DISSERTATION

AN INVESTIGATION OF WATER QUALITY CONSIDERATIONS FOR PREMISE PLUMBING SYSTEMS IN BUILDINGS

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Summer 2021

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ABSTRACT

AN INVESTIGATION OF WATER QUALITY CONSIDERATIONS FOR PREMISE PLUMBING SYSTEMS IN BUILDINGS

Providing potable and palatable water to their consumers is a top priority for drinking water treatment utilities in the US. To ensure the safety of the drinking water, disinfection methods have been applied for over a century. Chlorine is the most extensively used disinfectant to control waterborne pathogen activities. Despite its effectiveness, chlorine is known to react with natural organic matter (NOM) and produce disinfection by-products (DBPs) (e.g., trihalomethanes and haloacetic acids) that are known to be harmful to humans.

Currently, DBPs are regulated at the distribution system level. However, premise plumbing systems are unique and different from water distribution systems. Moreover, there are knowledge gaps for premise plumbing in residential and non-residential buildings under routine operations, and that has not been fully understood for different operation scenarios (e.g., use of water-efficient fixtures in conventional buildings) and building types (e.g., green-certified buildings).

The primary purpose of this dissertation was to contribute to the body of knowledge on water quality in premise plumbing systems by addressing some of the knowledge gaps identified in the literature. This dissertation comprises three independent but complementary studies. Each study focused on essential aspects of water quality in premise plumbing systems as follows: i) identifying the effects of building type (e.g., conventional vs. green-certified) on water quality in premise plumbing systems, ii) providing a comprehensive literature review on existing

contaminant prediction models for premise plumbing systems, and iii) developing a DBP prediction tool for premise plumbing systems.

In the first study, effects of building type on premise plumbing water quality were addressed. For this purpose, trihalomethanes (THMs) and water quality parameters, including temperature, pH, free chlorine levels, and total organic carbon (TOC) were collected and compared between a combined conventional and green-certified (i.e., water-efficient) building drinking fountains. Even though the distributed water quality to the green and conventional building sides was the same, statistically significant differences in water quality parameters and TTHMs were observed due to the changes in water chemistry in the premise plumbing systems. The study findings point out the importance of the plumbing pipe age and its impacts on water chemistry.

In the second study, a state-of-the-art review was conducted to provide background information on water quality and indoor air quality models that have been implemented in residential and non-residential building premise plumbing systems and indoor air environments. A systematic literature search was conducted in the Compendex, Web of Science, IEEE Explore, Science Direct, and PubMed databases. A total of 22 contaminant prediction modeling studies for premise plumbing and 12 for indoor air quality were reviewed in this study. Among the premise plumbing models, lead and copper prediction models have drawn more attention from researchers than any other contaminants. Due to increased inhalation exposure levels, shower models have been excessively included in risk exposure studies. This review aimed to draw attention to the research needs in modeling approaches, identify the gaps in the literature, and provide a baseline for future research attempts.

In the third study, a chloroform prediction model was developed and incorporated into a simulation software to predict chloroform concentrations in a premise plumbing system for eight hours of water stagnation. The model coefficients were determined with the bench-scale experiments based on water quality parameter ranges that can be seen in premise plumbing systems. Chloroform concentrations were tested in a two-story townhouse; experimental and model prediction results were compared. The chloroform prediction model underpredicted chloroform concentrations by 27-37% compared with the house measurements. This study represents an important initial attempt in developing a simulation-based water quality prediction model, which can be implemented in premise plumbing systems.

This study contributes to the body of knowledge on water quality in premise plumbing systems by providing a better insight into the effects of conventional and green-certified buildings, shedding light on the current state of numerical modeling research, and implementing a chloroform prediction tool in premise plumbing systems.

ACKNOWLEDGEMENTS

I would like to thank my advisors, Dr. Mehmet Ozbek and Dr. Pinar Omur-Ozbek, for their invaluable supervision, continuous support, and patience during my Ph.D. study.

I also would like to thank the other members of my committee, Dr. Neil Grigg and Dr. Gregory Dooley, for their generous contributions to this work.

My deep appreciation goes out to Brian Cranmer, Jenifer Marley, and Susanne Cordery, who were always helpful throughout my dissertation.

I would also like to say a heartfelt thank you to my family for always believing in me and encouraging me during this challenging period.

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CHAPTER. 1:Introduction

Water is essential for all living organisms. Access to clean drinking water and sanitation is recognized as a human right by the United Nations. According to Resolution A/RES/64/292, water should be sufficient, safe, acceptable, physically accessible, and affordable for everybody (UN, 2010). In the United States, The Safe Drinking Water Act (SDWA), a federal law passed in 1974, protects the public health by regulating public water systems. The SWDA delegates responsibility to the United States Environmental Protection Agency (EPA) to establish the maximum contaminant levels (MCL) of microorganisms, disinfectants, disinfection by-products (DBPs), radionuclides, and inorganic and organic chemicals in drinking water (USEPA, 2017). For over a century, chlorine has been extensively used as a disinfection agent to control waterborne pathogen activities (CDC, 2016). Despite its effectiveness, chlorine is known to react with natural organic matter (NOM) and produce DBPs (e.g., trihalomethanes and haloacetic acids) that are known to be harmful to humans (Richardson et al., 2007).

Currently, DBPs are regulated at the distribution system level. However, premise plumbing systems are unique and different from water distribution systems due to a large surface area to-water volume ratio, smaller pipe diameters, intermittent and frequent stagnation conditions, higher residence times, elevated and variable temperature, redox potentials, deposit accumulation, biofilm growth, and lower flow rates (Nguyen et al., 2012; Zheng et al., 2015). Moreover, the previous research shows that higher water quality deterioration occurs in buildings than in water distribution systems (Chowdhury et al., 2011; Dion-Fortier et al., 2009). Currently, there are knowledge gaps for premise plumbing in residential and non-residential buildings under routine operations that has not been fully understood for different operation scenarios (e.g., use of water-efficient fixtures in conventional buildings) and building types (e.g., green-certified buildings) (Julien et al., 2020). A recent study identified five main topics for building premise plumbing as needing urgent research: i) stagnation, ii) water use, iii) standards, iv) risk and disease modeling, and v) safety and sustainability (Julien et al., 2020).

