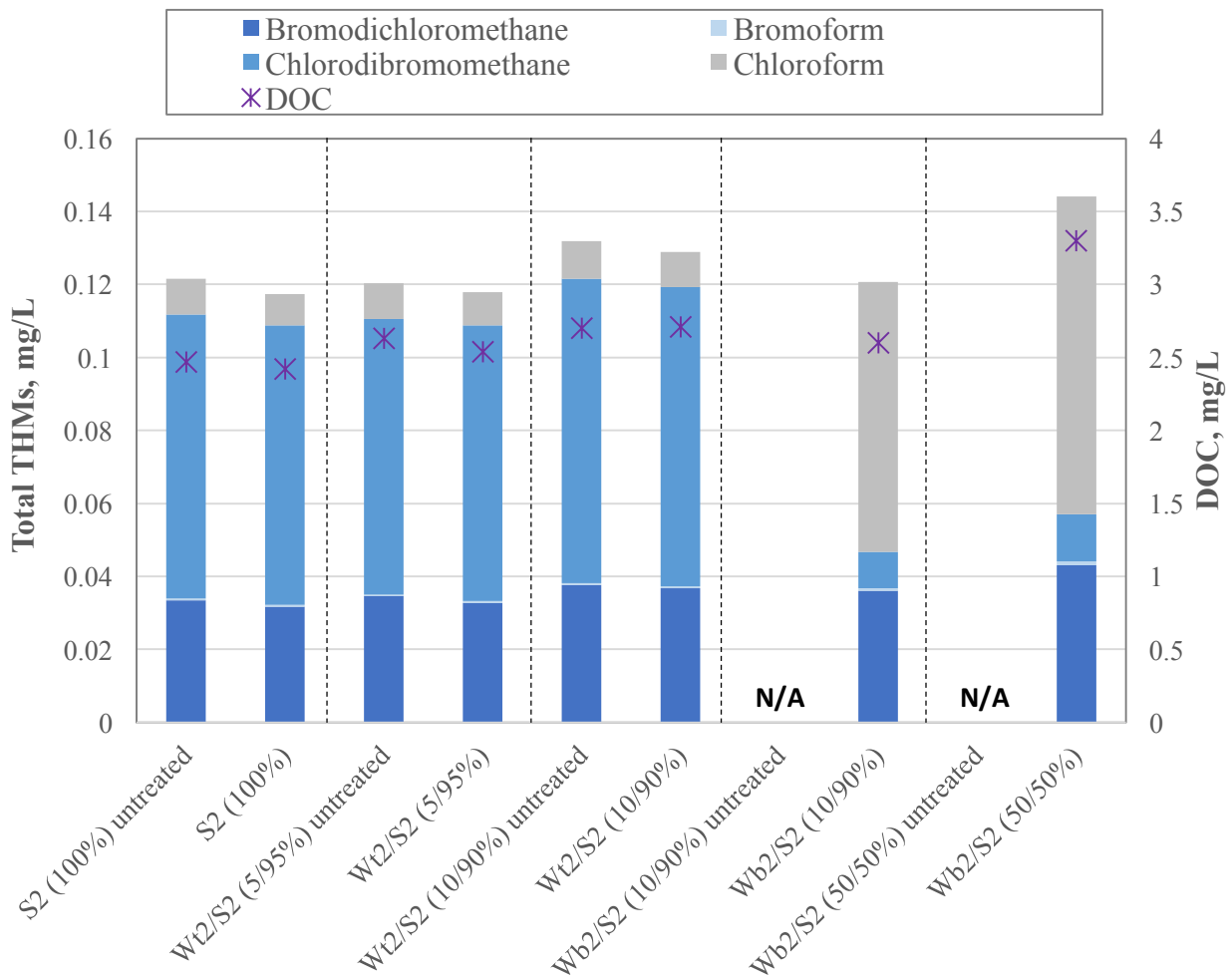
Figure 5. Trihalomethane Formation Potential Test results across Utility 2 for treated and untreated samples

For Utility 3, the blended and non-blended groundwater samples in Figure 6 contained significantly less TTHM and DOC concentrations compared to the surface water samples from Utility 1 and 2. DOC concentrations decreased as the blend ratio of RO-treated water increased from 10% to 50% in both pasteurized and non-pasterized blends. The reduction in DOC concentration in the higher recycled water blend ratios corresponded to a decrease in TTHM concentration. Although, blending appeared to largely reduce THM concentrations, the 10% Wp_3/G_3 blend resulted in a higher THM concentration compared to the non-blended groundwater sample (G_3). Moreover, compared to the surface water-impacted blends, all test waters from Utility 3 contained a higher percentage of the brominated THM species which stemmed from the partial and full substitution of bromine on the hydrogen atoms of the methane molecule. The high portion of brominated THM species that formed in Utility 3 were more toxic compared to the chlorinated forms. Bromide ions more readily react with oxidants yielding HOBr that, just like HOCl, form THMs in the presence of NOM (Hong et al., 2013). The brominated species forms at a higher rate compared to the chlorinated species as the bromide concentration increases due to the higher substitution ability of HOBr (Symons et al., 1993). This suggests that using treated groundwater as a source for blending reclaimed water may result as a potential health risk if adequate bromide removal is not performed prior to disinfection.
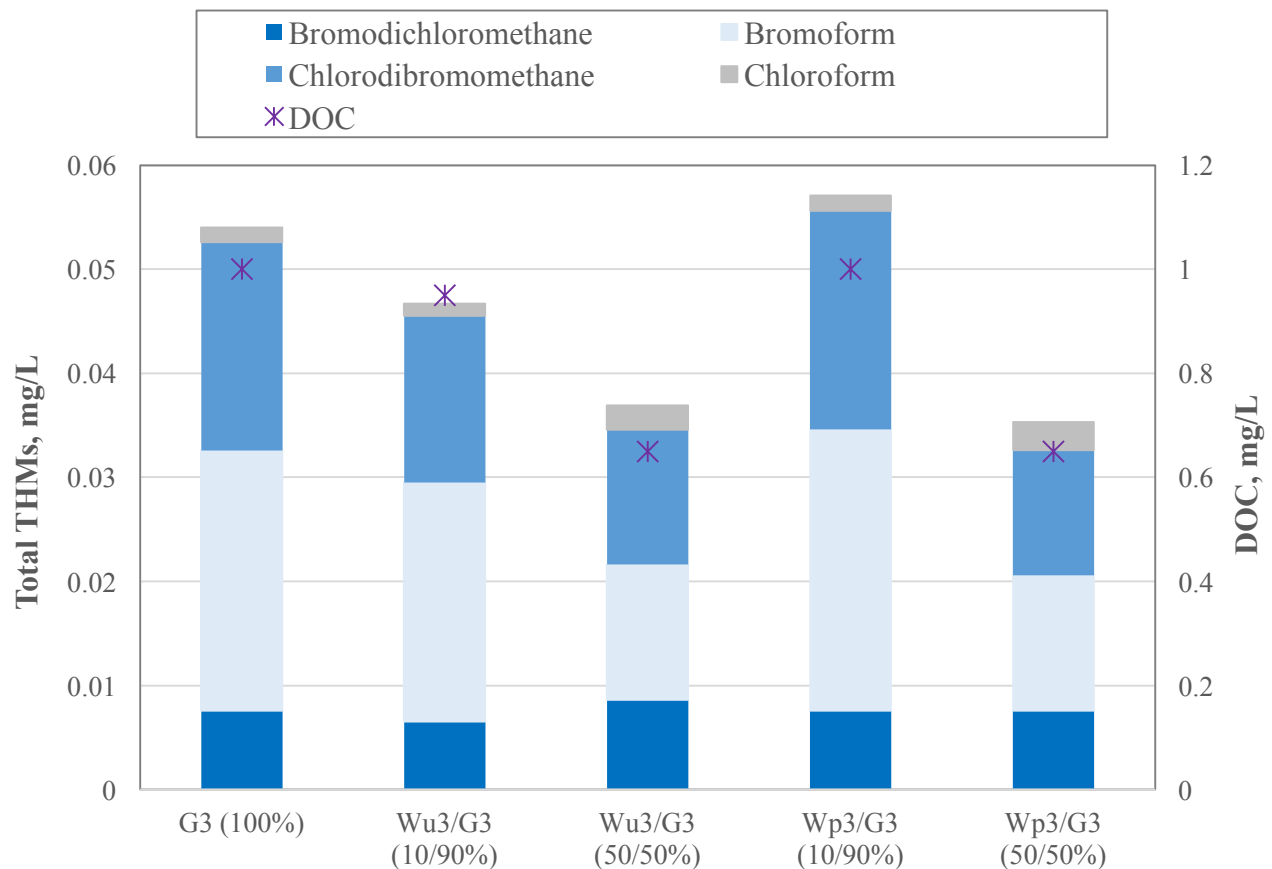
Figure 6. Trihalomethane Formation Potential Test results across Utility 3

In Figure 7, DOC and TTHM concentration trends for Utility 4 matched, showing that surface water sources typically have higher DOC values which results in more elevated THM yields than groundwater samples. Unblended reclaimed waters from both scenarios [(Wm4 (100%) and Wab4 (100%)) had low THM concentrations as a consequence of the MF-RO-UV/AOP treatment efficiency which reduced the concentration of potential organic precursors (>85%). Blending 10% RO-treated water with surface water in the first scenario did not sufficiently attenuate the THM concentration (0.098 mg/L), which spiked above the 0.08 mg/L threshold. In this case, further increasing the recycled water blend ratio could decrease THM

concentrations, demonstrating that blending may be a beneficial alternative to mitigate THM formation when a similar surface water quality is being used.
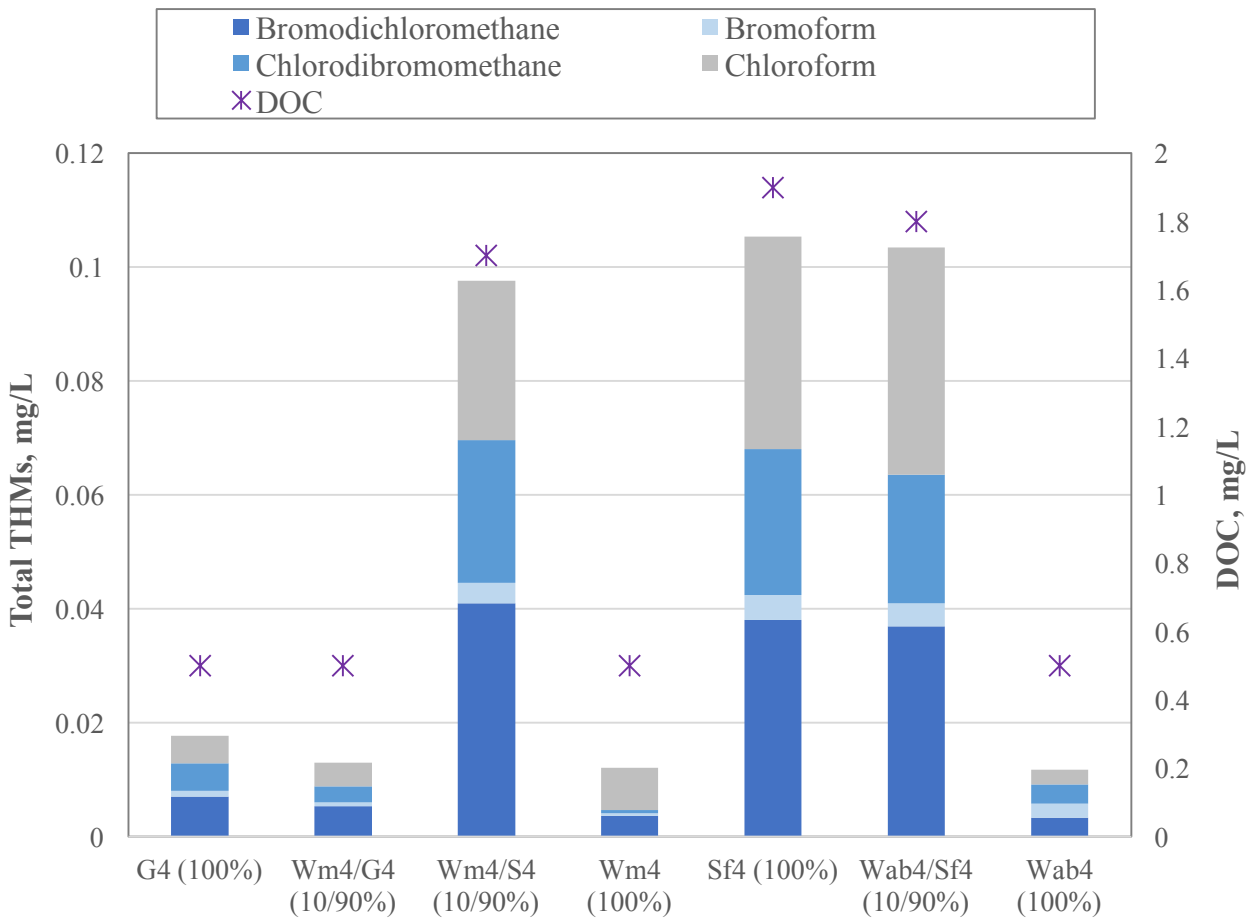
Figure 7. Trihalomethane Formation Potential Test results across Utility 4

In the second scenario, THM concentrations for the finished surface water sample (Sf_4) and the 10% RO-treated blend (10% Wab_4/ Sf_4) contained elevated THMs that exceeded the acceptable MCL, 0.105 mg/L and 0.103 mg/L, respectively. Increasing the percentage of recycled water to finished surface water slightly decreased the measured THM concentration; however, further tests would have to be performed to determine an appropriate recycled water blend ratio which would decrease THM yields to acceptable concentrations.

Samples were measured after bench-scale treatment (Test B') to evaluate the impacts of blending and treatment on THM formation. Unblended and tertiary treated blends from Utility 2 were also analyzed before treatment (Test A) to measure ambient THMs present in the source water and in the recycled water blends. In Figure 8, the effects of dosing the samples with chlorine resulted in higher THM concentrations in the treated samples compared to the untreated samples.
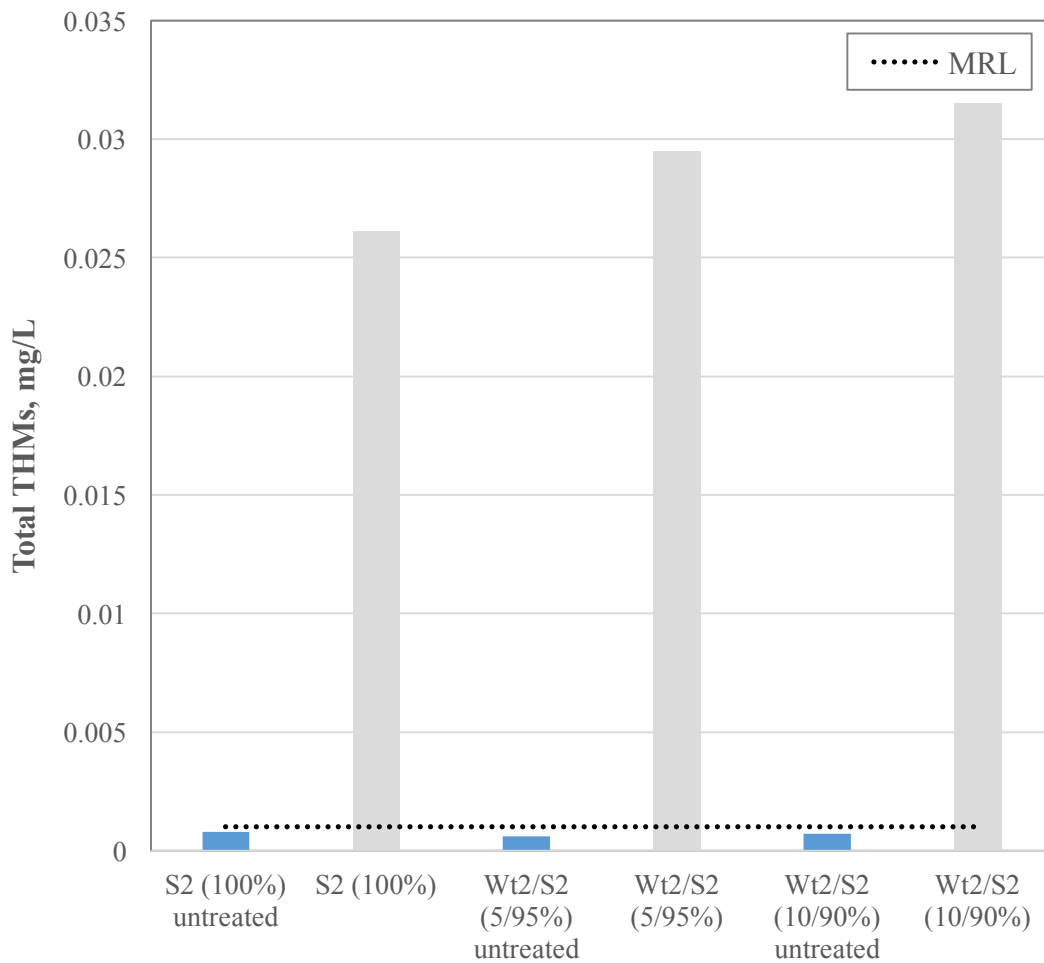
Figure 8. TTHM concentrations in treated and untreated tertiary-treated waters and non-blended raw surface water from Utility 2

Results obtained from measuring THM concentrations after treatment (Test B') are shown in Figure 9 for samples analyzed from Utility 1 and 2, and in Figure 10 for Utility 3 and 4

samples. Compared to THM-FP tests, THM concentrations measured from Test B' were lower due to the lower applied disinfectant dose, which was intended to sustain a residual not maximize THM formation. Nonetheless, similar trends were observed between Test B and B' in the formation of THMs as the percentage of recycled water increased, with the exception of the RO-treated blends from Utility 1. In Figure 9, THM concentrations increased irrespective of treatment as the ratio of reuse water increased. However, increasing the ratio of ozone-biofiltered water in Utility 2 had more of a negative impact on THM yields compared to ozone-biofiltered waters from Utility 1. Therefore, depending on the quality of the source water, caution should be practiced in blending high ratios of ozone-biofiltered waters. The surface water samples from Utility 1 were collected at different dates, and blended with the respective recycled water effluents, resulting in a variable quality of effluent. Hence, the batch used to produce the 10% ozone-biofiltered blend generated fewer THMs than expected when observing THM concentrations measured in the 10% and 50% RO-treated blends.
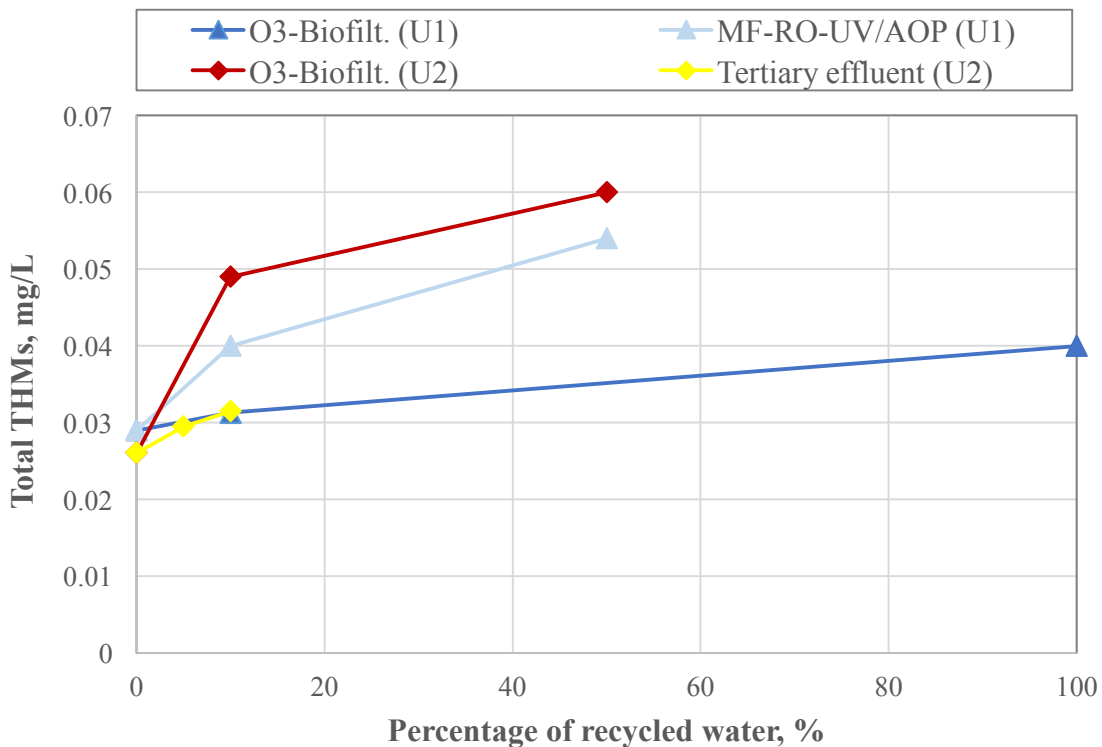
**Figure 10. TTHMs measured as the percentage of recycled water increases for Utility 3
(U3) groundwater samples, and Utility 4 (U4) groundwater and treated surface water
samples**

In Utility 3, when the UV-RO-UV/AOP blend ratio increased THM concentrations

decreased, indicating a similarity with THM-FP tests which exhibited the same behavior.

However, the opposite effect occurred when the percentage of pasteurized-UV-RO-UV/AOP

water increased from 10% to 50% which resulted in a spike of THMs from 0.021 to 0.035 mg/L.

For Utility 4, increasing the percentage of MF-RO-UV/AOP recycled water had a minimal effect

on THM formation in both scenarios. Compared to the non-blended samples [(G$_4$ (100%) and Sf$_4$

(100%)], the THM concentrations remained largely unchanged in the reclaimed samples [(Wm$_4$

(100%) and Wab$_4$ (100%)), which contained significantly low TTHM concentrations, 0.0022 and

0.0005 mg/L, respectively.

In Figure 11, the influent (Test C) and effluent (Test D) test waters collected before and after pipe rig incubation were analyzed for THMs. The 10% and 50% Wb_2/S_2 influent blends from Utility 2 contained significantly higher THM concentrations compared to all other test waters, indicating that when chlorine was used as a disinfectant the THM formation increased. The TTHM concentration further increased in the 10% and 50% ozone-biofiltration effluents after 48-hour contact time with chlorine, resulting in concentrations above regulatory drinking water limits, 0.105 and 0.104 mg/L, respectively.

Figure 11. Influent and effluent TTHM and TOC concentrations for all Utilities. Error bars indicate +/- 1 standard deviation.

The relatively high pH levels (~8) measured for Utility 2 influent and effluent blends may have contributed to the elevated THM yields. The average pH values measured at the influent and effluent approached or exceeded 8, especially for the 5% and 10% tertiary-treated blends which had average influent pH values above 8 (Figure 12).
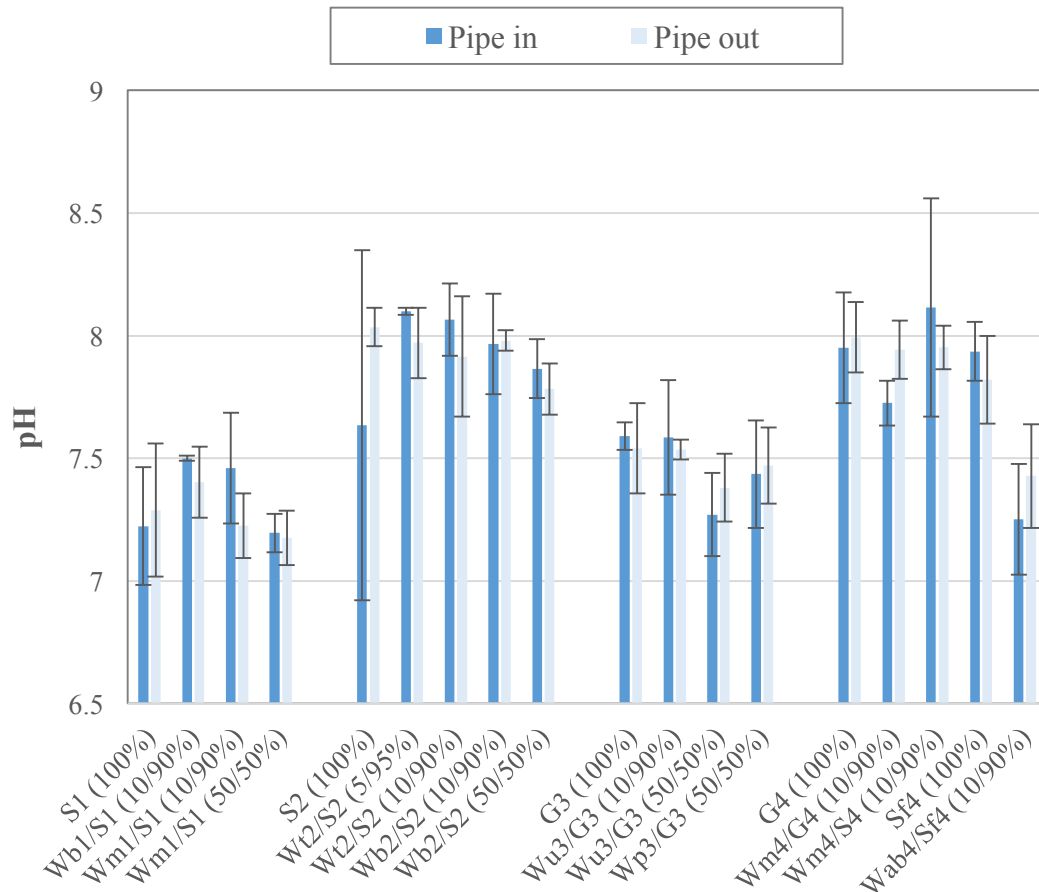
Figure 12. Average influent and effluent pH values for all Utilities. Error bars indicate +/- 1 standard deviation.

Doederer et al. (2014) demonstrated that chlorination of high pH waters (>8), resulted in the formation of more THMs compared to analogous waters at pH 5.5. High pH conditions were likely to favor THM formation because, as other DBPs hydrolize, they become readily available

as decomposition products and act as THM precursors. Contrarily, chloramines tend to produce more THMs at low pH conditions due to the degradation of chloramines to free chlorine.

For Utility 1, the higher TOC levels measured in the 10% and 50% Wm_1/ S_1 blends compared to the S_1 and 10% Wb_1/ S_1 waters contributed to the higher levels of TTHMs that formed in the former RO-treated blends. Thus, TOC was a suitable indicator used to predict the THM formation potential. As the RO-treated blend ratio from Utility 1 increased from 10% to 50%, TOC levels decreased due to the rejection of TOC from the RO membranes. But, contrary to expected, even though the TOC concentration was lower in the 50% RO-treated blend, the average THM concentration was higher in the 50% Wm_1/ S_1 blend compared to the 10% Wm_1/ S_1 blend due to the higher chloramine dose applied to the 50% Wm_1/ S_1 blend. Although, the TOC levels were higher in the 10% RO-treated blend, the 50% RO-treated blend was potentially dosed with a higher chloramine concentration. Within Utility 1, the more elevated THM levels observed in the RO-treated blends compared to test waters from scenario I (S_1 and 10% Wb_1/ S_1) were mostly a result of the higher TOC levels measured in the RO-treated blends (specifically S_1). In this case, blending using RO-treated waters had a reduced effect on attenuating TOC concentrations compared to the ozone-biofiltered blend due to quality of raw surface water. Thus, although RO membranes have TOC rejection rates that are typically >85%, adequate TOC removal depends on the influent TOC concentration entering the RO membrane.

Effluent TTHM concentrations from Utility 3 did not exceed the MCL, but the non-blended groundwater sample (G_3) contained the highest THM concentration when compared to THMs measured in the RO-treated blends. The non-blended groundwater sample was not expected to yield high THM concentrations considering the TOC concentration was similar to the TOC values of the other samples within Utility 3.

Disinfectant type and residual concentration also have an effect on THM yields. In chlorinated systems, longer contact times between free chlorine and organic precursors tend to increase the formation of THMs in distribution systems. In some cases, the opposite effect can occur for HAAs, which can degrade over time when low disinfectant residuals are measured (Tung & Xie, 2009). For utilities 1, 3 and 4, chloramines were used as secondary disinfectants, resulting in THM concentrations below the regulatory MCL. For Utility 2, THM thresholds were higher compared to concentrations measured in the other Utilities, especially in the 10% and 50% ozone-biofiltered blend effluents, which exceeded the 0.08 mg/L regulatory limit due to the use of chlorine as a secondary disinfectant. Despite the relatively similar TOC levels in the surface water-impacted waters from Utility 1 and 2, THM levels in Utility 2 were higher. Therefore, the implementation of chloramines to replace chlorine in disinfection practices can help mitigate THM and HAA concentrations downstream in distribution systems as the finished water becomes available to consumers. However, using chloramines can have its disadvantages especially because chloramines can break down over time to ammonia, which can lead to nitrification in distribution systems.

In Figure 13, the influent and effluent total chlorine and ATP concentrations were measured to understand the importance of maintaining a chlorine residual, in the absence of which biological activity can increase. The 10% RO-treated blend from Utility 1 had the highest effluent ATP concentration (101.92 pg/mL) due to the low chlorine residual measured in the effluent (0.03 mg/L). Compared to Utilities 3 and 4, the lower target disinfectant doses applied to Utility 1 and 2 samples translated into lower total chlorine concentrations measured in the influent and effluent samples. Although, lower chloramine and chlorine target doses were applied for Utility 1 and 2 samples, more THMs formed in these samples compared to samples

from the other Utilities (with the exclusion of the unblended groundwater sample from Utility 3). The higher THM concentrations measured in Utility 1 and 2 can be a result of the higher reactivity of the surface water organic precursors with the disinfectant.
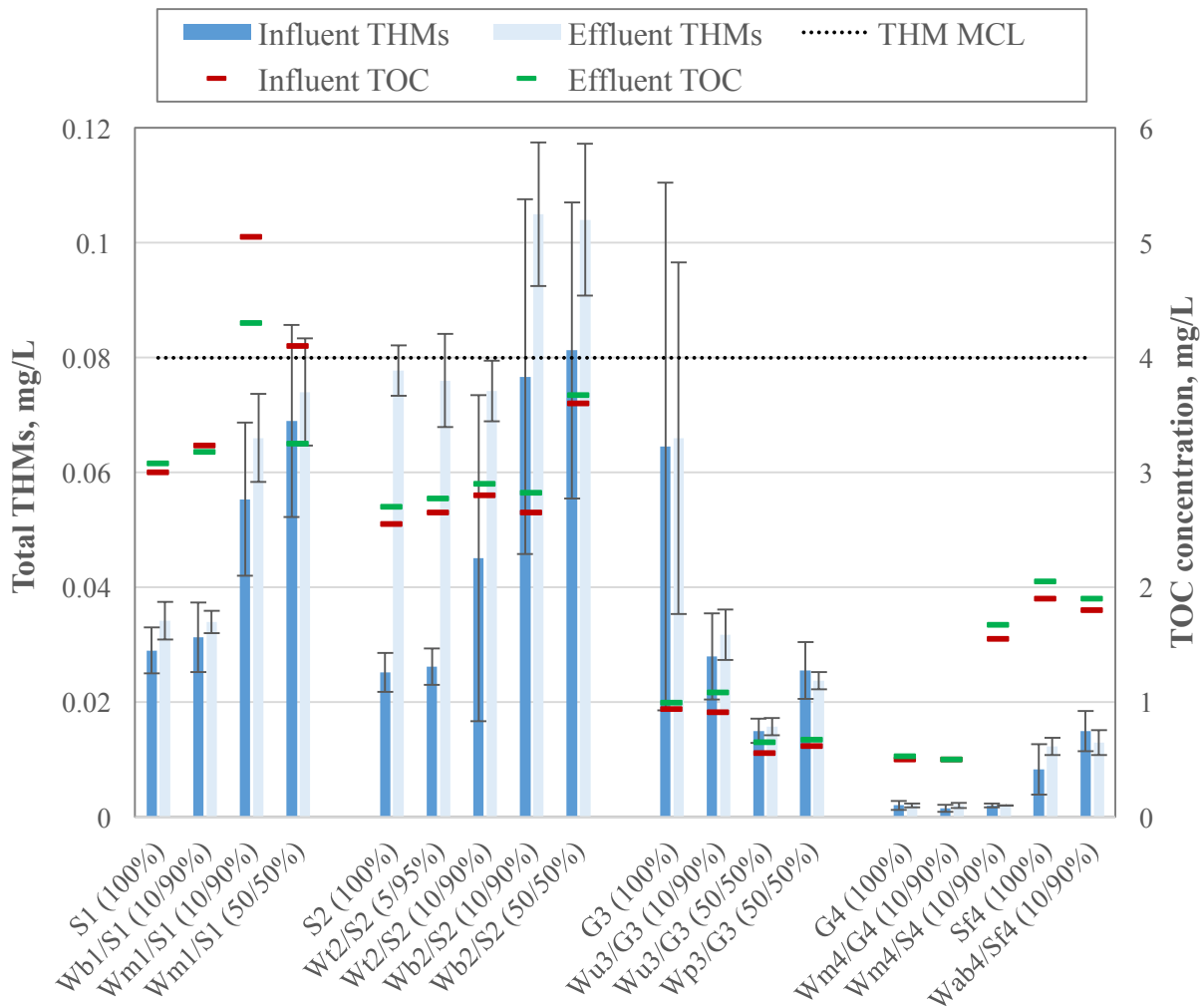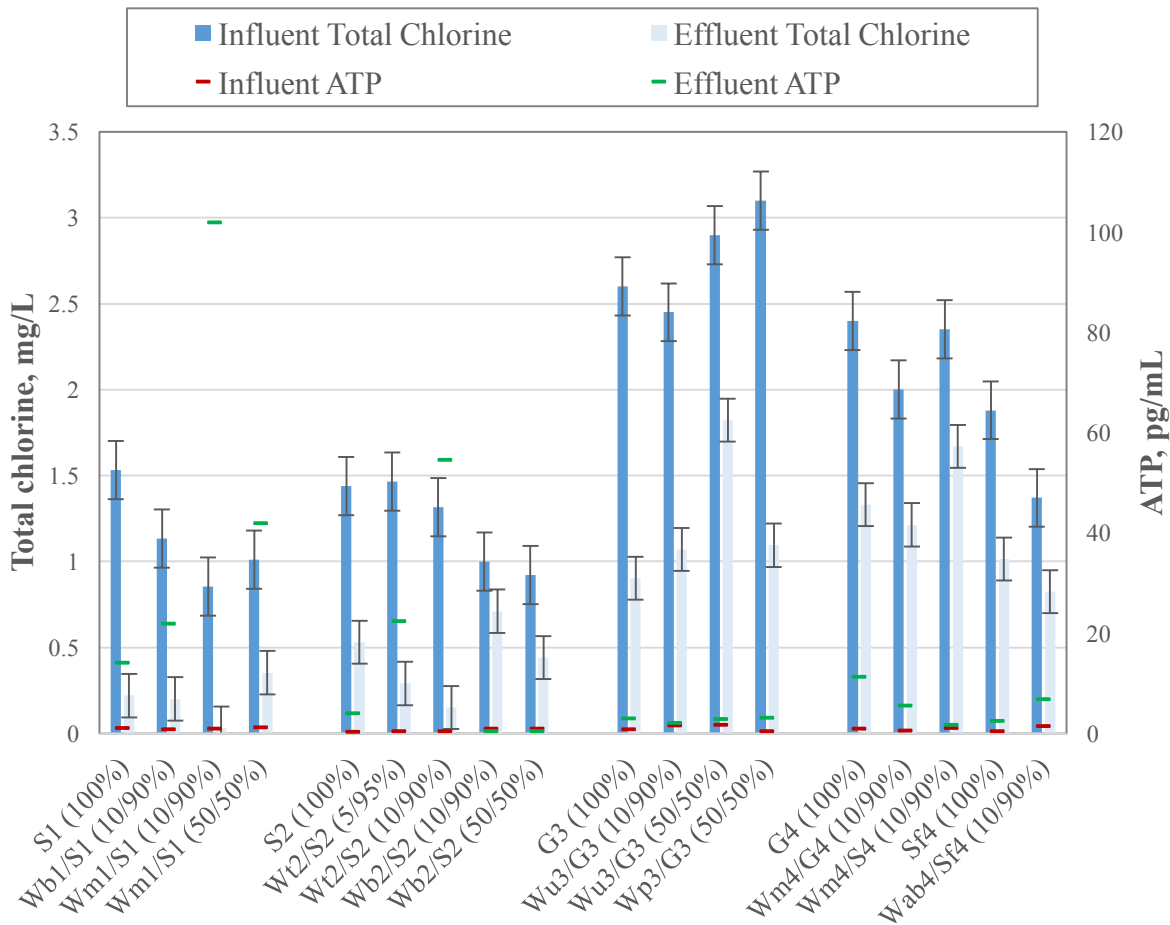

Figure 13. Influent and effluent total chlorine and ATP concentrations for all Utilities. Error bars indicate +/- 1 standard deviation.