The primary purpose of this dissertation was to contribute to the body of knowledge on water quality in premise plumbing systems by addressing some of the knowledge gaps identified in the literature. This dissertation comprises three independent but complementary studies. Each study focused on essential aspects of water quality in premise plumbing systems as follows: i) identifying the effects of building type (e.g., conventional vs. green-certified) on water quality in premise plumbing systems, ii) providing a comprehensive literature review on existing contaminant prediction models for premise plumbing systems, and iii) developing a DBP prediction tool for premise plumbing systems.

This dissertation was initially motivated by the observations of increased water quality deterioration in green-certified buildings compared with conventional buildings (Rhoads et al., 2016). To investigate these findings further, selected water quality parameters (i.e., temperature, pH, free chlorine residual, and total organic carbon (TOC)) and trihalomethanes (THMs) were compared between the drinking fountains of a combined conventional and green-certified building in the first study. The building selected for the study has a unique structure with a conventional design on one side of the building, while the other side is green-certified. Therefore, this sampling location provides a unique opportunity for cross-comparisons of water quality parameters between conventional and green-certified buildings by eliminating some uncontrollable factors such as distance to the water utility entrance point, water usage rate, and variations in distributed water quality to the buildings.

The literature review conducted as a part of the first study displayed the scarcity of contaminant prediction model applications for premise plumbing systems. Thus, in the second study, a comprehensive literature review was conducted to shed light on the current state of the modeling research on premise plumbing systems. The second study's findings revealed that even though water quality models have been excessively used for water distribution systems (Chowdhury et al., 2009), this trend was not observed for the water quality model implementations in premise plumbing systems. In the third study, a DBP prediction and simulation tool was developed based on the premise plumbing conditions to address this gap.

1.1. Three-Article Dissertation Organization

The three-article dissertation format is used in this dissertation, which comprises three independent but complementary studies focusing on varying aspects of water quality in premise plumbing systems. The three articles together highlight the importance of the premise plumbing system's effects on water quality at the point of use. The findings from this dissertation could be used to identify strategies for improving water quality in residential and non-residential buildings and support decision-making for public health risk management.

A brief research summary for each study is provided as follows:

Chapter 2: A Case Study: Comparison of Disinfection By-product Formations Between Green and Conventional Buildings

The first study aimed to identify and compare the effects of conventional and green-certified premise plumbing on drinking water quality. For this purpose, Total THMs (TTHMs) and water quality parameters (temperature, pH, free chlorine residuals, and TOC) were collected from the four drinking fountains located on the second and third floors of a combined conventional and green-certified building. The building was selected as the sampling location considering its unique structure to eliminate the effects of variables such as distance to the water utility entrance point, water usage rate, and variations in distributed water quality to the buildings. The findings of this study showed that even though the same quality of water was distributed to the green and conventional building sides, statistically significant differences in water quality parameters and TTHM formations were observed between some of the drinking fountains due to the changes in water chemistry in the premise plumbing systems. This study points out the impacts of the physical factors (e.g., system age) on water quality.

Chapter 3: A State-of-the-Art Review of Contaminant Prediction Models for Premise Plumbing Systems and Indoor Air Environments

The second study provides a comprehensive review of existing contaminant prediction models that could be implemented in residential and non-residential buildings, specifically for premise plumbing systems. In the review, considering the importance of inhalation exposure due to contaminated water use in indoor environments, contaminant prediction models for indoor air quality were also included. A systematic literature search was conducted in the Compendex, Web of Science, IEEE Explore, Science Direct, and PubMed databases. The inclusion and exclusion criteria were applied to select the relevant studies for this review. After three publication screening steps, a total of 22 modeling studies for premise plumbing and 12 for indoor air quality were reviewed. This study provides an insight into the current state of premise plumbing and indoor air quality modeling. Additionally, this study identifies the research gaps and highlights future research trends.

Chapter 4: Development of a Disinfection By-product Prediction Simulation Model in a Premise Plumbing System

The third study aimed to implement a first-order chlorine decay model to predict and simulate chloroform concentration within a premise plumbing system for eight hours of stagnation. For this purpose, bench-scale experiments were conducted to determine prediction model coefficients considering the water quality parameter ranges reported for premise plumbing systems. The fitted model coefficients were incorporated into simulation software. Chloroform concentrations were tested in a two-story townhouse; experimental and model prediction results were compared. The prediction model underpredicted the chloroform concentrations compared with the house measurements. This study is an important initial attempt in developing a simulation-based water quality prediction model, which can be implemented in premise plumbing systems and can be used by building and facility managers as a decision-making tool to improve water quality at the point of use under normal operations and during extended building closures such as the ones caused by COVID-19.

In the following chapters, three articles are presented with their introduction and purpose, literature review, methodology, results and discussions, and conclusions with further research directions. The significant findings of the studies, research contributions, and future research directions are summarized in the final chapter.

1.2. References

Centers for Disease Control and Prevention. (2016). Disinfection by-products. Retrieved from https://www.cdc.gov/safewater/chlorination-byproducts.html

Chowdhury, S., Champagne, P., and McLellan, P. J. (2009). "Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review". *Science of the Total Environment,* 407(14), 4189-4206.

Chowdhury, S., Rodriguez, M. J., Sadiq, R., and Serodes, J. (2011). "Modeling DBPs formation in drinking water in residential plumbing pipes and hot water tanks". *Water Research,* 45(1), 337-347.

Dion-Fortier, A., Rodriguez, M. J., Sérodes, J., and Proulx, F. (2009). "Impact of water stagnation in residential cold and hot water plumbing on concentrations of trihalomethanes and haloacetic acids". *Water Research,* 43(12), 3057-3066.

Julien, R., Dreelin, E., Whelton, A. J., Lee, J., Aw, T. G., Dean, K., and Mitchell, J. (2020). "Knowledge gaps and risks associated with premise plumbing drinking water quality". *AWWA Water Science,* 2(3), e1177.

Nguyen, C., Elfland, C., and Edwards, M. (2012). "Impact of advanced water conservation features and new copper pipe on rapid chloramine decay and microbial regrowth". *Water Research,* 46(3), 611-621.