In Figure 14, ammonia concentrations were higher in samples from Utility 1, 3 and 4, for which monochloramines and pre-formed chloramines were used as secondary disinfectants. Overall, ammonia concentrations were conservative when comparing influent and effluent concentrations across all utilities. Increases in effluent ammonia levels were apparent for Utility 3 samples, especially for the 50% RO-treated blend (50% Wm_3/ G_3) which contained 1.17 mg/L

NH$_3$-N in the influent and 1.5 mg/L NH$_3$-N in the effluent. The increase in effluent ammonia

concentration can be attributed to the higher amount of chloramines breaking down, which were

used to satisfy the demand of the higher blend ratio of RO-treated water. Moreover, the influent

ammonia concentration for the 50% Wm$_3$/G$_3$ blend was higher compared to the other samples

due to a higher potential breakthrough of ammonia from the RO filter membranes. However, the

high influent ammonia concentration could have also been a result of an overestimation of the

chloramine dose for the higher recycled water blend ratio.
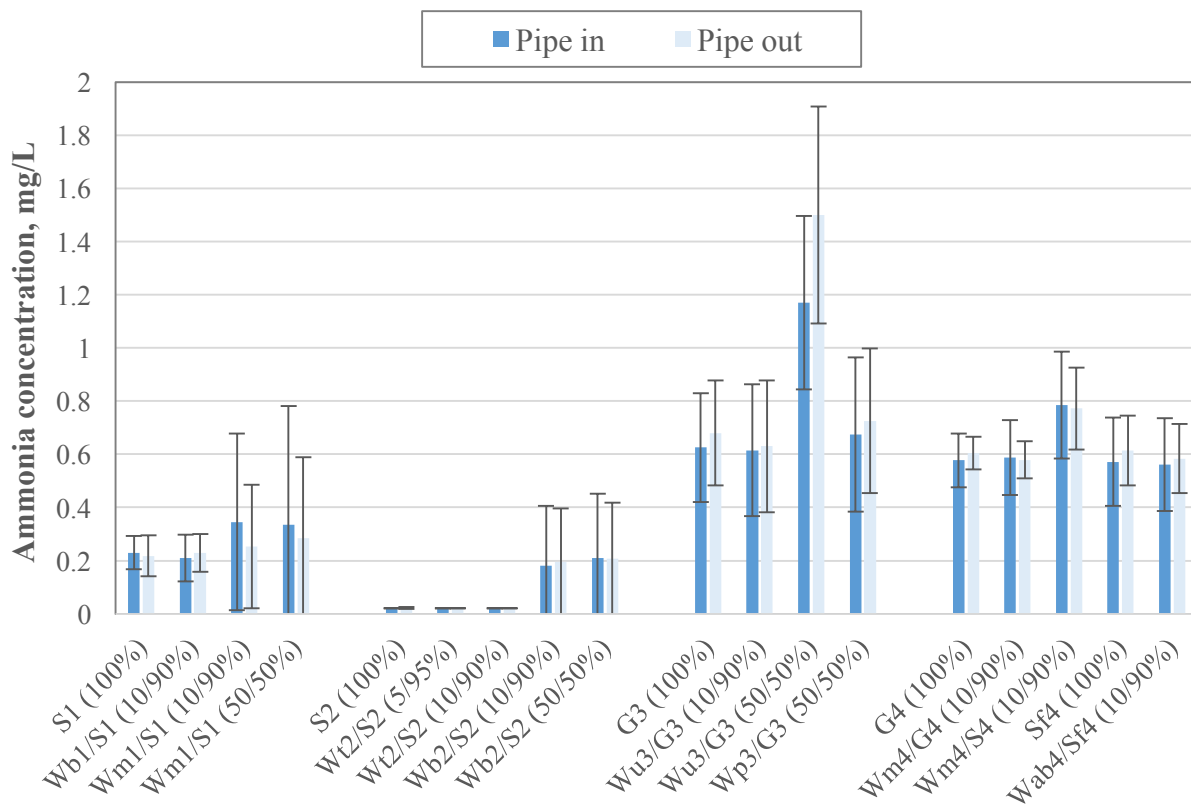
Figure 14. Average influent and effluent ammonia (NH$_3$–N) concentrations for Utilities 1, 2, 3 and 4. Note Utilities 1, 3 and 4 have adopted chloramination in the disinfection protocol. Error bars indicate +/- 1 standard deviation.

Influent and effluent nitrate concentrations were measured, considering that nitrate in

drinking water is regulated by the USEPA at an established MCL of 10mg/L NO$_3$-N. The presence

of elevated nitrate concentrations in finished waters can be a result of nitrification in distribution systems, especially in chloraminated systems where nitrifying bacteria are responsible for the oxidation of ammonia to nitrate. Nitrification negatively impacts drinking water quality because it depletes the chloramine residual, promotes corrosion issues in pipes, and decreases pH and DO concentrations (Wang et al. 2014).

For all utilities, results in Figure 15 show that the average nitrate concentrations between the influent and effluent remained largely unchanged. Although, none of the samples exceeded the 10 mg/L regulatory limit, the 50% ozone-biofiltered blend from Utility 2 contained the highest amount of nitrate compared to all other samples. The 10% Wb_1/S_1 blend from Utility 1 had similar effluent nitrate concentrations to the 10% Wb_2/S_2 blended sample from Utility 2, 2.0 mg/L and 1.5 mg/L NO_3-N. Both samples had lower nitrate concentrations than the 50% Wb_2/S_2 bio-filtered sample, indicating that blending high ratios of ozone-biofiltered water can have an adverse effect on the quality of the finished water. The treated goundwater sample and the 10% RO-treated blend (G_4 and 10% Wm_4/ G_4) from Utility 4 also contained elevated levels of nitrate. In this case, blending decreased the nitrate concentration in the 10% RO-treated blend, showing that nitrate should be monitored in source waters just as much as in recycled waters. When comparing the treated surface water sample and the 10% RO-treated blend (Sf_4 and 10% Wab_4/ Sf_4), the nitrate concentrations increased when the RO recycled water ratio increased. Assuming the RO recycled water blend ratio increased above 10%, nitrate concentrations would have potentially peaked, and exceeded the 10 mg/L MCL.
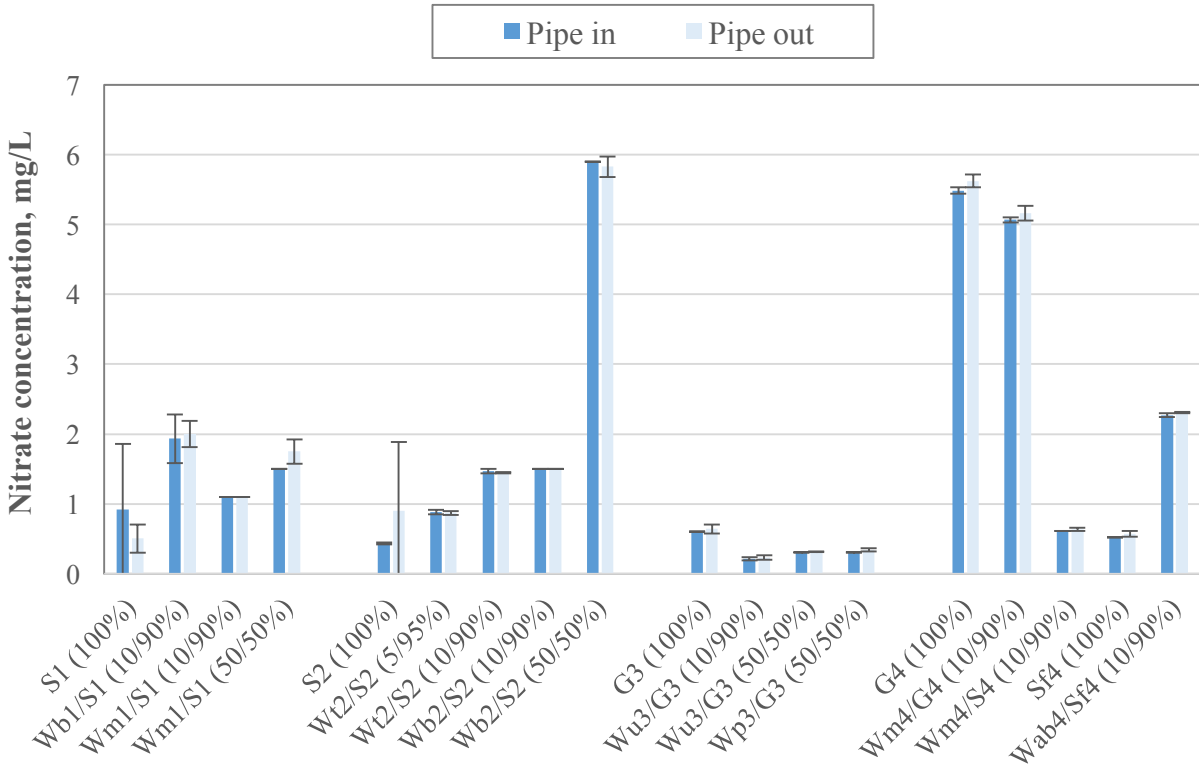
Figure 15. Average influent and effluent nitrate (NO$_3$-N) concentrations for Utilities 1, 2, 3 and 4. Error bars indicate +/- 1 standard deviation.

Other environmental factors like temperature may impact THM formation in distribution systems, especially in regions affected by seasonal variability. However, the test waters for this study were not subjected to temperature changes since the influent test waters were brought to room temperature before sampling, and effluent test waters from the pipe rigs were incubated at room temperature. Metal ions are also known to have a catalytic effect on DBP formation in chlorinated systems depending on the source water and characteristics of the NOM precursors (Zhao et al., 2016). Spikes in lead and copper concentrations in the effluent may have minimally contributed to the increase in DBP concentrations, however no control pipe rigs were tested in parallel (in the absence of brass coupons) to verify the potential effects of metals on THM formation.

3.4   Statistical Analysis

Correlation analyses of two water quality parameters were performed applying the Student's *t*-test method. Output variables were generated using linear regression in the StatPlus (AnalystSoft Inc. for Mac OS®, Version v6) statistical analysis program. A Model type I regression was used to estimate the dependence of one variable on another, where the random variable Y was the dependant variable and the fixed variable X was the independent variable. The correlation coefficient, r was employed with n-2 degrees of freedom to determine the calculated *t* value, which was compared to a tabulated two-tailed *t* value. Significant correlation of the two parameters was verified when the calculated *t*-value was greater than the tabular *t*-value at a 95% confidence level.

For effluent TTHM and HAA concentrations, significant correlation was observed with effluent TOC concentrations, indicating that TOC was an optimal surrogate that can be used for estimating disinfection by-product yields. Effluent TTHM and HAA concentrations were also compared to influent UV_{254} and SUVA values, for which significant correlations were confirmed more significantly for influent SUVA. When influent SUVA was the dependent variable, a stronger correlation with DBP formation was observed ($p<0.01$) compared to influent UV_{254} ($p<0.05$). Typically, waters with high SUVA values contain a higher fraction of total organics that absorb light at a 254 nm wavelength. Elevated SUVA values usually indicate that there are potentially higher portions of humic and/or aromatic compounds that have a higher affinity to react with oxidants to form DBPs. However, results showed the opposite trend, where higher DBP concentrations correlated to lower influent SUVA values. Hence, an inverse relationship was observed in the correlation between effluent THM and HAA concentrations and influent

SUVA values. Table 6 summerizes which pair of parameters had significant correlation with respect to Student's *t*-test confidence levels.

Table 6. Regression analyses for various parameters across all utilities.

Parameters		Figure number	Correlation coefficient, r and coefficient of determination r^2		Calculated *t* test for significance of correlation coefficient, r	Two-tailed t tabulated for 16 degrees of freedom	
						2.12	2.92
Independent	Dependent		r	r^2		p<0.05	p<0.01
Effl. TOC	Effl. TTHMs	12	0.676	0.457	3.67		X
Effl. TOC	Effl. HAAs	13	0.692	0.479	3.84		X
Effl. TTHMs	Infl. UV_{254}	14	0.514	0.264	2.39	X	
Effl. HAAs	Infl. UV_{254}	15	0.563	0.317	2.72	X	
Effl. TTHMs	Infl. SUVA	16	0.652	0.452	3.44		X
Effl. HAAs	Infl. SUVA	17	0.681	0.464	3.72		X

Once significance of the correlations was established, 95% upper and lower confidence limits were set for the regression line of each pair of parameters to generate biconcave confidence limits using equations from Sokal & Rohlf (1981).

For effluent THM and TOC concentrations, the scatter distribution ($R^2 = 0.457$) of sample means showed that half of Utility 1 values were within the confidence limits while nearly all of Utility 2 values were outside the upper range, with the exclusion of the 10% tertiary-treated blend (Figure 16). Although, both Utility 1 and 2 have similar effluent TOC concentrations, the disinfectant type was causing the effluent THM concentrations to be higher for Utility 2 test waters. The use of chlorine in Utility 2's disinfection protocol was potentially triggering THM levels to spike above the upper confidence limits, which was established from determining a fitted regression line.

Figure 16. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent TTHMs vs. effluent TOC

Chloramines were used to disinfect Utility 1 samples, illustrating the binary relationship with Utility 2 samples which displayed similar TOC values to Utility 1, but higher THM concentrations were measured in the effluent due to the use of chlorine for disinfection. Hence, the prevalent occurrence of THMs in chlorinated systems was used to justify higher THM yields in Utility 2 samples. Groundwater blends from Utility 3 were within the confidence limits, however the unblended groundwater was substantially outside the expected range. For Utility 4, surface water blends clustered away from the groundwater samples, suggesting a potential impact of source water quality on THM formation. Based on the effluent TOC values of the surface water blends, the 10% Wm_4/S_4 sample was expected to produce THM concentrations between 0.02 – 0.04 mg/L,

while the Sf_4 and 10% Wab_4/ Sf_4 samples were expected to produce THMs in the 0.02–0.05 mg/L range. This behavior can be explained by the smaller portion of reactive organics present in the surface water blends that produced less than expected THM yields. In Utility 4, the use of chloramines also may have mitigated the overall effluent THM concentrations in both the surface water and groundwater samples.

Figure 17. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent HAAs vs. effluent TOC

In Figure 17, the higher coefficient of determination (R^2 = 0.479) extrapolated from the linear regression analysis of effluent HAAs and TOC concentrations, indicated an improved correlation of the two parameters compared to the regression between effluent THMs and TOC. Nonetheless, effluent HAAs and TOC concentrations exhibited similar trends in the clustering of

sample means with effluent THM and TOC. However, none of the effluent HAA concentrations exceeded the 0.06 mg/L regulatory threshold, indicating that during the 48-hour incubation period a fraction of HAAs may have degraded over time.

Figure 18. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent THMs vs. influent UV254

In Figure 18, weaker correlation was observed on the regression of effluent THM and influent UV_{254} concentrations compared to the previous examples. Based on the scatter distribution ($R^2 = 0.265$), half of the values placed inside the bounds of the confidence limits, and the other half laid outside the confidence limits. The sample means, positioned from plotting effluent HAA and influent UV_{254} concentrations, were better fitted to the predicted regression line ($R^2 = 0.317$) as shown in Figure 19.

Figure 19. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent HAAs and influent UV254

SUVA values, used to determine significance of correlation between the reactive species of DOC and DBP yield, were calculated by taking the ratio of influent UV_{254} to influent DOC concentration and multiplying by 100. Influent DOC concentrations (Test C) were obtained by filtering the samples through a 0.45 μm pore size filter.

Based on the scatter plot distribution in Figure 20, a negative slope was generated from the regression analysis of effluent THMs and influent SUVA concentrations. Most of Utility 1 and 2 sample means clustered on the left side of the plot, whereas Utility 3 and 4 sample means arranged across the right side, revealing a pattern in the grouping of the sample means similar to the grouping observed in the other regression scenarios. Although the arrangement of the sample

means appeared to shift from right to left, the positioning of the sample means remained constant in relation to one another. In the regression analysis of effluent HAAs and influent SUVA, the coefficient of determination ($R^2 = 0.464$) was closer to 1 when compared to the R^2 value of effluent THMs and influent SUVA concentrations ($R^2 = 0.397$).
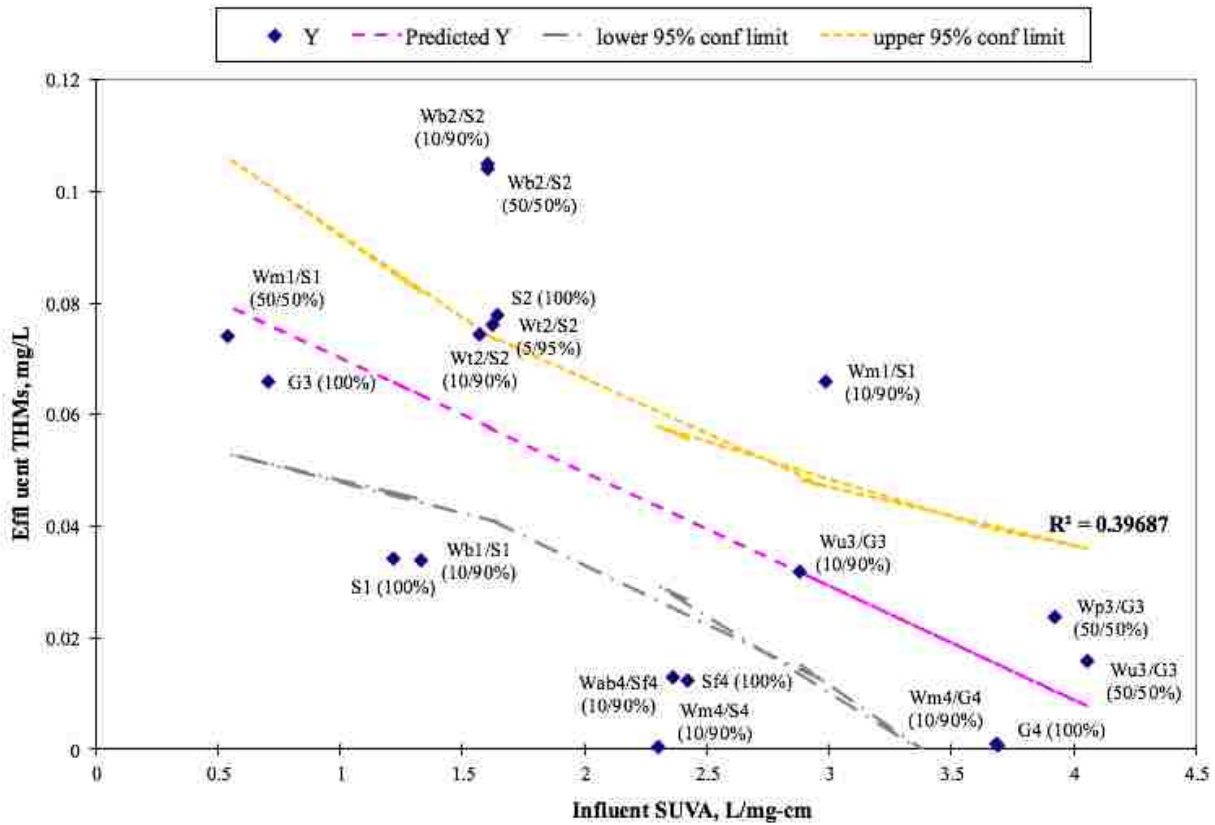
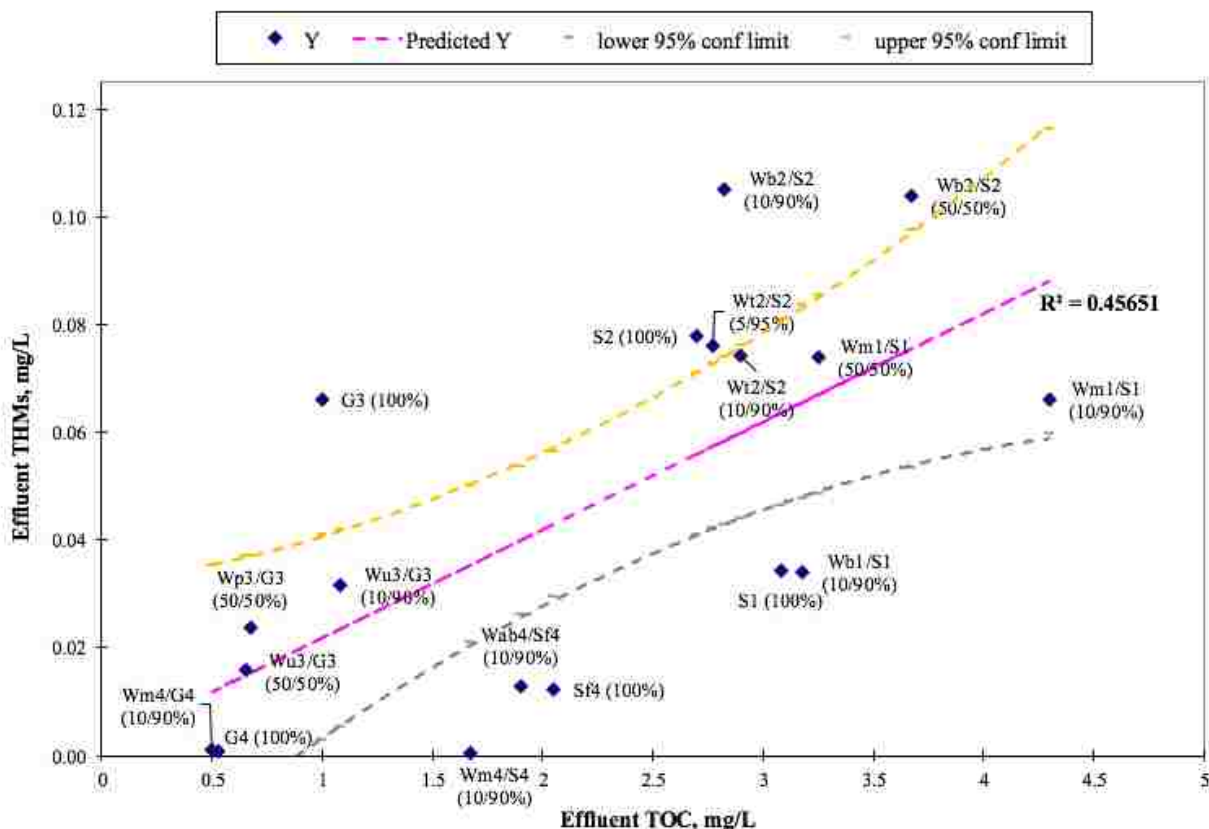**Figure 20. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent THMs vs. influent SUVA**