Rhoads, W. J., Pruden, A., and Edwards, M. A. (2016). "Survey of green building water systems reveals elevated water age and water quality concerns". *Environmental Science: Water Research & Technology,* 2(1), 164-173.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., and DeMarini, D. M. (2007). "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research". *Mutation Research,* 636(1), 178-242.

U.S. Environmental Protection Agency. (2017). Ground Water and Drinking Water. Retrieved from https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Byproducts

United Nations General Assembly. (2010). *Resolution A/RES/64/292*. Retrieved from https://www.un.org/waterforlifedecade/human_right_to_water.shtml#:~:text=On%2028%20July%202010%2C%20through,realisation%20of%20all%20human%20rights.

Zheng, M., He, C., and He, Q. (2015). "Fate of free chlorine in drinking water during distribution in premise plumbing". *Ecotoxicology,* 24(10), 2151-2155.

CHAPTER. 2: A Case Study: Comparison of Disinfection By-product Formations Between Green and Conventional Buildings

2.1. Introduction and Purpose

Disinfection by-products (DBPs) have challenged water authorities since the 1970s. During a routine water quality check, Rook (1974) observed new spikes on the chromatograph and determined the spikes were results of reactions between chlorine and natural organic matter (NOM) in water, such as humic substances. Today, testing can identify hundreds of halogenated DBPs in drinking water; some of the halogenated DBPs are trihalomethanes (THMs), haloacetic acids (HAAs), halo ketones (HKs), haloacetonitriles (HANs), cyanogen chloride, chloral hydrate, and chloropicrin (CP) (Singer, 1994). THMs are the most ubiquitous DBPs in drinking water and are extensively investigated in the literature. Chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$), and bromoform ($CHBr_3$) are THMs, and the sum of individual THMs' concentrations make up the total THMs (TTHMs).

Upon THMs' discovery, many epidemiological and toxicology studies have been conducted, and some of THMs are identified as probable human carcinogens (e.g., bromodichloromethane), while some are trans-species carcinogens (e.g., chloroform) (Richardson et al., 2007). The long-term exposure to chlorinated water was linked to an increased risk of colon cancer in males (King et al., 2000). In another study, bladder cancer risk was found to be 1.63 times more for 35 years of exposure or more compared to 10 years of exposure to chlorination by-products (King & Marrett, 1996).

These studies have promulgated the water quality standards for THMs, and over the years, the compliance requirements have been improved to protect public health by limiting exposure to these contaminants. Currently, THM and five haloacetic acid (HAA5) levels are regulated at the level of public water systems (PWSs) according to Stage 1 and Stage 2 Disinfectants and Disinfection By-products Rules (DBPRs). The maximum contaminant level (MCL) allowed in drinking water determined by the Environmental Protection Agency (EPA) is 0.080 mg/L for the THMs and 0.060 mg/L for the HAA5.

Currently, drinking water quality is regulated at the distribution system level. However, premise plumbing systems are unique and different from water distribution systems due to a large surface area to-water volume ratio, smaller pipe diameters, intermittent and frequent stagnation conditions, higher residence times, elevated and variable water temperatures, redox potentials, deposit accumulation, and lower flow rates (Nguyen et al., 2012; Zheng et al., 2015). Moreover, the previous research shows that higher water quality deterioration occurs in buildings compared to the water distribution systems (Chowdhury et al., 2011; Dion-Fortier et al., 2009). A recent study revealed that there are still knowledge gaps for premise plumbing in residential and non-residential buildings under routine operations; and water quality has not been fully understood for different operation scenarios (e.g., use of water-efficient fixtures in conventional buildings) and building types (e.g., green-certified buildings) (Julien et al., 2020).

Given this gap, this study's purpose is to identify the effects of building type on premise plumbing water quality. For this purpose, temperature, pH, free chlorine levels, total organic carbon (TOC) and TTHM levels taken from the drinking fountains were compared between a combined conventional and green-certified building. As such, this study contributes to the body of knowledge by providing a better understanding of the effects of green building practices on drinking water quality.

2.2. Literature Review

2.2.1. Influential Factors on Chlorine Decay and THM Formation Kinetics

Despite the existence of other disinfection methods (e.g., chloramines, ultraviolet light, potassium permanganate, and ozone), chlorine is the most commonly used disinfectant due to its effectiveness in controlling microbiological growth, easy application, sustained residual levels, and cost-effectiveness (Al-Jasser, 2007). However, chlorination requires relatively tight control. Low chlorine doses can exacerbate microbial activities, whereas excess chlorine doses promote DBPs formation. To overcome this issue, and considering chlorine is a limiting factor for DBPs formation, many researchers investigated: i) reaction kinetics of chlorine with organic and inorganic compounds and ii) predictive DBP models to assist decision-makers in their management decisions (Chowdhury et al., 2009). Since monitoring DBPs can be time-consuming and often requires expensive techniques, predictive modeling has gained importance in quantifying DBP levels (Sadiq & Rodriguez, 2004). Most models utilize statistical methods such as non-linear regression using one or more field and laboratory water sample results in the prediction process (Sadiq & Rodriguez, 2004). Prediction models are outside of the scope of this study, and detailed information on these models can be found elsewhere (See Chowdhury et al., 2009; Sadiq & Rodriguez, 2004).