Similarities on regression between effluent THMs-influent SUVA and effluent HAAs-influent SUVA were observed comparing the distribution of sample means (Figures 20 and 21). Although, there appears to be significant correlation between influent SUVA and effluent DBP concentrations, in both cases nearly half of the sample means lay outside the confidence limits. This behavior likely implied that the influence of other sources of variation can affect the formation

of DBP. Identifying the chemical structure and molecular weight of the organic compounds in the blended waters may help further improve the interpretation of the results. However, varying one parameter to observe the effects of THM concentrations is not always a simple cause and effect rationale, by which the change in concentration of one variable causes the change in concentration of the other. Often times, covariation of multiple variables may occur coincidentally or due to the variation of a common source, resulting in a faulty correlation. Hence, regression analysis may have limitations for predicting DBP yields. Nonetheless, it is a reliable tool that can immediately recognize causal trends and patterns, and make associations to improve drinking water quality.
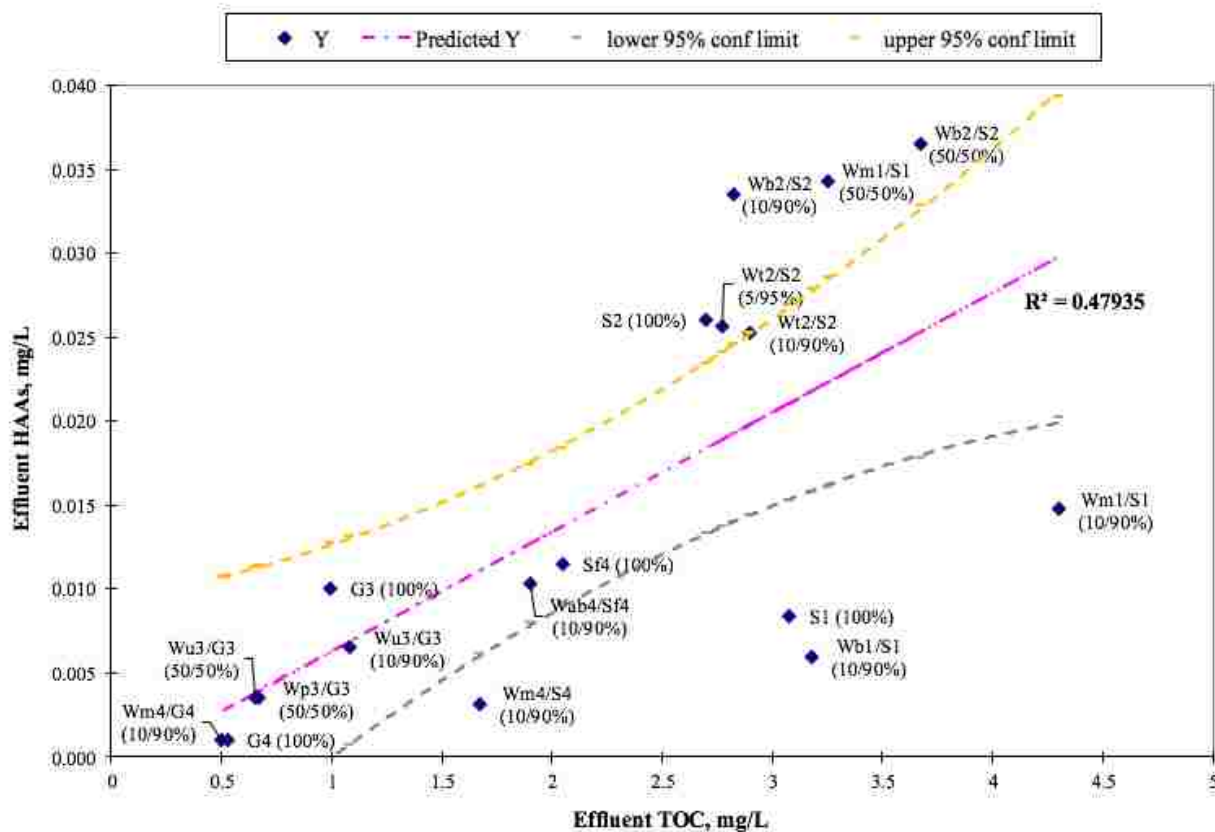

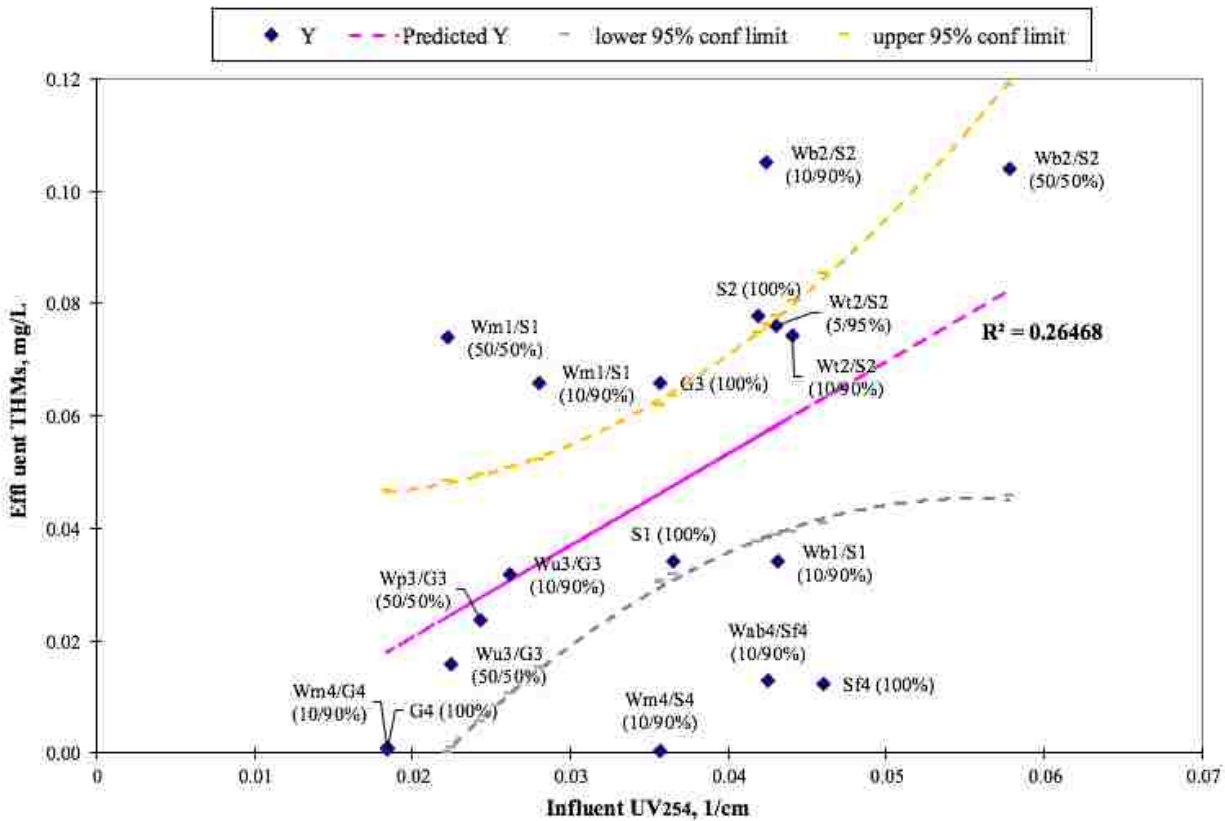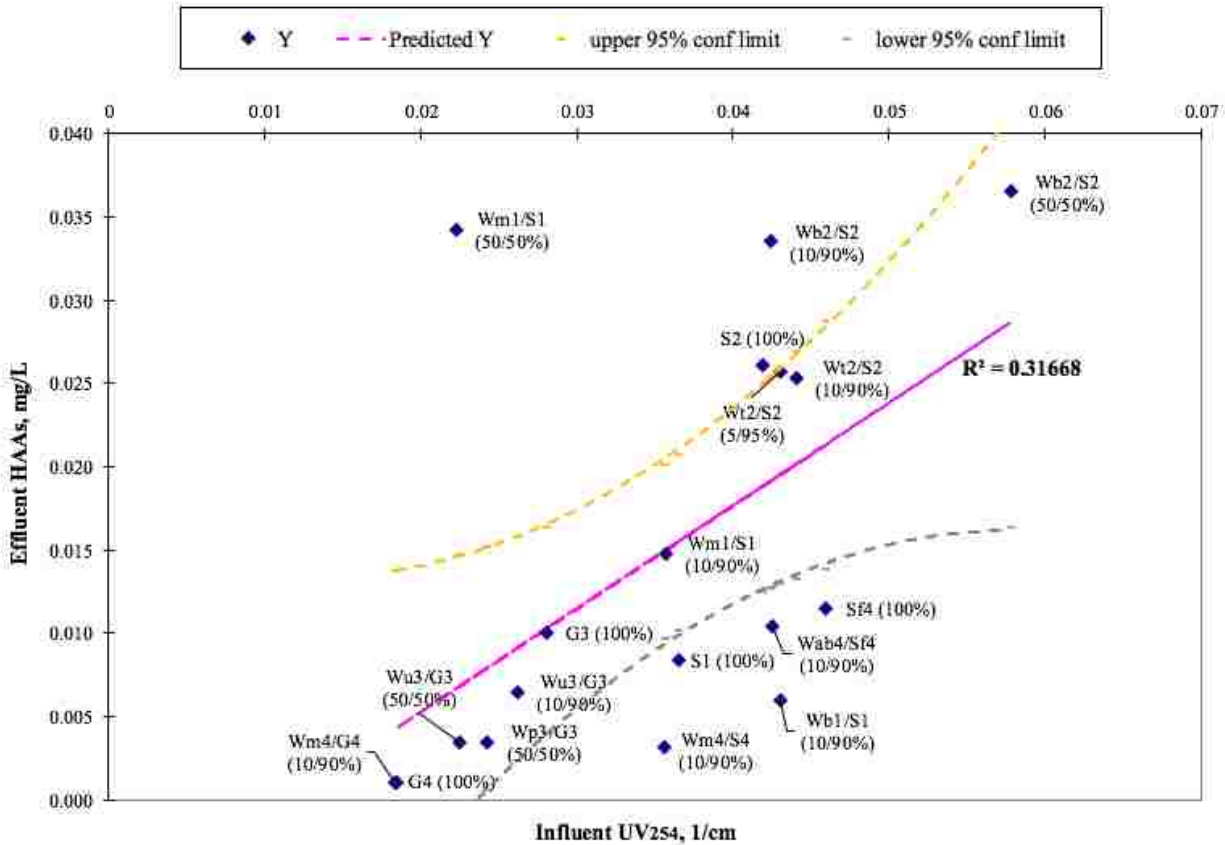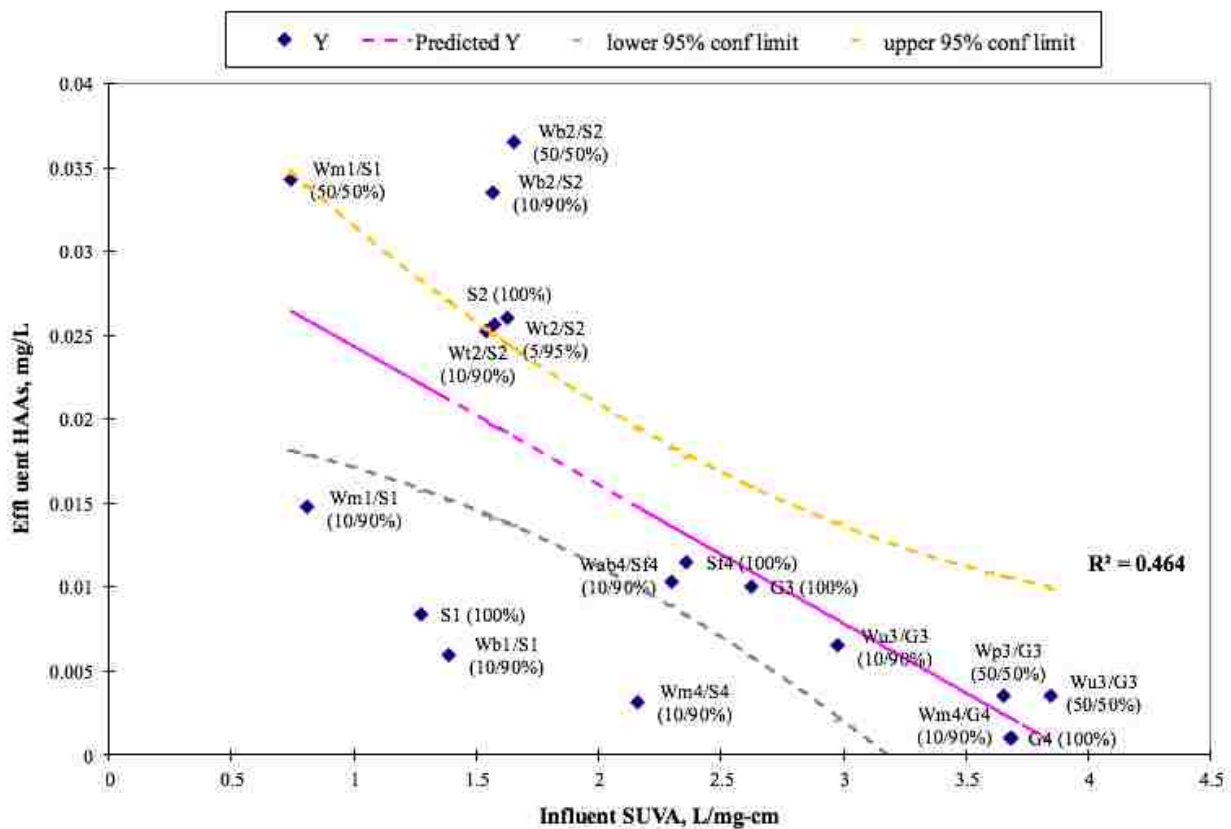**Figure 21. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent HAAs vs. influent SUVA**

3.5   Discussion

Ozone-biofiltered blends from Utility 2 contained effluent THM concentrations that exceeded the 0.08 mg/L MCL. Consequently, the DOC in ozone-biofiltered waters were suspected to contain transformation products and soluble microbial products that increased the number of DBP precursors, and fostered substrate availability for biological activity. As a strategy to improve the removal of oxidized organics produced from the exposure to ozone in the ozone-biofiltered blends from Utility 2, additional treatment of the recycled water prior to blending can be performed by adding a treatment barrier after O_3-Biofiltration such as Microfiltration. Another alternative to mitigate THM formation would be to switch secondary disinfectant. Instead of using chlorine, Utility 2 may want to start applying chloramines, while still monitoring for nitrogenous DBPs that may potentially form. Moreover, chloramines are more prone to penetrate into the deeper layers of the biofilm than chlorine, resulting in detachment of biomass into the finished water.

Better correlation was observed between effluent DBPs and influent SUVA than effluent DBPs and influent UV_{254}, indicating that DBP formation more reliably depended on the aromaticity of the dissolved organic matter rather than on the UV absorbance at 254 nm of the dissolved organics. Usually, higher SUVA values indicate a higher reactivity to form chlorinated THMs and HAAs because of the aromatic rings that have been shown to function as major precursors (Li et al., 2000). However, results generated from comparing influent SUVA values and effluent DBP concentrations showed the opposite effect, where THM and HAA yields increased as influent SUVA values decreased (Table 7). In order to further understand the reaction rates of the precursors in the different blends, it would be useful to characterize the organics. Based on the molecular weight and hydrophobicity of the drinking water sources and

the reclaimed waters, the nature of the DOC can be used to predict treatment efficiency, and consequently affinity to form THMs. For example, DOC with low SUVA values (< 2 L/mg-C *m) prevalently have low molecular weight, non-humic and hydrophilic compounds that can hamper DOC removal during coagulation (Hu et al., 2016).

Table 7. Mean effluent THM concentrations, and mean influent DOC and SUVA values across all utilities

Utility	Test waters	Mean Infl. DOC (mg/L)	Mean Infl. SUVA (L/mg*cm)	Mean Effl. THMs (mg/L)
1	S1	2.9	1.3	0.0342
	Wb1/ S1 (10/90%)	3.1	1.4	0.0340
	Wm1/ S1 (10/90%)	4.4	0.8	0.0660
	Wm1/ S1 (50/50%)	3.0	0.7	0.0740
2	S2	2.6	1.6	0.0778
	Wt2/ S2 (5/95%)	2.7	1.6	0.0760
	Wt2/ S2 (10/90%)	2.9	1.5	0.0742
	Wb2/ S2 (10/90%)	2.7	1.6	0.1050
	Wb2/ S2 (50/50%)	3.5	1.7	0.1040
3	G3	1.1	2.6	0.0660
	Wu3/ G3 (10/90%)	0.9	3.0	0.0318
	Wu3/ G3 (50/50%)	0.6	3.8	0.0158
	Wp3/ G3 (50/50%)	0.7	3.7	0.0238
4	G4	0.5	3.7	0.0008
	Wm4/ G4 (10/90%)	0.5	3.7	0.0010
	Wm4/ S4 (10/90%)	1.7	2.2	0.0005
	Sf4	2.0	2.4	0.0123
	Wab4/ Sf4 (10/90%)	1.9	2.3	0.0130

3.6   Summary

The objective of this part of the research was to evaluate the effects of blending recycled waters with groundwater and surface water sources on the formation of Trihalomethanes (THMs). THMs and other water quality parameters were tested at different sampling points to determine optimal blend ratios as water age increased, and identify correlation in sample mean concentrations using statistical methods.

From the THM-FP tests, DOC concentrations were shown to increase as THM concentrations increased for all blended and non-blended waters. Overall, surface water-impacted blends from Utility 1, 2 and 4 had higher DOC and THM concentrations compared to groundwater samples, as a result of the natural filtration that occurs in the overlying soil that improves water quality of groundwater basins. Recycled water blends treated from MF(UF)-RO-UV/AOP treatment trains contained a higher fraction of brominated THMs, which could be due to the potential breakthrough of bromide from the RO membranes. Although, RO effectively rejects bromide, reuse water influents typically have a higher bromide concentration compared to natural source waters. Surface water sources in the United States usually contain low bromide concentrations ranging between 0.014-0.2 mg/L (USEPA, 1996), but recycled waters may contain more brominated DBPs produced from the discharge of bromide from industrial sites. THM concentrations in groundwater blends were low, however the non-blended groundwater effluent from Utility 3 had a higher THM mean concentration compared to all other groundwater blends, and to the non-blended groundwater effluent from Utility 4. The higher fraction of Bromoform and Chlorodibromomethane species in the blended and non-blended groundwater samples may have been the result of bromide derived from bromine-containing minerals, which are more prevalent in groundwater sources compared to surface water sources.

With some exceptions, results from Test B mostly agreed with observed trends from Test B2. Contrary to THM-FP tests, Test B THMs produced from Utility 2 increased in concentration as the RO recycled water ratio increased from 10% to 50%. For Utility 3, THM concentrations appeared to decrease in THM-FP tests as the Pasteurized-RO-treated blend ratio increased, however the opposite effect occurred in Test B where the THM concentration in the 50% Pasteurized-RO blend was higher than in the 10% Pasteurized-RO blend. Finally, an

incongruence between the two tests was observed in the THM concentrations measured in the treated surface water samples. In THM-FP tests, blending decreased THM yields, whereas Test B results showed invariable THM concentrations as the RO recycled water ratio increased from 0% to 100%.

Influent and effluent THM concentrations measured before (Test C) and after (Test D) pipe rig incubation were compared to the blends among each Utility based on the effects of TOC and disinfectant type. The ozone-biofiltered blends from Utility 2 contained the highest effluent THMs that exceeded regulatory limits. Even though, the ozone-biofiltered blends from Utility 2 had TOC values similar to Utility 1, more THMs formed in Utility 2 due to the use of chlorine as a disinfectant rather than chloramines. Therefore, caution must be practiced when blending ozone-biofiltered waters with source waters at TOC values close to 3. Preventative strategies may include switching to chloramines or adding a treatment barrier after ozone and biofiltration to mitigate THM formation.

Significance on regression was confirmed at a 95% confidence level for effluent THMs and HAAs on effluent TOC, influent UV_{254} and influent SUVA. The observed scatter of the concentration means consistently showed Utility 2 blends distribute along or above the upper confidence limits. Utility 4 test waters had the lowest effluent THM concentrations compared to all other Utility blends. However, an overestimation of the expected THM concentration in the surface water blends from Utility 4 was observed in relation to influent SUVA values from the clustering of the concentration means in the lower confidence limits. The low THM yield in the surface water blends from Utility 4 may have been a result of a reduced reactivity of the DOC.

CHAPTER 4. CHEMICALLY AND BIOLOGICALLY INDUCED CORROSION FROM

THE ANALYSIS OF METALS AND NUISANCE BACTERIA

4.1   Introduction

Lead and copper leaching may occur in distribution pipes due to corrosion reactions that

occur among the disinfectant, water dissolved constituents, and the metal surface. These

reactions may also cause the chlorine residual to deplete, affecting the chemical and biological

stability of the finished water. Copper release can arise in low pH conditions causing soluble

forms of Cu(II) to react with dissolved oxygen and generate soluble and precipitate corrosion

products including various forms of copper oxides. Some common copper corrosion products

that may form in distribution systems include cupric hydroxide [$Cu(OH)_2$], cuprite [Cu_2O] and

tenorite [CuO] (Zhang & Andrews, 2012).

EPA's Lead and Copper Rule (LCR) established that a 1-liter first draw sample from the

tap should be used to determine if 90% of samples collected are below the 15 ppb lead action

level and 1.3 ppm copper Maximum Contaminant Level Goal (MCLG) (U.S. EPA, 2016). These

health-based thresholds, used to monitor lead and copper, were adopted for use as acceptable

limits in this study assuming the LCR provision can help guide utilities to appropriately manage

blending reuse water in the same way conventional source waters are monitored.

4.2   Materials and Methods

The sampling method for measuring lead and copper potentially simulates water

consumption of a typical household because a 48-hour incubation period could be representative

of the time water is stored in a water storage tank or distribution system pipes for the weekend

when a family is out of town. The sampling approach was based on the same concept of sampling aged water as the LCR monitoring process, which requires at least a six-hour stagnation period before collecting tap water samples for compliance with lead and copper limits (GPO, 2011). Metals were measured (Test D) by collecting incubated effluent waters from the pipe rigs into amber glass bottles. Copper was measured following EPA method 200.8, according to which pretreatment steps included filtering a $\geq$20mL aliquot of sample water through a 0.45 μm membrane filter, and adding nitric acid for preservation purposes. Then, prior to analysis the filtrate was placed into a 50 mL centrifuge tube to which was added a predetermined volume of nitric acid to adjust the sample concentration to a 1% (v/v) nitric acid solution. The sample was mixed, and analyzed for copper using inductively coupled plasma – mass spectrometry. For lead analysis, EPA method 200.9 was adopted. Similarly, samples were filtered and acidified to a pH of less than 2, and transferred into a centrifuge tube where nitric acid was added so that the sample concentration reached 1% (v/v) of nitric acid solution. The sample was capped, mixed and analyzed using a graphite furnace atomic absorption spectrophotometer.

4.3   Results

4.3.1   Metals and corrosion potential of pipe distribution systems

Comparing changes in concentration from pre-incubation influent to post-incubation effluent, results from this phase of the study showed that lead and copper leaching occurred during pipe rig incubation. Particularly, effluent lead concentrations exceeded the EPA action level (> 0.015mg/L) for all samples from Utility 1, G_3 and Wp_3/G_3 effluents from Utility 3, and Sf_4 and Wab_4 effluents from Utility 4. Figure 22 shows average lead concentrations for all test waters before (Pipe in) and after (Pipe out) pipe rig incubation. The Method Reporting Limit is

indicated by the black dashed line labelled MRL. The lead action limit is labelled using a green dashed line to show there is a lead leaching potential in some of the incubated effluent blends.

Figure 22. **Distribution of average lead concentrations for all utilities before and after 48-hour pipe rig incubation.** Error bars show +/- 1 standard deviation.

For Utility 1, the elevated lead concentrations may have been partially caused by the low alkalinity (36 – 80 mg/L) of the finished waters, which means that potential for scale formation on the pipe walls or fittings would be minimal. Parameters such as alkalinity, pH, calcium concentration, TDS, and temperature were utilized in the next section to calculate the Langelier Saturation Index (LSI) to understand the effects of water quality on corrosion potential in finished waters. A similar distribution between effluent lead and effluent copper concentrations was observed for Utility 3, where higher effluent copper was measured in the unblended groundwater (G_3) sample and in the 50% pasteurized RO-treated (50% Wp_3/ G_3) sample compared to the other blends (Figure 23). Thus, the source water quality and/or the effects of

pasteurization as a pretreatment step to mitigate biological fouling of the UF and RO membranes may have caused effluent lead and copper concentrations to increase. For Utility 4, significant lead leaching occurred in the finished surface water (Sf_4) sample and in the 10% RO-treated (10% Wab_4/ Sf_4) industrial blend. Although, the reclaimed water source was stabilized, further treatment of the finished surface water may have reduced the occurrence of lead corrosion in the blended and unblended samples. The addition of zinc orthophosphate in the 10% Wm_4/ S_4 surface water blend maintained lead and copper concentrations low, < 0.00365 mg/L and <0.0274 mg/L, respectively. Therefore, including zinc orthophosphate in the treatment of the Sf_4 sample and 10% Wab_4/ Sf_4 blend could have potentially reduced lead leaching.
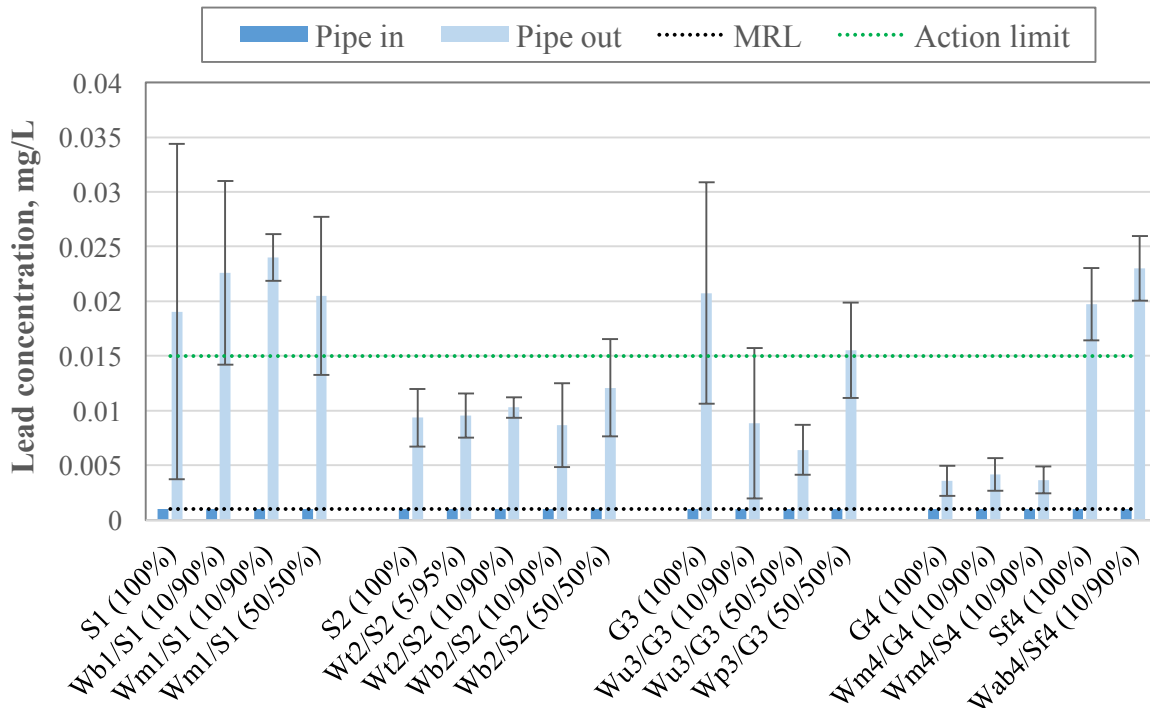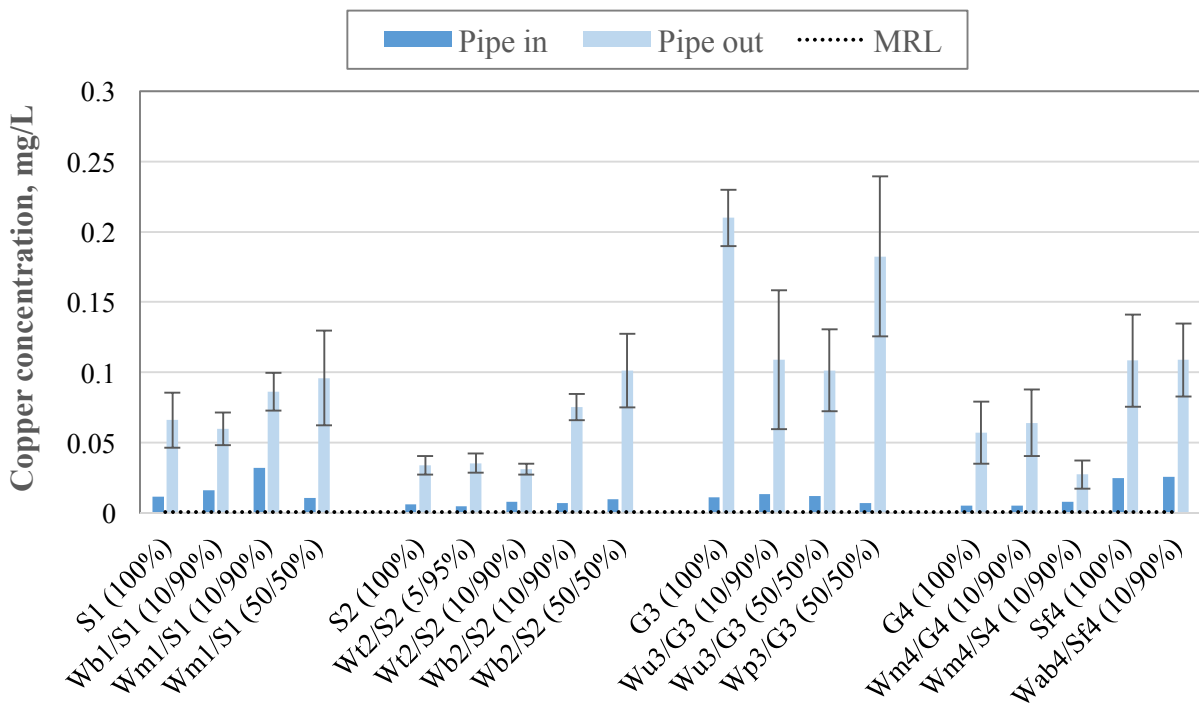

Figure 23. Distribution of average copper concentrations for all utilities before and after 48-hour pipe rig incubation. Error bars show +/- 1 standard deviation.

As shown in Figure 23, all effluent copper concentrations were far below the 1.3 mg/L copper action level. However, within Utility 3 the G_3 and 50% Wp_3/G_3 samples exceeded 0.2

mg/L and 0.15 mg/L, respectively. The elevated levels of copper in the unblended groundwater sample decreased as the RO-treated blend ratio increased from 10% Wu_3/G_3 to 50% Wu_3/G_3, suggesting that the higher alkalinity (287 mg/L) and hardness (730 mg/L as $CaCO_3$) of the unblended groundwater sample did not prevent copper corrosion as well as the Wu_3/G_3 blended samples did. The added pasteurization step of the 50% Wp_3/G_3 blend resulted in a higher effluent copper concentration compared to the 10% and 50% non-pasteurized RO-treated blends. Thus, the influence of bacteria on the formation of copper corrosion products may have contributed to the higher copper concentrations measured in the G_3 and 50% Wp_3/G_3 samples compared to the other blends.

4.3.2   Langelier Saturation Index

The test waters' corrosion potential was estimated based on the calculated LSI values shown in Table 8. The LSI values were derived using measured water quality parameters of the blended and unblended waters immediately after treatment (Test B) assuming a temperature of 21°C. Waters with LSI values greater than zero exhibited a higher scale-forming potential as a result of more divalent ions (i.e. calcium, magnesium) in solution that can form precipitates that coat and protect the surface of the brass coupons in the pipe rigs against corrosion. Although less corrosive waters inhibit the dissolution of metals from the brass fittings, excessively hard water can increase the rate of scale formation to the point that thick layers can decrease the flow efficiency in pipes and gum up filters and heat exchangers. Waters with negative LSI values are potentially corrosive, and tend to dissolve existing deposits on the surface of plumbing networks. Ideal LSI values range between -0.5 – 0.5, and are likely to reach equilibrium as the LSI value approaches 0.

Table 8. Calculated LSI values for finished waters across all utilities

Utility	Finished waters	LSI
1	F1[1]	**-0.792**
	S1	**-1.201**
	Wb1/ S1 (10/90%)	**-1.249**
	Wm1/ S1 (10/90%)	**-0.786**
	Wm1/ S1 (50/50%)	**-1.762**
2	F2[1]	-0.060
	S2	0.306
	Wt2/ S2 (5/95%)	0.127
	Wt2/ S2 (10/90%)	0.088
	Wb2/ S2 (10/90%)	0.400
	Wb2/ S2 (50/50%)	0.411
3	G3	0.617
	Wu3/ G3 (10/90%)	0.539
	Wu3/ G3 (50/50%)	-0.299
	Wp3/ G3 (10/90%)	0.642
	Wp3/ G3 (50/50%)	-0.225
4	G4	0.313
	Wm4/ G4 (10/90%)	-0.144
	Wm4/ S4 (10/90%)	**-0.614**
	Wm4	**-0.929**
	Sf4	**-1.283**
	Wab4/ Sf4 (10/90%)	**-1.227**
	Wab4	-0.144

[1]The full-scale treated unblended surface water samples
Note: **Bold LSI** values indicate high corrosion potential (<-0.5)

For Utility 1, LSI values were all negative, especially for the 50% RO-treated blend suggesting that increasing the ratio of MF-RO-UV/AOP treated water increased the corrosivity of the finished water. Lead and copper concentrations were later evaluated using statistical methods to evaluate the significance of the correlation between lead leaching and LSI. Finished waters from Utility 2 tended more towards neutral or slightly positive LSI values. Utility 3 had positive LSI values for the unblended groundwater sample and 10% RO-treated blends (pasteurized and non-pasterized), and negative LSI values for the 50% RO-treated blends (pasteurized and non-pasterized) showing that irrespective of the source water, higher ratios of RO-UV/AOP treated water increased corrosion potential of the blended water. Overall, the

hardness and alkalinity decreased when increasing the RO-UV/AOP recycled water ratio. Hence, blending treated groundwater with RO-treated water can decrease the waters' scale-forming ability. A larger fraction of monovalent and divalent cations and anions are removed by UF and RO membranes compared to O_3-biofiltration processes, often reducing pH and the scale-forming potential of the blended waters compared to O_3-biofiltration processes.

Although recycled waters from Utility 4 were stabilized prior to blending, LSI values were negative for both the 100% reclaimed water (Wm_4) in Scenario 1 and for the 100% reclaimed water (Wab_4) in Scenario 2. This indicates that the addition of calcium chloride did not reduce the corrosion potential of these blended waters for both the groudwater and surface water blends. Moreover, the addition of zinc orthoposhate in the final step of treatment for the surface water blend did not reduce the corrosion potential. Instead it decreased the LSI from -0.144 in the goundwater blend to -0.614 in the surface water blend. In the second scenario, stabilization of the reclaimed water with calcium chloride increased the LSI of the 100% reclaimed water compared to the reclaimed water from the first scenario. In the second scenario of Utility 4, the negative LSI values of the unblended finished suface water (Sf_4) and 10% RO-treated blend (Wab_4/ Sf_4) could be a result of coagulation of the surface water at the drinking water treatment plant, which may have reduced the pH, and consequently increased the corrosion potential.

4.4   Statistical Analysis

Within each water utility, the effects of treatment approach and blend ratio were statistically compared to the unblended finished waters using analysis of variance (ANOVA) and Student's *t*-test. Effluent-Influent delta values for lead and copper concentrations were used as output variables in establishing sources of variation ($\alpha = 0.05$). The blended and unblended

waters in each utility were treated as dependant variables to determine if treatment and blend ratio had an effect on metal leaching. Significant differences among means were established at the 95% confidence level for the metals shown in Tables 9 and 10. Computed F values and their associated *p* values were compared to a $p < 0.05$ threshold level for significance. The calculated F value can be compared to the tabular F value to evaluate the degree of variance in the amount of lead and copper leaching from the brass fittings.