Chlorine dose, pH, temperature, water, and pathogen characteristics are considered to be highly influential on chlorination efficiency (Brown et al., 2011). Vasconcelos et al. (1997) suggested that chlorine demanding reactions with organic and inorganic compounds, biofilm on the pipe wall, corrosion, and mass transfer of chlorine between bulk water and pipe wall should all be considered in chlorine dose selection. Chlorine chemistry is pH dependent; at lower pH values (3-7) hypochlorous acid (HOCl) predominates whilst above 7.5 HOCl further disassociates into hypochlorite ions (OCl^-) and hydrogen ions (H^+) and OCl^- becomes the dominant species (Gordon & Tachiyashiki, 1991; Hung et al., 2017). Thus, lower pH values are favored to maintain higher HOCl levels in drinking water due to its inactivation power on pathogens (Brown et al., 2011). Mutoti et al. (2007) found that a 10 °C increase in water temperature (21 °C vs. 31 °C) tripled chlorine consumption rates. Beyond the factors given above, different premise-plumbing pipe materials showed variability in reacting with free residual chlorine. For instance, higher chlorine decay rates were observed for copper pipes compared to galvanized iron and polyvinyl chloride (PVC) (i.e., copper > galvanized iron > PVC), suggesting that higher chlorine concentrations should be considered for copper plumbing pipes. Cleaning the pipe deposits in the copper pipes enhanced the kinetic reactions significantly between chlorine and cleaned copper surfaces, resulting in higher chlorine decay rates. This finding implies that deposits slow the oxidization process between free chlorine and copper pipe walls. When the deposits were cleaned in PVC and galvanized iron pipes, less difference in decay rates was observed (Zheng et al., 2015). Vasconcelos et al. (1997) found that pipe diameter and chlorine reactions on the pipe wall are inversely related.

Similar to chlorine, other significant factors have been identified for THM formation. According to Liang and Singer (2003), nature and concentration of NOM, pH, water temperature and season, disinfectant dose and residual level, contact time, and bromide concentration are the most substantial factors. Gallard and von Gunten (2002) looked into THM formation potentials based on slow and fast-reacting THM precursors and found that resorcinol and phenol type structures might be considerable on fast and slow THM formations, respectively. Different organic fractions of NOM (e.g., hydrophobic acids, hydrophilic charged acids, hydrophilic neutral compounds) yielded various THM formation rates suggesting that most of the THMs were formed from hydrophilic charged acids (61.7%) (Jegatheesan et al., 2008). The molecular weight fraction of NOM also impacts chlorine demand and TTHM formation rates; a smaller molecular weight fraction of NOM yielded increased TTHM formation while chlorine demand was high for bigger molecular weights (Gang et al., 2003). In another study, Gang et al. (2002) found that alum coagulation reduced DBP formation (i.e., reduced TTHM and HAA formation potentials by 54%) by decreasing chlorine demand and removing some of the organic carbon composition. Adin et al. (1991) observed increased THM formations when pH increased from 4 to 8. The authors explained the relationship between high pH and THM formations with i) increased base-catalyzed hydrolysis (i.e., THM formation mechanism) under alkaline conditions and ii) increased ionization, solubility, and stability of humic molecules at high pH values yielding more contact sites for chlorine attack eventually forming more THMs. Chowdhury et al. (2011) found that THM concentrations were significantly higher during warm months than cold months, and this result was also reported in an earlier study (Golfinopoulos et al., 1998). According to Singer (1994), seasonal effects might occur due to increased water temperature; therefore, increased reaction rates between chlorine and organic compounds and, eventually, increased THM formation is expected.

It is known that chlorine decay can occur in bulk water and on inner pipe surfaces (Vasconcelos et al., 1997). Xu et al. (2018) found chlorine decay and THM formation were higher in the pipes with biofilm depositions than the pipes without biofilm under the same operating conditions, suggesting that reactions with depositions and diffusion into biomass profoundly influence chlorine decay mechanisms. Biofilm properties were also pointed as an important factor in chlorine decay and THM formation in the study. Bromide ion (Br^-) presence in water is another critical factor in DBP formation. As the amount of Br^- increased, the formation of brominated THMs increased while the formation of chlorinated THMs decreased (Clark et al., 2001; Hong et al., 2007). The strength of oxidizing agents explains this phenomenon, as hypobromous acid (HOBr) is stronger than HOCl (Symons et al., 1993).

Most of the research on this topic has been conducted using samples taken from distribution systems; therefore, these samples do not reflect conditions in premise plumbing systems. Premise plumbing systems differ from distribution systems by a large surface area to-water volume ratio, smaller pipe diameter, intermittent and frequent stagnation conditions, higher residence times, elevated and variable temperature, redox potentials, deposit accumulation and, lower flow rates (Nguyen et al., 2012; Zheng et al., 2015). Previous studies have found higher THM levels in premise plumbing than in water distribution systems. Chowdhury et al. (2011) found that THM levels are 136%-181% higher in premise plumbing than in water distribution systems. In another study, the residents' exposure to DBPs in premise plumbing was found to be higher than in distribution systems; based on the collected water samples from six houses supplied by three municipal systems, higher levels of THMs (22.1 µg/L, 43.4 µg/L, 37 µg/L for systems 1, 2, and 3, respectively) and HAAs (8.4 µg/L, 21.4 µg/L, 18 µg/L for systems 1, 2, and 3, respectively) were measured in first drawn water samples compared to the distribution systems (Dion-Fortier et al., 2009).

2.2.2. Water Quality in Green Buildings

Leadership in Energy and Environmental Design (LEED) is one of the most commonly used green rating systems and aims, among other things, to reduce potable water use and wastewater generation by utilizing efficient landscaping systems and using innovative potable water conservation technologies (Benjamin, 2019). The most recent version of LEED (v4 at the time of this study) promotes water efficiency in various sources of water usage (e.g., indoor water use reduction and outdoor water use reduction) in buildings. High-efficiency fixtures, waterless urinals, and composting toilet systems are used in green buildings for purposes of water conservation (Haselbach, 2008). Past research shows that experiences with these water-conservation-related innovations were discrepant among professionals involved with green buildings (Chambers et al., 2017). The baseline water consumption for fixtures (e.g., toilet (water closet): 1.6 gallons per flush (gpf), urinal: 1.0 gpf) listed under LEED v4-WE Prerequisite: Indoor Water Use Reduction can be found in U.S. Green Building Council (2014). Apart from the WE Prerequisite Indoor Water Use Reduction category, further indoor water use reduction is awarded. The credit points might change depending on the building type; however, up to 6 credits could be earned for new construction for a 50% water reduction under this category.

DeOreo et al. (2016) compared indoor water use in single-family residential buildings and found that the average water usage was reduced from 177 gallons per household per day (gphd) in 1999 to 138 gphd in 2016, indicating a 22 percent decrease. This reduction was attributed to water-efficient washing machines and toilets. In another study, comparisons in water use between new and existing single-family houses in the US were made. The results showed that lower water use was observed in new houses with water-efficient features (110 gphd) compared to the houses built before 1995 (177 gphd) and houses built after 2001 (140 gphd) (DeOreo et al., 2011).