Table 9. ANOVA for the effect of treatment blend on measured post-incubated total lead concentration – Utility 3.

Utility	Source of variation	Sum of squares	Degrees of freedom	Mean square	F value	*p* value
3	Between means (or treatments)	0.000509	3	0.000169	3.88	0.03765
	Within samples (or error)	0.000523	12	4.36×10^{-5}		
	Total	0.00103	15			

Table 10. ANOVA for the effect of treatment blend on measured post-incubated total copper concentrations – Utilities 2 and 3.

Utility	Source of variation	Sum of squares	Degrees of freedom	Mean square	F value	*p* value
2	Between means (or treatments)	0.0144	4	0.00361	20.88	0.0001
	Within samples (or error)	0.00259	15	0.00017		
	Total	0.017	19			
3	Between means (or treatments)	0.0371	3	0.0123	7.21	0.00504
	Within samples (or error)	0.0205	12	0.0017		
	Total	0.0577	15			

For lead, only for Utility 3, did treatment blend have a significant effect ($p<0.05$) on lead sample means (Table 9). Treatment blend did not have a significant effect on lead sample means for Utilities 1, 2 and 4 (Table S1).

For copper, treatment blend had a significant effect ($p < 0.05$) on sample mean copper concentrations for Utility 2 and Utility 3 (Table 10). For Utilities 1 and 4, no significant effect of treatment blend was observed for lead and copper sample means (Table S2). Fisher's Least Significant Difference (LSD) test and Duncan's Multiple Range Test (Alder & Roessler, 1964) were performed to identify which combination of treatment blend produced significant differences among the sample means for Utility 2 and 3. The LSD test is a series of pairwise comparisons of all combinations of sample means. Duncan's Multiple Range test compares differences among sample means to a series of shortest significant ranges, Rp that are a function of sample size, chosen confidence interval and sample variance. Evaluations of sample means are performed for every combination of treatment-blend condition to determine which differences were greater than the tabulated Rp values. Duncan's smallest Rp value provided more rigour to the analysis by reducing possibility of false positives for significance. However, for all significant cases, the difference in means was not lower than the LSD.

Comparisons among the difference of means showed that there was no significant difference in copper levels between the unblended surface water and the 5%, 10% tertiary treated blend from Utility 2. However, significant differences among the sample mean copper concentrations were observed when comparing unblended and tertiary treated blends with the ozone-biofiltered blends (Table 12). The clustering of the groupings suggested that advanced treatment by ozone and biofiltration may have had an effect on the amount of copper being released into water.

Table 11. Duncans Multiple Range test results for effect of treatment approach and blend on mean changes in total lead (ΔPb)

Utility	Treatment	Mean ΔPb	Grouping		
3	G_3	0.0198	A		
	50% Wp_3/50% G_3	0.0145		AB	
	10% Wu_3/90% G_3	0.0078			B
	50% Wu_3/50% G_3	0.0054			B

Table 12. Duncans Multiple Range test results for effect of treatment approach and blend on mean changes in total copper (ΔCu)

Utility	Treatment	Mean ΔCu	Grouping		
2	50% Wb_2/50% S_2	0.0914	A		
	10% Wb_2/90% S_2	0.0684		B	
	5% Wt_2/95% S_2	0.0305			C
	S_2	0.0279			C
	10% Wt_2/90% S_2	0.0233			C
3	G_3	0.1990	A		
	50% Wp_3/50% G_3	0.1757		B	
	10% Wu_3/90% G_3	0.0955			C
	50% Wu_3/50% G_3	0.0895			C

For Utility 3, significant differences among the sample mean lead concentrations were observed between the unblended groundwater samples and the 10% and 50% RO-treated waters (Table 11). For copper, significant differences among the sample concentration means were determined for the 50% pasteurized RO-blend with respect to the unblended groundwater sample and non-pasteurized blended waters. Based on the grouping arrangements, significant differences among sample mean copper concentrations were also observed for the unblended groundwater and the non-pasteurized blended waters. For Utility 4, both scenarios were evaluated independently because the recycled waters were blended with different source waters. Moreover, the recycled waters were not collected from a common source. In the first scenario, the reuse water was retrieved from a municipal wastewater source, while the reuse water from the second scenario was treated wastewater effluent retrieved from an industrial site. Although the recycled waters from Utility 4 were processed using the same treatment barriers (i.e., MF-RO-UV/AOP),

reliable comparisons cannot be made unless variations are made strictly with respect to changes in blend and treatment.

For all utilities, average lead concentrations in the effluent were compared to calculated LSI values using linear regression. Significant correlation between effluent lead and LSI were confirmed at 99% confidence ($p<0.01$), suggesting a dependance of lead corrosion on the solution's estimated LSI. Effluent total and combined chlorine concentrations were compared to effluent lead concentrations to predict the effects of disinfectant on the dissolution rate of solid lead. Table 13 shows higher correlation between the effluent total chlorine and effluent lead concentrations ($p<0.02$) compared to the effluent combined and free chlorine with effluent lead concentrations ($p<0.05$). During prolonged storage periods, elevated concentrations of total chlorine may cause shifts in redox potential and pH, which potentially promote corrosion of lead. Moreover, differences in oxidation-reduction potential for chlorine and chloramines could influence the nature of the lead corrosion products.

Table 13. Regression and correlation analysis for various parameters across all utilities

Parameters		Figure number	Correlation coefficient, r and Coefficient of determination, r^2		Calculated t test for significance of correlation coefficient, r	Two-tailed t tabulated for 16 degrees of freedom	
						2.12	2.58	2.92
Independent	**Dependent**		**r**	**r^2**		**p<0.05**	**p<0.02**	**p<0.01**
LSI	Effluent Pb	22	0.636	0.404	3.29			X
Effluent Total Cl_2	Effluent Pb	23	0.569	0.323	2.76		X	
Effluent Combined Cl_2	Effluent Pb	24	0.523	0.273	2.45	X		
Effluent Free Cl_2	ΔCu	25	0.485	0.235	2.22	X		

For the regression of LSI on effluent lead concentrations in Figure 24 with $R^2 = 0.404$, the distribution of the sample means appears to be clustering on the right side of the plot towards a condition of carbonate equilibrium. Most of the sample means were within the bounds of the 95% confidence limits with the exception of six sample means out of eighteen from Utility 1, 3 and 4. Three out of the six [G_4 (100%), 10% Wm_4/ G_4 and 10% Wm_4/ S_4] effluent lead sample means that laid outside the acceptable range for positive regression were from Utility 4, suggesting poor correlation between effluent lead and LSI was observed for those blends. The unblended groundwater sample from Utility 3 was oddly positioned in the zone above the upper 95% confidence limit. Therefore, it had an effluent lead concentration above the regulatory limit even though the LSI was slightly scale forming. Nonetheless, more than half of the effluent lead sample means exhibited significant correlation with LSI, indicating that LSI measurements can confidently help predict the stability of lead-containing pipe solder after prolonged storage periods.

Figure 24. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent lead vs. Langelier Saturation Index (LSI).

The scatter plot, generated using mean concentration values of effluent lead and effluent total chlorine along with 95% confidence limits, was evaluated in Figure 25 to establish a pattern in the grouping of the blends for each Utility. Most of the sample means appeared to arrange along the inner and outer edge of the confidence limits, resulting in a coefficient of determination of 0.323. A distinct separation in the distribution of sample means was observed in the clustering of Utility 1 and 2 on the left side of the plot, and Utility 3 and 4 on the right side.

Figure 25. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent lead vs. effluent total chlorine residual.

Similarly, for the scatter plot of effluent lead and effluent total chlorine (Figure 25), a negative slope was obtained for the relationship between the sample means for effluent lead and effluent combined chlorine. The distribution of sample means in Figure 26 was analogous to the observed clustering of Utility blends in Figure 25, where Utility 1 blends were grouped in the upper left bounds of the confidence limits and Utility 2 blends were arranged along the lower left bounds of the confidence limits. Utility 3 sample means were more scattered across the middle to right hand side of the plot. For Utility 4, Scenario 1 blends were clustered on the right side of the lower confidence limits, and the Utility 4 Scenario 2 scenario two blends laid outside the confidence limits in the upper zone of the plot.
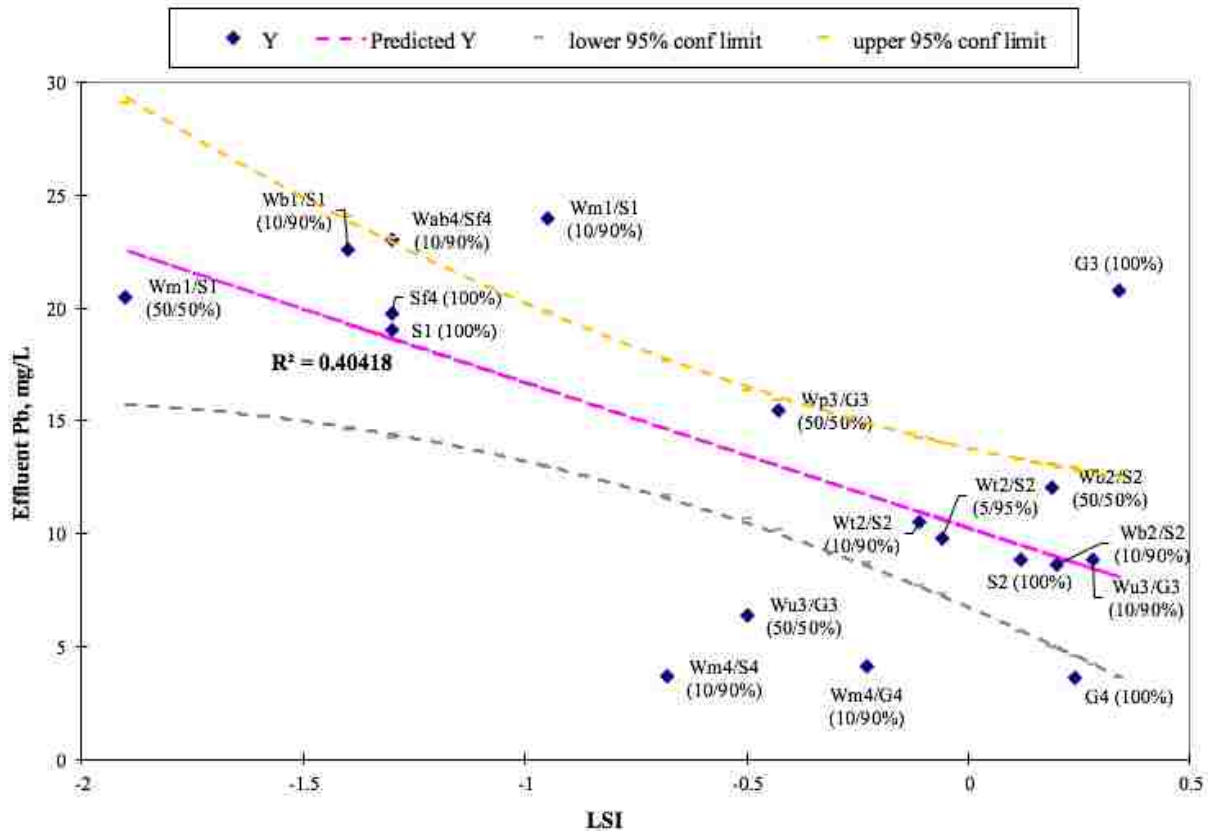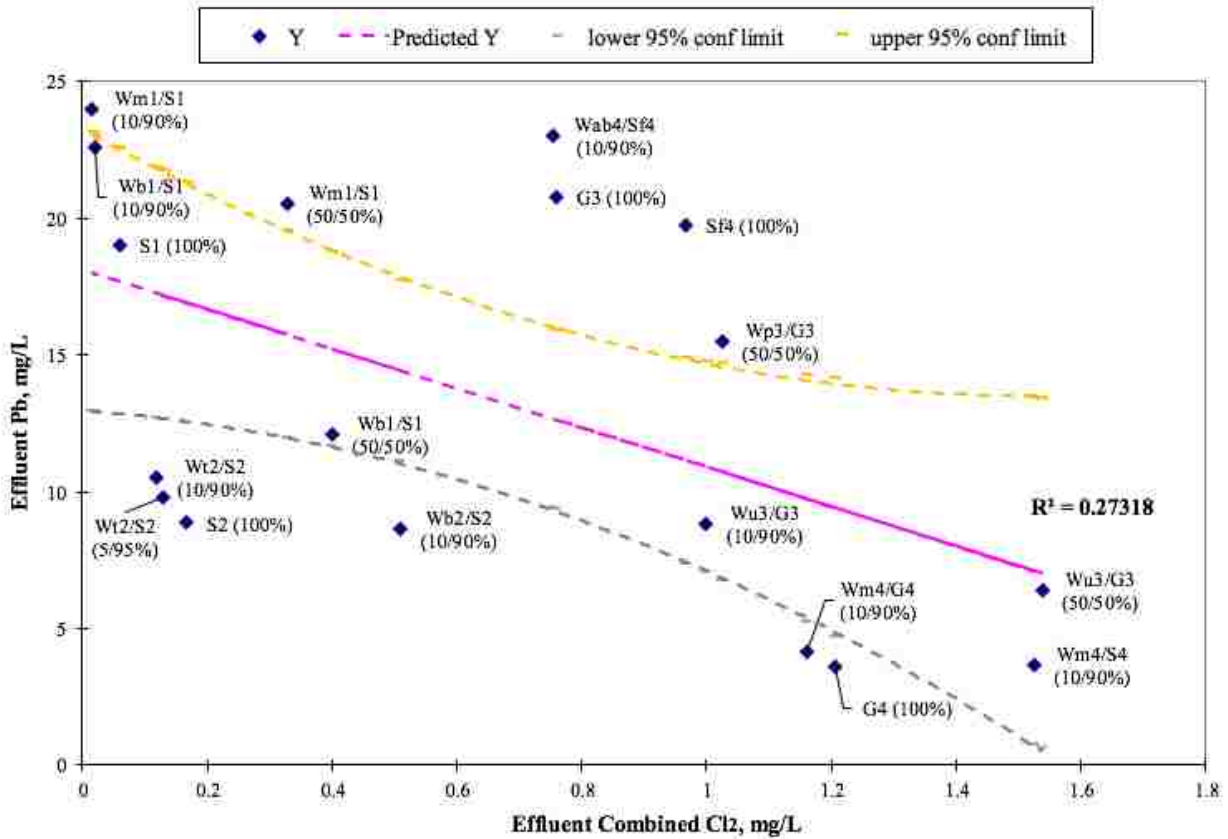
Figure 26. Least squares linear regression and biconcave upper and lower 95% confidence limits for effluent lead vs. effluent combined chlorine residual.

In Figure 27, scattering of the sample means for delta copper and effluent free chlorine resulted in a lower R^2 value (0.235) compared to the other pairs of parameters tested for significance on regression. The clustering of the Utility blends' sample means was inconsistent, mostly accumulating on the bottom left to middle side of the plot. Half of the sample means laid within the confidence limits indicating that high residual chlorine concentrations may affect the dissolution rate of copper. Since the slope of the predicted sample means on regression was not very steep (0.391(mg/L Cu) / (mg/L free Cl_2)), increases in effluent free chlorine concentration on copper corrosion were not as constant and linear compared to the correlation analysis of parameters with larger slope values.
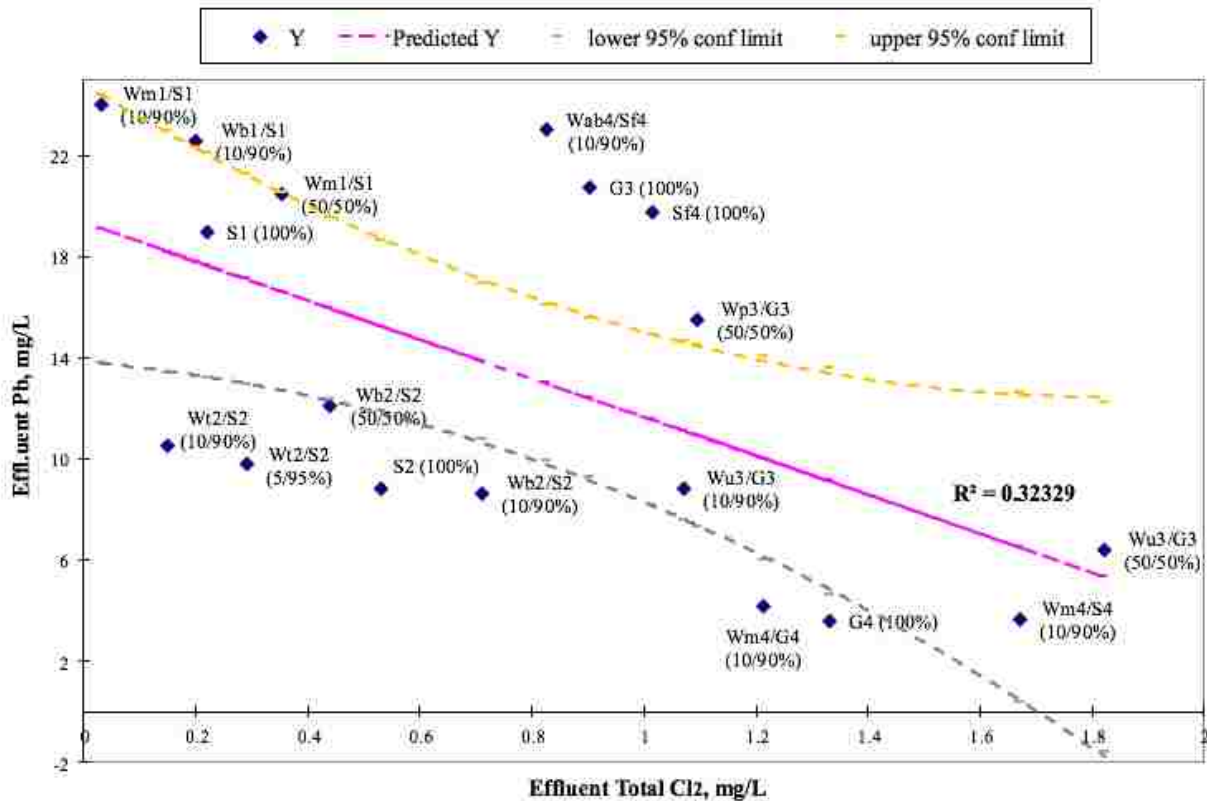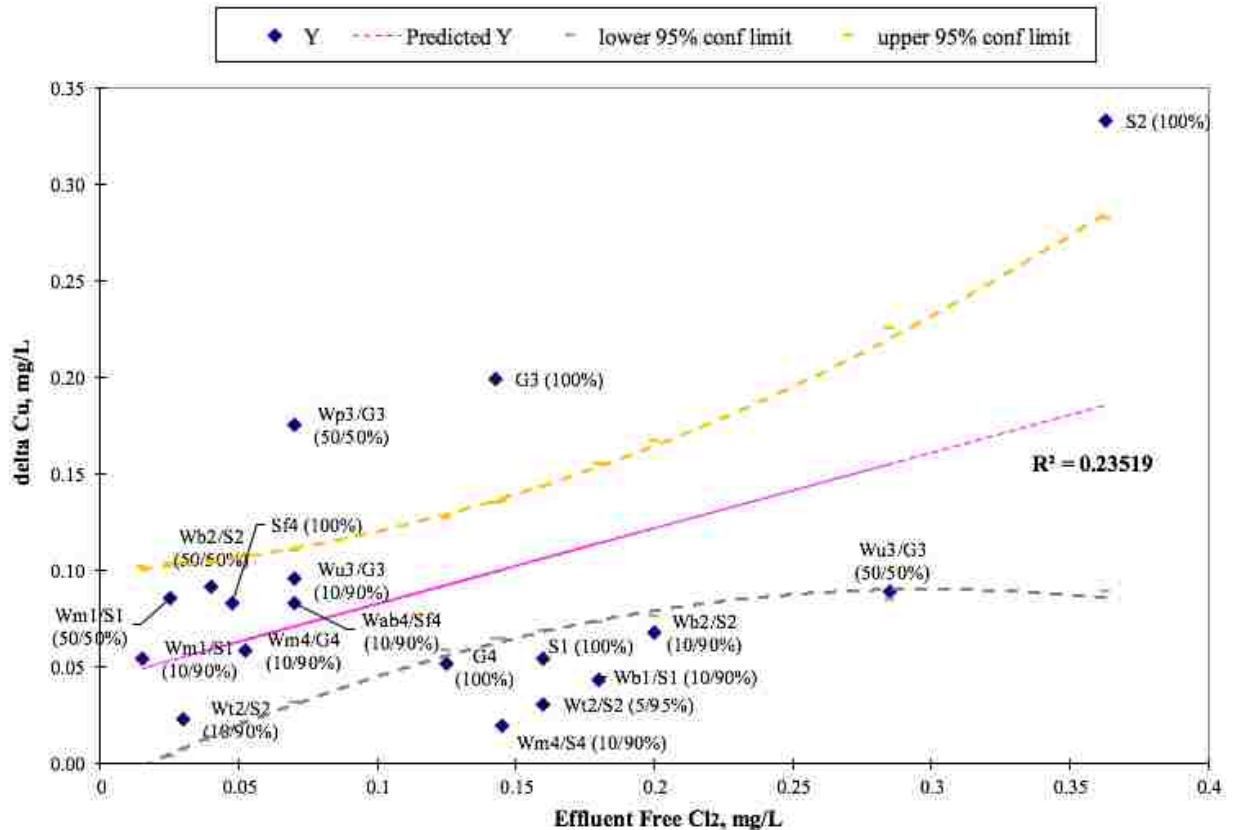
Figure 27. Least squares linear regression and biconcave upper and lower 95% confidence limits for delta copper vs. effluent free chlorine residual.