Recently, increased water age has been linked to green premise plumbing. Problems such as rapid disinfectant decay rates, increased corrosion in the plumbing system, higher microbial growth rates, and temperature anomalies in cold and hot water systems due to higher water age are anticipated in green-building plumbing systems (Rhoads et al., 2015). Rhoads et al. (2016) found higher bacteria levels in green buildings than conventional buildings, and these deteriorations in water quality were attributed to increased chlorine decay due to increased water stagnation in premise plumbing and water heaters. Greater deterioration of the water quality was observed in the premise plumbing of a green residential building compared to the water in the distribution system (Salehi et al., 2018). In an institutional green building, Richard et al. (2020) found that 95% of the chlorine measurements were under detection limits over six months of sampling. According to another study conducted in a net-zero green building, higher TTHM formation was observed in premise plumbing compared with the water collected at the point of entry of the building. In that study, variations in the concentrations of TTHMs were observed across all fixtures for cold and hot water during different seasons (Salehi et al., 2020).

To date, most of the studies on this topic focused on THMs formation in distribution systems. In a few studies focusing on premise plumbing, water quality parameters were compared between green and conventional buildings; however, the building characteristics were different (e.g., conventional single house building vs. net-zero office building) (Rhoads et al., 2016), which could cause variations in cross-comparison attempts.

In this study, TTHM concentrations collected from water fountains in a combined conventional and green-certified building were compared. It is believed that the unique structure of this building would help isolate some of the uncontrollable factor impacts (e.g., distance to the water utility entrance point, water quality, and water usage rate).

2.3. Methods and Materials

2.3.1. Building Characteristics

A combined conventional and green-certified building located in Colorado, United States, was selected for water samplings. Both parts (conventional and green-certified) of the building are used for educational purposes and contain classrooms, offices, laboratories, and common areas. The conventional part is a 73,027 square feet building that was built in 1975. The green building addition (113,403 square feet) was completed in 2018, and it was awarded LEED Silver, according to LEED BD+C: New Construction (v2009). The water is conserved on the green building side by utilizing low-flow water closets, urinals, public laboratory sinks, and kitchen faucets. As a result of the design efforts, the annual water use was reduced by 42%, and 4 out of 4 possible points were earned under the WEc3 Water Efficiency category according to LEED BD+C: New Construction (v2009). No water conservation features were observed during the building visits on the conventional building side.

Tap water at the building sections is distributed by the public water utility (~5 miles away from the building) that provides water to more than 35,000 customers covering 35 square miles in the area. Chlorine is used as the primary disinfectant at the treatment plant, and the source water (from a river and the reservoir) is treated in the following order: pre-sedimentation basin, rapid mix, flocculation, sedimentation, filtering, clear well, and chlorine contact basin. The water utility brings drinking water to three main meter locations around the campus perimeter. Based on the closest main meter distances, the water travels through 2800 ft (Conventional Side) and 2600 ft (Green Side) of PVC (8") pipes in the campus loop and enters the utility rooms from the building sections' basement levels separately.

For the green building side, the plumbing blueprints were used to estimate the length and volume of the pipes. In this building section, the water is provided from the basement to the upper levels with 2 ½" copper pipes and carried to the drinking fountains with 2" copper plumbing on each floor after the riser runs (Table 1). The drinking fountains are the wall mount, bi-level water cooler stations with a flow rate of 1.1 gallons per minute (GPM) and manufactured by Elkay (Model: VRCTL8WSK). The drinking fountains are equipped with evaporator tanks (i.e., water collection tanks) with embedded thermostat units (Elkay, 2019). Once operated and cold water is drawn from the evaporator tank, the cooling system is triggered to chill freshwater from the premise plumbing up to the selected cooling temperatures.

On the conventional building section, wall mount fully recessed cooler units manufactured by Elkay (Model: Not available) are assembled on each floor. Although the conventional building as-built plumbing drawings were available from 1974, due to the plans' unreadability, the conventional building side's pipes' dimensional characteristics are not presented in Table 1. Later discussions with the facilities managers revealed that copper piping was installed on the conventional building side.

Table 1. Characteristics of the Green and Conventional Building Sides

Parameter	Green Building	Conventional Building
Building Year	2018	1975
Number of Building Floors	4	3
Square Footage	113,403	73,027
Plumbing Material	Copper	Copper
Length & Diameter & Volume of Pipe Feeding Fountains on 2nd-Floor	169 Ft. & 2 ½" and 2" & 5.35 CuFt.	NA
Length & Diameter & Volume of Pipe Feeding Fountains on 3rd-Floor	193 Ft. & 2 ½" and 2" & 5.98 CuFt.	NA
Number of Drinking Fountains	4, Bi-level	4

NA: Not Available

In Figure 1, the monthly water consumption of the building sides is shown for both buildings from October 2018 to December 2020. A two-sample t-test was conducted to identify if there are statistically significant differences between the building sides. The data was checked for two-sample t-test assumptions, and all assumptions are met (i.e., independent observations, observations are from a normal distribution, equal variances (p-value= 0.6744>0.10). The results showed that the mean water consumption differences for conventional and green building sides are not statistically significant at the 0.05 significance level (p> 0.9848). Although water-efficient plumbing components are utilized on the green building side, no statistically significant difference was observed in the water consumption levels between the building sections. This result can be attributed to the green building side having more classrooms and conference rooms, resulting in more occupants and higher water demand. The conventional building side is mainly comprised of private office spaces.