4.5 Microbial Activity and Biological Corrosion

The presence of nuisance bacteria in distribution systems may contribute to a series of problems that can compromise the aesthetic quality (e.g., discoloration, cloudiness, slime formations) of the finished water (DBI, 2004). Often, the proficiency of one analytical test can be limited in detecting a large variety of bacteria in a single sample that can pose risk downstream in distribution systems. Hence, the Biological Activity Reaction Tests (BART™) were developed by Droycon Bioconcepts Inc. to qualitatively and semi-quantitatively estimate the activity or "aggressivity" of a bacterial population based on a time lag correlation. The test consists of incubation of a measure of blended water with different growth media in sealed containers that

also contain a floating ball that limits the rate of diffusion of oxygen from the container headspace into the growth media. The differing levels of available oxygen at the top of the medium, near the ball and at the bottom of the container select for aerobic growth conditions and metabolism near the ball and anaerobic conditions, favoring anaerobic metabolism at the bottom of the container. The longer the time lag to the detection of a reaction in the BART™ biodetector, indicated by visual changes in color, cloudiness, etc., the smaller the aggressive population of the microbial consortium being determined. Conversely, the shorter the time lag, the higher the number of active cell populations in the sample, and the more aggressive the bacteria.

Growth rates and final densities of six bacterial groups were evaluated: Sulfate reducing bacteria (SRB), Acid producing bacteria (APB), Heterotrophic aerobic bacteria (HAB), Slime forming bacteria, Nitrifying bacteria, and Denitrifying bacteria. Results were obtained by monitoring the incubation containers for specific visual indicators to determine corrosion and/or biofouling potential of the target microbial species. The presence of SRB and/or APB were a positive indication of high corrosion potential, resulting in taste and odor problems in the finished waters, and potential for blackened waters. A positive test for HAB and/or slime-forming bacteria indicated high biofouling potential characterized by cloudiness, slime formations and plugging. The finished waters had a high nitrate generation potential if the test was positive for nitrifying and/or denitrifying bacteria. Positive visual indicators include (a) black growth at the base for anaerobic SRB or black growth on the ball for aerobic SRB (example in Figure 28); (b) cloudy solution and slime growth at the bottom of the vial for the slime-forming test (example in Figure 29); (c) foam around and under the ball for denitrifying bacteria (example in Figure 30); and (d) bleached solution for heterotrophic aerobic bacteria (HAB) (example in Figure S3).

The endpoint day for each test differed per the test kit's instructions. The HAB and

denitrifying bacteria tests ended after 4 days. The nitrifying bacteria tests ended after 5 days, and

the SRB, APB and slime-forming test endpoints ended after 8 days. Table 14 contains a

summary of the results obtained from the BART™ analysis for all four utilities.

Table 14. Qualitative and semi-quantitative[1] BART™ results

Test waters	Sulfate reducing bacteria[2]	Acid producing bacteria[2]	Heterotrophic aerobic bacteria[3]	Slime forming bacteria[2]	Nitrifying bacteria[4]	Denitrifying bacteria[3]
Utility 1	Present	Absent	Absent	Present	Absent	N/A
10% Wb1/ S1	Present	Absent	Absent	Present	Absent	N/A
10% Wm1/ S1	Present	Absent	Absent	Present	Absent	N/A
50% Wm1/ S1	Present	Absent	Absent	Present	Absent	N/A
Utility 2	2,200,000	Absent	Absent	1,750,000	Absent	1,800,000
5% Wt2/ S2	2,200,000	Absent	6,500	1,750,000	Absent	1,800,000
10% Wt2/ S2	2,200,000	70,000	6,500	1,750,000	Absent	1,800,000
10% Wb2/ S2	2,200,000	Absent	Absent	500	Absent	3,000
50% Wb2/ S2	2,200,000	<100	Absent	500	Absent	Absent
Utility 3	2,200,000	Absent	Absent	500	Absent	Absent
10% Wu3/ G3	2,200,000	Absent	6,500	500	Absent	3,000
50% Wu3/G3	2,200,000	Absent	Absent	500	Absent	3,000
50% Wp3/ G3	2,200,000	Absent	6,500	500	Absent	Absent
Utility 4	2,200,000	Absent	Absent	440,000	Absent	1,800,000
10% Wm4/ G4	2,200,000	Absent	Absent	440,000	Absent	1,800,000
10% Wm4/ S4	2,200,000	Absent	Absent	440,000	Absent	1,800,000
Sf4	6,000	Absent	Absent	350,000	Absent	215,000
10% Wab4/ Sf4	6,000	Absent	Absent	350,000	Absent	215,000

[1]Estimated microbial densities are in CFU/mL
[2]8-day test
[3]4-day test
[4]5-day test

The quantification of the bacteria was performed using the manufacturer's reference chart

that correlated each reaction day to an approximate population size of each bacterial group. The

underlined values were indicative of aggressive or rapid growing bacteria, occuring typically

within the first two days of the test. Non-undelined values implied the bacteria had a medium growth rate, and the <100 CFU/ml value indicated the bacteria were slow growers. The reaction day criteria are different for each test because the microbial groups have different growth curves. For example, a three-day reaction for slime forming bacteria is indicative of aggressive bacteria, but a three day reaction for denitrifying bacteria indicates a more moderate growth rate. Due to an initial misinterpretation of the BART™ method, Utility 1 was analyzed strictly based on a negative or positive test result (absent or present) at the end of the reaction period (after 4-10 days).

The sulfate reducing bacterial group (SRB) occurred in the highest densities in nearly all samples, detected as blackened slime present mostly at the base of the vial, and detected less frequently around the ball. This reaction pattern indicated that the dominant group of bacteria present belonged to the dense anaerobic SRB consortium, whereas black slime around the ball indicated the presence of aerobic bacteria. Regardless of the source water, a one-day reaction was observed for almost all samples with the exclusion of the finished surface water (Sf_4) and the 10% RO-treated industrial water blend (10% Wab_4/ Sf_4). The one-day reaction corresponded to an approximate population size of 2,200,000 CFU/mL. The culture medium (Postgate's medium; Postgate, 1963) selected for the test was specific for SRB (e.g., *Desulfovibrio, Desulfotomaculum),* which are microorganisms that use sulfate as an electron acceptor for cellular respiration and release hydrogen sulfide as a metabolic byproduct. The H_2S that reacted with the ferrous iron present at the base of the vial leads to the formation of black iron sulfides. Traces of black slime and foul "rotten egg" odor were an indication of H_2S that formed at the base of the column, which could consequentally form on the inside surface of pipes.

Figure 28. Utility 3. From left to right, 10% Wu$_3$/G$_3$ and duplicate, 50% Wu$_3$/G$_3$ and duplicate. Black growth at base indicates dense anaerobic SRB consortium were present. Black growth around ball indicates aerobic SRB consortium were present.

The presence of SRB in blended waters has a significant impact on corrosion in distribution systems, especially in pipes where iron is present (Yang et al., 2014). In low-flow conditions, waters with high concentrations of sulfate can increase the acidity in older infrastructures, and promote dissolution of iron. Although, the waters were not exposed to iron fittings, there would be a potential risk associated with releasing the blended waters in older distribution systems that contain iron.

Slime-forming bacteria were another group of reoccuring bacteria active in all samples, but were less numerous in Utility 3. The presence of these bacteria was established by the occurrence of specific visual indicators (i.e., cloudiness, dense slime observed at the base of the vial, and gel-like particulates visible upon gentle stirring; examples in Figures 28 and S2). A variety of visual characteristics were used to identify the dominant bacteria since slime forming bacteria include a very diverse microbial community. Particularly, the 10% and 50% Wb$_2$/ S$_2$ samples expressed most of the above described characteristics. Compared to the other samples in this scenario, the 10% Wb$_2$/S$_2$ sample (far left sample in Figure 28) contained larger size

particulates in the form of floating layered plates. Dominant slime-forming bacteria for the 10%

Wb_2/ S_2 sample may include some species of *Proteus* bacteria that accumulate in a disc-like

layer and form a cloudy solution when mixed. The estimated population size of the slime-

forming bacteria in the ozone-biofiltered samples from Utility 2 was less notably high (~ 500

CFU/mL) compared to the size of the slime-forming population in the tertiary-treated blends (~

1,750,000 CFU/mL). Although the ozone-biofiltered blends appeared more cloudy than the

tertiary-treated blends, both blending scenarios had slime growth at the base of the vial. Often,

the observer has to gently stir the vial against a light source at the end of each reaction day to

clearly see the slime-like particulates settled at the base (Hach, personal communication,

December 1, 2015). Thus, the ozone-biofiltered blends resulted in a 6-day reaction period for a

positive detection of slime-forming bacteria. The reaction patterns for the S_2 and tertiary-treated

blends from Utility 2 can be found in the Appendix (Figure S2).

Figure 29. Utility 2. From left to right, 10% Wb_2/S_2 and duplicate, 50% Wb_2/S_2 and duplicate. Cloudy solution and dense slime growth at base was a positive test for the presence of slime forming bacteria.

The presence of slime-forming bacteria typically result in the accumulation of slime-like

coatings around the surface of pipes and fittings in distribution systems (DBI, 2004). These

conditions can cause hydraulic problems related to decreased flow efficiency and slime

sloughing in the finished water. Slime can accumulate to form a biofilm which promotes

colonization of aerobic bacteria on pipe surfaces and anaerobic bacteria beneath the biofilm.

These bacteria produce metabolic accretions that cause corrosion issues, plugging, reduced

efficiency of heat exchangers, and degrades the aesthetics of the finished water, including

increased cloudiness, foul taste and odor (DBI, 2004). Slime forming bacteria are not directly

responsible for infection; however, the bottom layers of biofilm can provide optimal conditions

to harbor *E. coli* and other pathogenic bacteria.

Denitrifying bacteria were identified for all samples that had foam appearing throughout

the upper and lower zones of the column. An early detection of denitrifiers was observed for all

samples from Utility 4, and most samples from Utility 2 (S_2, 10% Wt_2/ S_2 and 5% Wt_2/ S_2) with

the latter shown in Figure 30. The 10% ozone-biofiltered blend from Utility 2 had a more

moderate growth rate compared to the raw surface water and tertiary treated blends from Utility

2. Also, the 10% and 50% non-pasteurized RO-treated blends from Utility 3 had moderate

growth rates (~ 3,000 CFU/mL).

Figure 30. Utility 2. From left to right, S_2 and duplicate, 10% Wt_2/ S_2 and duplicate, 5% Wt_2/ S_2 and duplicate. Foam around and under the ball was a positive test for denitrifying bacteria.

Nitrates in water can be reduced by denitrifiers into nitrites then into nitrogen gas (N_2), which is a major process in the nitrogen cycle. The presence of denitrifying bacteria could be an indication that the water source may be affected by pollution of leaking septic tanks, industrial contamination or nitrogen-rich spills. However, in this case, from observing Figure 15 nitrate concentrations in the influent were not significantly different from nitrate concentrations in the effluent. Therefore, it is likely that the nitrate concentration may have not been high enough relative to the denitrifying bacteria to affect the effluent nitrate concentrations during incubation periods.

4.6   Discussion

Effluent lead concentrations from Utility 1 exceeded the 15ppb EPA action level irrespective of blend ratio and treatment of the recycled waters. There is a lead leaching potential or risk associated with samples that have effluent lead concentrations above 15ppb for conditions

of prolonged exposure. However, the measured lead exceedances that resulted from prolonged laboratory incubation may not be representative of actual concentrations that might form from stagnant blended waters in a real distribution system. The elevated lead concentrations were associated with the low LSI values (<-0.5), which indicated a high corrosion potential. For Utility 3, higher effluent lead and copper concentrations were measured in the non-blended groundwater sample and in the 50% pasteurized-RO blend compared to the other non-pasteurized blended waters. Although, increasing the recycled water blend ratio increased the corrosion potential of the samples, the non-blended groundwater sample contained the highest amount of effluent lead and copper. Moreover, added treatment with pasteurization was expected to improve water quality rather than increase lead and copper concentrations compared to the 50% non-pasteurized blend. Therefore, in this case, corrosion of lead and copper may have been induced by the activity of bacteria that thrive in hot environments. Microbially induced corrosion (MIC) could explain how the presence of specific microorganisms like sulfate-reducing bacteria (SRB) can promote pitting in the form of black copper sulfide (Labuda, 2003). Biological Activity Reaction Tests (BART™) were utilized to assay the presence of active SRB, for which an estimated population size of 2,200,000 CFU/mL was observed for all test waters from Utility 3. This suggests that biological activity may have influenced copper corrosion. However, since all test waters from Utility 3 tested positive for SRB, the BART™ test was not useful to distinguish the composition of the pits to cause the G_3 and 50% Wp_3/G_3 samples to contain higher copper concentrations than in the non-pasteurized blends. Additional testing using Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS) would be required to map and characterize the elemental composition of the corrosion pits on the coupons, and identify exopolymeric material produced from bacteria.

The addition of zinc orthophosphate as a corrosion inhibitor in the surface water blend from Utility 4 mitigated both lead and copper concentrations in the effluents, which had the lowest measured values compared to all other samples. Stabilization of the reclaimed water from Utility 4-scenario 1 may have limited the leaching of metals. However, the LSI value in the 100% reclaimed water sample was higher than in the blended waters, indicating that the low effluent lead levels measured in the G_4 and 10% Wm_4/ G_4 samples were not influenced by LSI. Although, the reclaimed water from Utility 4-scenario 2 was stabilized, effluent lead concentrations increased when the treated surface water sample was blended with 10% RO-treated industrial water. The higher lead concentration of the blended sample (10% Wab_4/ Sf_4) compared to the non-blended sample (Sf_4) may suggest that the LSI of the reclaimed water was not sufficiently driven to equilibrium or that a corrosion inhibitor should have been added.

For the BART™ results, SRB were the most reoccuring and aggressive bacterial groups, appearing at the beginning of the reaction period. The presence of high levels of aggressive SRB were an indication of high corrosion potential, which can be associated with taste and odor problems, and blackened finished waters. However, due to the absence of iron in the brass fittings, the size of the bacterial populations may actually be overestimated. Alternatively, the production of cupric (I) sulfite may have occurred, which has a blackened color similar to iron sulfides. Further analysis of the elemental composition on the brass coupons may be necessary to verify for corrosion in the form of black pits. In Figure 31, effluent sulfate concentrations are shown to approach or exceed the non-enforceable secondary MCL[1] of 250 mg/L in Utility 2 and

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[1] The EPA has established non-mandatory water quality standards for 15 contaminants including sulfate to improve the aesthetic quality of finished waters. Retrieved from https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals#what-are-secondary Accessed 10/10/17.

3, respectively, suggesting that the presence of elevated substrate in the form of sulfate may have induced SRB proliferation.
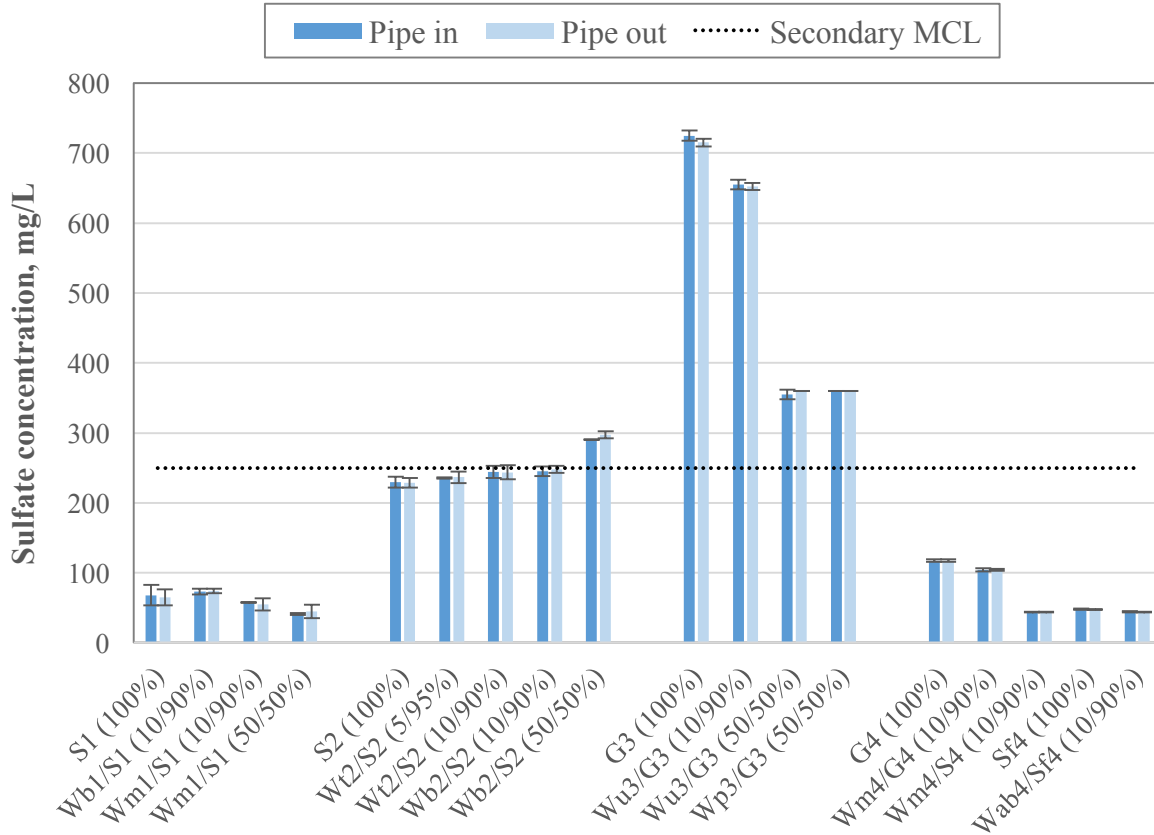
Figure 31. Distribution of average sulfate concentrations for all utilities before and after 48-hour pipe rig incubation.