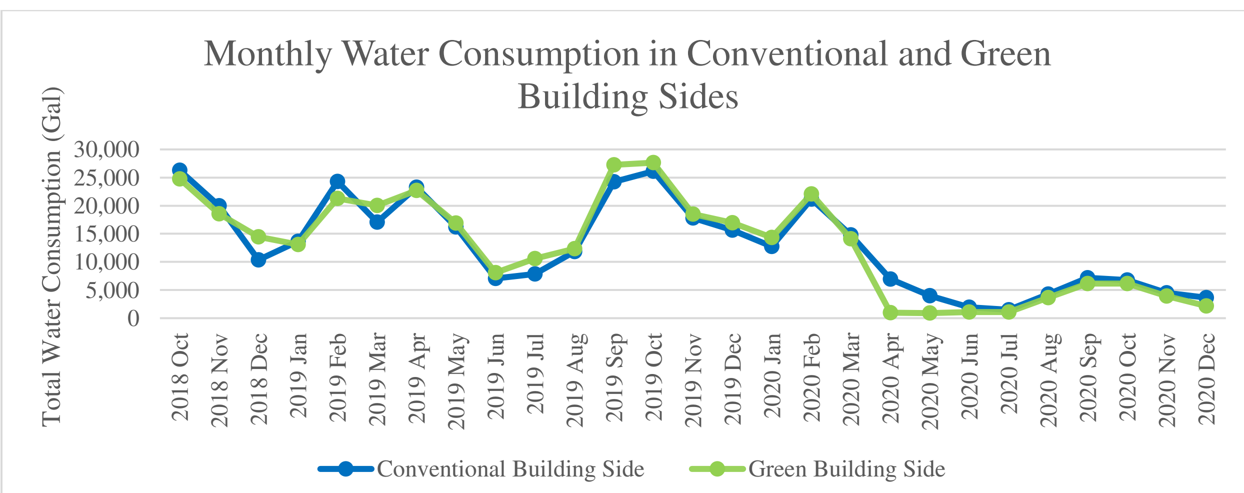

Figure 1. The Distribution of Total Monthly Water Use Based on Building Type

2.3.2. Sample Collection

Two sampling events were conducted inside the building. Sampling Event-1 was conducted from November 16, 2020, through December 1, 2020. Temperature, pH, free chlorine residuals, TOC, and THMs were sampled from a total of four drinking fountains that are located on the second (L2) and third (L3) floors of both green (Gre.) and conventional (Con.) building sections (One fountain each on L2 and L3 of the green building and one fountain each on L2 and L3 of the conventional building). During building visits, it was observed that the cooling unit in the first-floor conventional side fountain was not operating; therefore, the first-floor drinking fountains were excluded from the study. The fourth-floor drinking fountain on the green building side was not included in the study, considering the conventional building does not have the fourth floor. Grab samples from the service lines, hot and cold-water faucets in the restrooms, breakrooms, kitchens, and laboratories were not collected as they were not within the scope of this study. The measurements were taken three times a day (i.e., morning-7:00 AM, noon-12:00 PM, and evening-5:00 PM) for 16 days (including the weekends), yielding a sample size of 192 for THMs, free-chlorine, and temperature, individually. TOC measurements were taken during the morning and evening sampling trips. Due to a few instrumentation challenges, TOC and pH could not be measured on November 19, 20, and 21, 2020, resulting in a total sample size of 104 for TOC and 158 for pH.

Unexpected negative correlations between temperature, free chlorine residuals, and TTHMs collected in the Sampling Event-1 data set prompted another sampling effort; Sampling Event-2 was conducted from December 14, 2020, through December 20, 2020. In this case, the temperature and pH were measured in three sequential samples (40 mL) three times a day from the same fountains sampled in Sampling Event-1. Water samples were collected following the same floor order for both sampling events; Green-L2, Green-L3, Conventional-L3, Conventional-L2.

The building's operation and closure dates were also used in the analyses; the building was fully occupied (i.e., in-session) between November 16 and November 21, 2020. From November 21 to November 29, 2020, the building was closed due to the fall recess (i.e., not in-session). On November 30 and December 1, 2020, the building was accessible again (i.e., in-session). A timeline of sampling and building operation events is given in Figure 2.

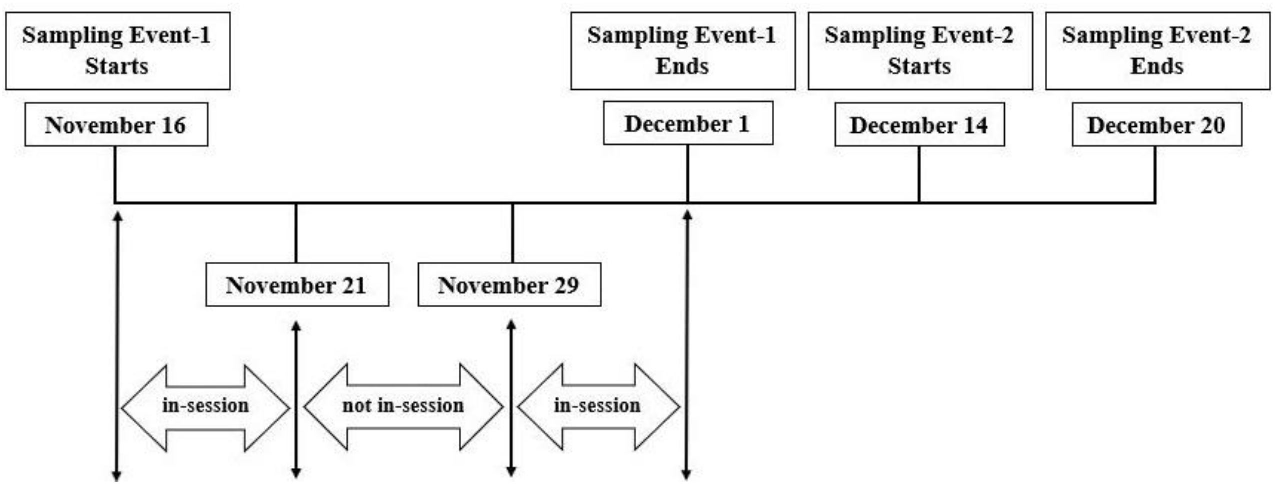

Figure 2. Timeline for Sampling and Building Operation Events

2.3.3. Sampling Preparation and Analytical Methods

40 mL amber glass vials with PTFE/silicone septum caps were used for the samples collected for THM and TOC measurements and were filled headspace-free. The vials for THM sampling were primed according to the USEPA 551.1 method; as specified, phosphate buffer and sodium sulfite reagents were added in the vials before sample collection to adjust pH and quench THM formation, respectively. Based on the recommendations in the followed method (HACH® Method 10129), preservative addition was not considered for the TOC samples. The water

samples were collected in 50 mL polypropylene bottles for pH and temperature measurements. Without prior flush-out, the water samples were immediately collected in the following order: 40 mL for THMs (first vial), 40 mL for temperature and pH (second vial), 10 mL for chlorine (third vial), and 40 mL for TOC (fourth vial). pH, temperature, and free chlorine measurements were taken on-site. Once collected, THM and TOC sample vials were transported in coolers to the laboratory, stored at 4 °C in the dark, and analyzed within 24 hours.

The USEPA 551.1 method was followed to analyze THMs using gas chromatography (Hewlett Packard HP 6890 Series) equipped with an electron capture detector and a DB-5 column (Agilent J&W). The calibration standard mixture (200 µg/mL) was purchased from Millipore-Sigma; a seven-point calibration curve was prepared (1 µg/L, 5 µg/L, 10 µg/L, 50 µg/L, 100 µg/L, 200 µg/L, and 500 µg/L) and analyzed daily for each set of experiments. Dibromochloropropane (DBCP) was used as a surrogate in all field and laboratory control samples.

TOC levels were measured according to HACH® Method 10129 with a HACH® DR/2500 Spectrophotometer. Free chlorine residual measurements were taken using a HACH® Pocket Colorimeter following the DPD (*N, N-diethyl-p-phenylenediamine*) method 8021. Temperature and pH measurements were performed with a handheld pH meter (Dr. Meter-PH 838) and calibrated weekly.

2.3.4. Data Analysis and Statistics

SAS (2015a) was used to perform statistical analysis. The normality of the data was tested; due to the observed non-normal distribution, the non-parametric Kruskal Wallis and the Wilcoxon Signed-Rank tests were utilized. Kruskal Wallis test was used if the water quality parameters and TTHM concentrations were statistically different between building type and floor levels. Morning, noon, and evening concentrations were compared at the fountain level. The impact of occupancy was also investigated by including the building's operation and closure dates; comparisons were conducted for each fountain individually. Kruskal Wallis test reveals the statistical significance but does not provide which groups are different from each other; therefore, a posthoc test, Dwass, Steel, Critchlow-Fligner multiple comparison procedure was followed after the Kruskal Wallis tests (SAS Institute Inc., 2015b). The Wilcoxon Signed-Rank tests were performed to reveal statistically significant differences in temperature and water pH between the first, second, and third grab samples by building type and floor. Pearson correlation analysis was conducted to identify relationships between the water quality parameters and TTHM formation.

2.4. Results and Discussion

2.4.1. Sampling Event-1 Results

2.4.1.1. Temperature and pH by Building Type, Building Floor, and Time of the Day

Table 2 presents the ranges of temperature and pH for the samples collected during the Sampling Event-1. The temperature profiles differed across the drinking fountains; the average temperature was 1-3 °C higher for the green building side (L2: 16.3 °C, L3: 17.3 °C) than the conventional side (L2: 14.1 °C, L3: 15.3 °C). At the 0.05 significance level, the four respective fountains' average temperatures were found statistically significantly different from each other (p-value $<.0001$). Temperature measurements from the morning, noon, and evening sampling events did not show variations by the fountain (p-value>0.05 for all comparisons); these steady water temperatures can be attributed to the thermostat-controlled cooler units in the drinking fountains. Previously, temperature increases (+3-10 °C) were reported in premise plumbing compared to the water entering buildings (Chowdhury et al., 2011; Salehi et al., 2020). In this study, the water temperature is expected to get warmer under stagnant conditions in the premise plumbing before chilled in the fountains. As samples were not collected from other building outlets and the service lines, identifying temperature changes in the premise plumbing is not possible without further sample collection.

Table 2. Sampling Event-1 Temperature and pH Results

Parameter	**Green Building Side**						**Conventional Building Side**					
	L2			**L3**			**L2**			**L3**		
	Mean	**10th % tile**	**90th % tile**	**Mean**	**10th % tile**	**90th % tile**	**Mean**	**10th % tile**	**90th % tile**	**Mean**	**10th % tile**	**90th % tile**
Temp, °C	16.3	15.1	17.3	17.3	16.6	18.0	14.1	12.9	14.8	15.3	14.5	16.0
pH	8.2	8.0	8.4	8.1	7.9	8.4	8.7	8.6	8.8	8.8	8.6	8.9

Including all pH values, 50.6% of the measurements were above the EPA's National Secondary Drinking Water Regulation limit of 8.5 (USEPA, 2020). Water pH was consistently higher on the 2nd-floor (8.3-9.1) and the 3rd-floor (8.6-9.1) conventional side drinking fountains than those of the green building side. Statistically significant differences were found between drinking fountains' pH values except for between the conventional 2nd-floor and 3rd-floor fountains (p-value 0.9101). Morning, noon, and evening pH measurements were not statistically significantly different for any fountains (p-value>0.05 for all comparisons). The pH values reported by the public water utility were used as a benchmark for the in-building measurements. At the entry point of the distribution system, the average water pH taken for three days during the study period was approximately 8, and on those days, most of the pH measurements at the fountains exceeded the public utility measurements. Table 3 shows the average daily water pH at the drinking fountains compared to the public utility measurements. These results might indicate an increase within the building plumbing and support others' findings (Dion-Fortier et al., 2009;

Salehi et al., 2020). The greater pH in the conventional building side drinking fountains was assumed to be resulting from higher alkalinity and mineral scale build-up due to the plumbing system's age (Water Systems Council, 2007); however, further data collection is needed by including other water quality parameters (e.g., alkalinity and hardness) to justify this assumption.