Correlation analyses between BART™ population sizes and effluent metal concentrations were performed, resulting in significant correlations for effluent lead with SRB ($p<0.01$) and effluent lead with DNB ($p<0.05$), and delta zinc with DNB ($p<0.05$) (Table 15). Even though the numerical ranges associated to the population sizes were approximate values (relative to the manufacturer's table), significance was obtained. In some cases, the results of the correlations may not indicate causation but instead could indicate covariance with the metals data; nonetheless, high metabolic activity and slime growth associated with high population sizes may

have contributed to the high effluent lead and high delta zinc through creation of anaerobic surface conditions that could support erosion of the lead or zinc from the metal surfaces.

Table 15. Regression and correlation analysis for metals and bacterial densities from BART™ analysis across Utilities 2, 3 and 4.

Parameters		Correlation coefficient, r and coefficient of determination, r^2		Calculated *t* test for significance of correlation coefficient, r	Two-tailed t tabulated for 12 degrees of freedom	
					2.12	2.92
Independent	Dependent				p<0.05	p<0.01
		r	r^2			
Sulfate reducing bacteria	Effluent Pb	0.681	0.464	3.22		X
Denitrifying bacteria	Effluent Pb	0.570	0.325	2.41	X	
Denitrifying bacteria	ΔZinc	0.547	0.299	2.26	X	

4.7   Summary

In this part of the research, corrosion potential of the blended waters was evaluated relative to chemical and biological contaminants measured in the pipe rig effluents. Lead, copper and several bacterial groups were quantified as a means to identify ideal blend ratios for DPR applications. Results were further analyzed to establish statistical significance on regression and/or variance of the sample mean concentrations.

Effluent lead concentrations exceeding the EPA action level were measured in all of Utility 1 samples, the non-blended groundwater and 50% pasturized-RO blend from Utility 3, and the treated surface water and 10% RO-treated industrial blend from Utility 4. Although, copper leaching occurred in all the pipe rig effluents, none of the effluent concentrations exceeded the 1.3ppm LCR limit.

Significant variation among sample means was observed for copper in Utility 2, where the ozone-biofiltered blends were significantly different from each other, and with respect to the

other samples. In this case, both blend ratio and treatment of the recycled water influenced the amount of copper that leached from the brass fittings. For Utility 3, some similarities were observed in the differences among lead and copper sample means. For both lead and copper the non-pasturized RO blends were always significantly different ($p < 0.05$) from the non-blended groundwater sample. However, for lead, the pasteurized-RO blend was not significantly different from the other sample means, while for copper the pasteurized-RO blend was significantly different from the other sample means.

Regression significances were established between effluent lead concentration means and LSI of the finished waters ($p<0.01$), effluent lead and total chlorine concentration means ($p<0.02$), effluent lead and combined chlorine concentration means ($p<0.05$), and delta copper and free chlorine concentration means ($p<0.05$). As indicated by the clustering of the sample means, high corrosion potential strongly correlated to lead leaching for (1) Utility 1 samples, (2) the non-blended finished surface water and (3) 10% RO-treated industrial blend from Utility 4. For the distribution of effluent lead and total chlorine concentration on the regression plot, Utility 1 and 2 sample means aggregated along the edge of the upper and lower 95% confidence limits, respectively. Higher scatter was associated with Utility 3 and Utility 4 sample means; however, Utility 4 sample means in the first scenario grouped separately from the Utility 4 sample means in the second scenario. The non-blended groundwater sample, 10% RO-treated groundwater and surface water blends from Utility 4 grouped outside the lower zone of the 95% confidence limit, while the non-blended finished surface water and 10% RO-treated industrial blend grouped outside the upper zone of the 95% confidence limits.

BART™ results showed that the most predominant bacterial groups were sulfate-reducing bacteria, slime-forming bacteria and denitrifying bacteria. In Utility 2, reductions in slime

forming bacteria and denitrifying bacteria were observed after treatment by ozone and biofiltration of the tertiary treated effluent (10% Wb_2/ S_2 and 50% Wb_2/ S_2). While the non-blended groundwater sample and 50% pasteurized-RO blend from Utility 3 tested absent for denitrifying bacteria, the 10% and 50% non-pasteurized RO-treated blends contained moderate bacterial densities (3,000 CFU/mL). For Utility 4, aggressive population sizes were quantified in both scenarios for sulfate reducing bacteria, slime forming bacteria and denitrifying bacteria.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

- For Utility 1, blending RO-treated water resulted in higher THM concentrations compared to the unblended and ozone-biofiltered samples due to the higher TOC concentrations measured in the RO blends. The surface water samples blended for Utility 1 scenario I and scenario II were collected on different dates, resulting in variable TOC concentrations which could explain the higher THM concentrations in the RO-treated blends. Both the ozone-biofiltered blend and RO-treated blends contained effluent lead concentrations that exceeded the LCR action level, suggesting that blending did not help minimize lead leaching potential.

- For Utility 2, blending ozone-biofiltered effluent increased effluent THM concentrations above regulatory limits. The addition of another treatment process after ozone and biofiltration could potentially remove organic precursors to help mitigate THM yields. Characterization of the DOC can help identify the presence of low or high molecular weight compounds. Consequently, the molecular weight distribution could help determine a sustainable treatment option preferred over RO (e.g., UF or MF).

- For Utility 3, blending non-pasteurized-RO-treated water helped improve finished water quality by reducing effluent THMs, and effluent copper and lead concentrations. Increasing the non-pasteurized-RO blend ratio from 10% to 50% would be recommended to optimize the blending requirements for Utility 3.

- Blending RO-treated water for Utility 4 scenario I also helped reduce effluent THMs, and effluent copper and lead concentrations. In the second scenario, blending RO-treated water from an industrial source had nearly no effect on reducing effluent THMs nor effluent copper concentrations. However, the 10% RO-treated blend contained higher

effluent lead concentrations than the unblended sample, suggesting the need for further treatment of the RO-treated industrial water before blending.

- Regression analyses conducted for effluent THM/ effluent HAA concentrations and effluent TOC concentrations resulted in significant correlations at the 99% confidence level ($p<0.01$). The clustering of the sample means from Utility 2 appeared mostly outside the bounds of the 95% upper confidence limit. Although, Utility 1 and 2 had similar TOC values, Utility 2 yielded more THMs and HAAs due to the use of chlorine in the disinfection protocol. Hence, the best recommendation for Utility 2 would be to further treat the ozone-biofiltered effluent with an additional treatment barrier like Microfiltration prior to blending. Another alternative would be to switch disinfectant type from chlorine to chloramines. However, adding chloramines during secondary disinfection can lead to nitrification issues, especially if chloramines were applied to the 50% ozone-biofiltered blend, which contained the highest nitrate concentration.

- Better correlations were observed between effluent THMs/ effluent HAAs and influent SUVA values ($p<0.01$) compared to effluent THMs/ effluent HAAs and influent UV_{254} values ($p<0.05$). In these two comparisons, the regression plots showed an inverse relationship, where the UV_{254} values increased as effluent DBP concentration increased, and influent SUVA values decreased as effluent DBP concentrations increased. Although, the correlation trends may help predict THM and HAA formation, improved characterization of the organic matter is recommended to better understand the reactivity of the DBP precursors.

- Regression analysis of effluent lead on the LSI of the finished waters indicated there was significant correlation at the 99% confidence level ($p<0.01$). The clustering of the sample

means from Utility 1 around the upper 95% confidence limit indicated that the reclaimed

waters, irrespective of treatment, would require stabilization and/or addition of a

corrosion inhibitor before discharge into a distribution system. Although, the reclaimed

industrial effluent from Utility 4 was stabilized, blending appeared to increase effluent

lead concentrations. Therefore, further treatment of the reclaimed water source is

recommended followed by pH adjustment of the finished surface water prior to blending.

The lead exceedance measured in the non-blended groundwater sample from Utility 3

showed poor correlation with LSI, indicating that the high scale-forming potential did not

limit lead corrosion. Although, effluent lead concentrations in both the non-blended

groundwater and 50% Pasteurized-RO-treated blend from Utility 3 exceeded EPA action

levels, smaller densities in the denitrifier population size were measured compared to the

non-pasteurized RO-treated blends. The 50% pasteurized-RO-treated blend from Utility 3

had a higher effluent lead concentration compared to the 50% non-pasteurized RO-

treated blend, suggesting that, without elemental analysis of the corrosion pits in the pipe

rigs, Utility 3 should exclude pasteurization in their reclaimed water treatment train.

- Significance of regression results showed better correlation between effluent lead and

total chlorine concentration ($p<0.02$) than between effluent lead and combined chlorine

concentrations ($p<0.05$). This comparison may suggest that both the chlorine-containing

compounds and free chlorine ions mutually influence dissolution of solid lead, rather than

exclusively when combined chlorine was present. However, from observing the

clustering of the sample means, Utility 2 grouped consistently below the lower 95%

confidence limits in the effluent lead and total/combined chlorine regression plots. This

pattern indicated that the use of chlorine in the disinfection protocol may have helped

reduce lead corrosion. An inverse relationship was observed between delta copper and free chlorine concentrations for Utility 2, where higher free chlorine concentrations correlated with higher copper corrosion. Therefore, chlorine disinfection may reduce lead leaching but potentially produce more copper corrosion products compared to chloramines. However, the regression plot showed that the non-blended surface water from Utility 2 was the only sample mean with the highest delta copper concentration. Hence, blending would be recommended for Utility 2 as a measure to reduce copper corrosion.

- Blended and non-blended effluents from all utilities contained high levels of sulfate reducing bacteria, and high-moderate levels of slime forming and denitrifying bacteria. Hence, the aesthetic quality of the finished waters may be compromised, especially for the non-blended surface water and tertiary treated blends from Utility 2. Subsequent treatment of the tertiary treated effluent by O_3-Biofiltration reduced the production of slime forming bacteria and denitrifying bacteria, suggesting that blending ozone-biofiltered waters would be recommended for Utility 2 to alleviate corrosion induced by these bacteria. Although, sulfate reducing bacteria densities were not reduced after treatment by O_3-Biofiltration, an overestimation of the population size may have occurred due to the nature of the culture medium in the BART™ reaction vials. For sulfate reducing bacteria, Postgate's medium was employed by design in the BART™ tests to stimulate and enhance the growth rate of these specific bacteria. The growth medium was characterized by a lactate-yeast extract containing ferrous sulfate, ascorbate and thioglycolate (Postgate, 1963). Compared to other modifications that were performed to the medium, the cysteine-free medium gave more reliable colony counts of sulfate-

reducing bacteria for natural water samples. Therefore, the environment in the column may have increased the rate of bacterial growth, which resulted in shorter time lags in bacterial growth rates.

- Some limitations to consider when evaluating these bench-scale laboratory results include: 1) prolonged incubations of the bench-scale samples might generate higher concentrations than would be produced in a full-scale distribution system, 2) the variability of the disinfectant contact time (not standardized) which may have skewed the THM correlation analysis, 3) the lack of data for the unblended surface water from Utility 4 (S_4) which limits the ability to compare concentrations in blended and unblended waters for Utility 4.

APPENDIX. SUPPLEMENTARY DATA

Figure S1. Pipe rigs with CDA brass bar simulating distribution system with premise plumbing

Table S1. ANOVA for the effect of treatment blend on measured post-incubated total lead concentrations – Utilities 1, 2 and 4.

Utility	Source of variation	Sum of squares	Degrees of freedom	Mean square	F value	*p* value
1	Between means (or treatments)	0.000298	3	9.95×10^{-5}	2.85	0.08216
	Within samples (or error)	0.000419	12	3.49×10^{-5}		
	Total	0.007176	15			
2	Between means (or treatments)	0.000027	4	6.85×10^{-6}	0.74	0.58035
	Within samples (or error)	0.000139	15	9.28×10^{-6}		
	Total	0.000167	19			
4[1]	Between means (or treatments)	0.001641	4	0.000410	42.8	4.93×10^{-8}
	Within samples (or error)	0.000144	15	9.58×10^{-6}		
	Total	0.001784	19			

[1]Note: Utility 4 *p* value is significant ($p < 0.01$), however non-significance was determined because the source waters and reclaimed waters were different for both scenarios so a comparison of variance would not be valid.

Table S2. ANOVA for the effect of treatment blend on measured post-incubated total copper concentrations – Utilities 1 and 4.

Utility	Source of variation	Sum of squares	Degrees of freedom	Mean square	F value	*p* value
1	Between means (or treatments)	0.00383	3	0.00128	2.80	0.08527
	Within samples (or error)	0.00547	12	0.00046		
	Total	0.00930	15			
4[1]	Between means (or treatments)	0.01118	4	0.00279	4.89	0.01004
	Within samples (or error)	0.00858	15	0.00057		
	Total	0.01976	19			

[1]Note: Utility 4 *p* value is significant ($p < 0.05$), however non-significance was determined because the source waters and reclaimed waters were different for both scenarios so a comparison of variance would not be valid.
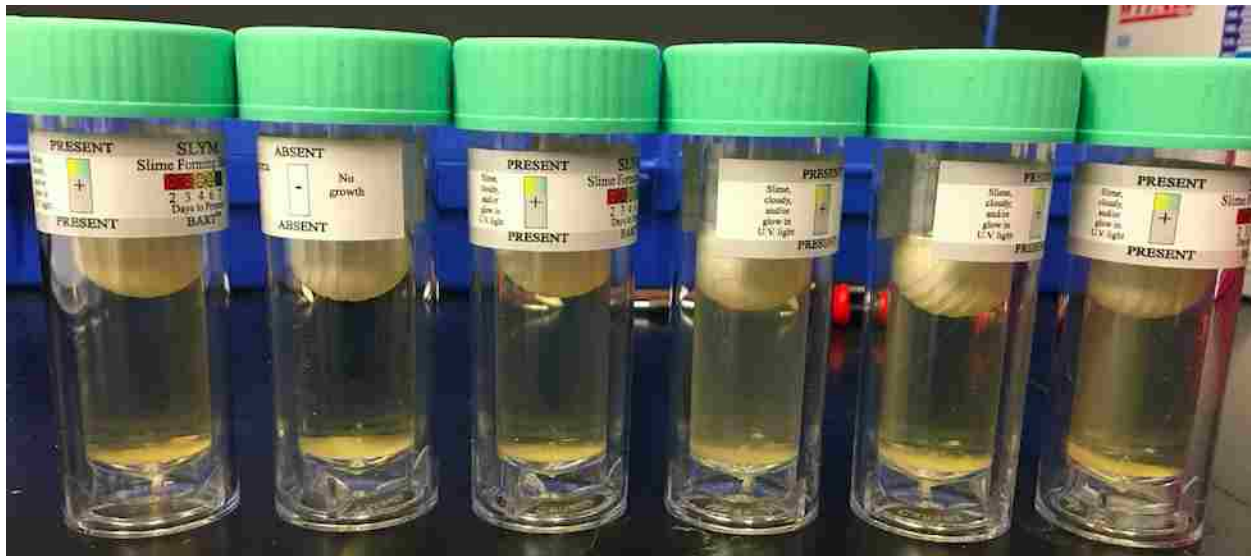

Figure S2. Utility 2. From left to right, S_2 and duplicate, 10% Wt_2/ S_2 and duplicate, 5% Wt_2/ S_2 and duplicate. Dense slime growth at base was a positive test for slime forming bacteria.
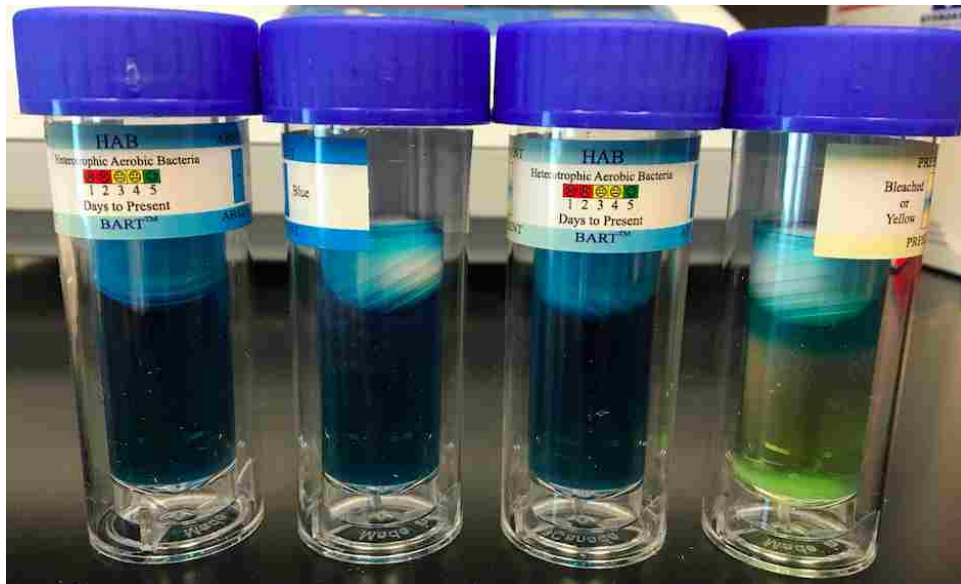
Figure S3. Utility 3. From left to right, G_3 and duplicate, 50% Wp_3/ G_3 and duplicate. The bleached solution indicated positive for heterotrophic aerobic bacteria.

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CURRICULUM VITAE

The Graduate College

University of Nevada, Las Vegas

Assumption Grace Grimaldi

grimaldi.assumption@gmail.com

Degrees:

Bachelor of Science in Chemistry, 2013

University of Nevada, Las Vegas

Master of Science in Civil and Environmental Engineering, 2017

University of Nevada, Las Vegas

Thesis Title: Evaluating the Chemical and Biological Stability of Finished Waters Blended for

Direct Potable Reuse in a Simulated Distribution System

Thesis Examination Committee:

Advisory Committee Chair, Dr. Dave James, Ph.D.

Advisory Committee Member, Dr. Eric Dickenson, Ph.D.

Advisory Committee Member, Dr. Daniel Gerrity, Ph.D.

Graduate College Representative, Dr. Patricia Cruz, Ph.D.