Table 3. Water pH at the Entrance of the Distribution System and the Fountains

Date	Public Utility Measurement	Green Building Side		Conventional Building Side	
		L2	L3	L2	L3
11/16/2020	7.9	8.3	8.4	8.6	8.7
11/23/2020	8	8.1	8.1	8.7	8.7
12/1/2020	8	8.0	8.0	8.8	8.8

2.4.1.2. Chlorine Residual, TOC and TTHM Concentrations by Building Type, Building Floor, and Time of the Day

Chlorine residuals, TOC, and TTHM measurements collected during the Sampling Event-1 are presented in Table 4. The average free-chlorine residuals across drinking fountains were around 0.04-0.05 mg/L-Cl_2. 100% of the samples (n=192) were less than the recommended minimum chlorine residual levels (0.2-0.5 mg/L) at the point of use (WHO, 2011). Undetectable chlorine residuals, specifically in green-certified buildings, were observed in previous studies (Ra et al., 2020; Rhoads et al., 2016; Salehi et al., 2020). A study conducted in an institutional green building showed that 98% of the first draw and 97% of the second draw chlorine measurements were less than the method detection limit (0.02 mg/L-Cl_2) through the six-month sampling period (Richard et al., 2020). In the presented study, lower chlorine residuals resulting from high water stagnation were expected on the green building side fountains considering the water conservation efforts. However, there was no statistically significant difference in chlorine residuals between the conventional and green building fountains at different building levels (e.g., Gre-L2 vs. Gre-L3 vs. Con-L2 vs. Con-L3) (p-value>0.05 for all comparisons). A potential change in disinfectant residuals during the daytime was also investigated; the morning, noon, and evening levels were compared for each drinking fountain individually. Despite the free chlorine concentrations taken five hours apart, the measurements did not show significant changes (Morning vs. Noon, Noon vs. Evening, Morning vs. Evening; p-value >0.05 for all comparisons). Assuming that the freshwater with higher free chlorine levels was not drawn from the distribution system between the sampling times, observed low chlorine levels might imply the lack of water use in the building. The lowest pH value was 7.8 in the building; thus it is expected that OCl^- was the dominant chlorine species (Hung et al., 2017).

Table 4. Sampling Event-1 Free Chlorine Residual, TOC, and TTHM Results

Parameter	**Green Building Side**						**Conventional Building Side**					
	L2			**L3**			**L2**			**L3**		
	Mean	**10th % tile**	**90th % tile**	**Mean**	**10th % tile**	**90th % tile**	**Mean**	**10th % tile**	**90th % tile**	**Mean**	**10th % tile**	**90th % tile**
Free Cl_2, mg/L	0.05	0.02	0.09	0.05	0.02	0.08	0.04	0.02	0.08	0.05	0.02	0.08
TOC, mg/L	1.4	0.6	2.1	1.6	0.7	2.1	1.5	0.4	2.6	1.4	0.5	2.1
TTHM, µg/L	45.7	32.5	55.1	44.9	35.6	58.4	52.6	43.6	63.2	54.1	40.5	69.2

Average TOC levels showed similar trends for all drinking fountains (i.e., Gre-L2: 1.4 mg/L; Gre-L3: 1.6 mg/L; Con-L2: 1.5 mg/L; Con-L3: 1.4 mg/L). Figure 3 shows a box and whisker plot (the minimum, the lower quartile, the median, the upper quartile, the maximum, and the outliers are shown) for TOC concentrations by building type and floor. On November 16, 2020, a TOC level of 1.38 mg/L was reported by the public utility at the distribution system entrance. This value was mostly less than the building measurements taken on the same day (i.e., Gre-L2: Morning: 1.6 mg/L-Evening: 0.9 mg/L; Gre-L3: 1.3-2.1 mg/L: Con-L2: 2.5-1.5 mg/L; Con-L3: 2.1-1.9 mg/L). The highest TOC level was observed (6.9 mg/L) in the 3rd-floor green building drinking fountain and occurred only once. This outlier might result from the water quality changes in the distribution systems due to hydraulic disturbances (Gauthier et al., 1999) or could be an instrumentation error. Statistically significant differences in TOC levels were not found between the drinking fountains (p-value 0.8215) and also not observed when morning and evening concentrations were compared for each drinking fountain separately (p-value >0.05 for all comparisons).

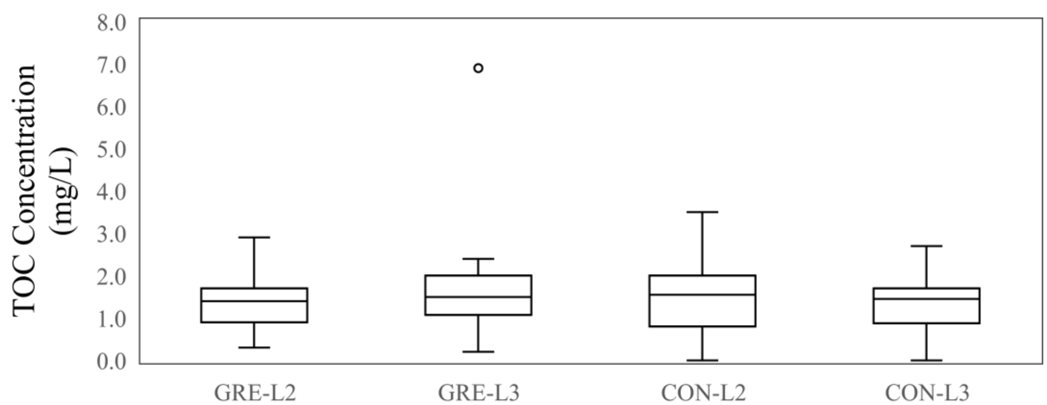

Figure 3. The Box Plot for TOC Variations for Green and Conventional Building Drinking Fountains

Chloroform contributed to the highest proportion of TTHMs (average of 90% of TTHMs in Con., 89% of TTHMs in Gre.), while bromoform accounted for the lowest percentages (average of 0.11% of TTHMs in Con., 0.12% of TTHMs in Gre.).These findings are expected for surface waters with low bromide ion concentrations (Clark et al., 2001) and observed in other studies (Dion-Fortier et al., 2009). Hohner et al. (2016) tested bromide concentrations at the public utility intake and did not detect bromide in surface waters that feed water to the city.

Greater average TTHM levels were found in the conventional building side (L2: 52.6 µg/L, L3: 54.1 µg/L) than green building side drinking fountains (L2: 45.7 µg/L, L3: 44.9 µg/L). Figure 4 shows TTHM concentration changes (i.e., daily highest TTHMs) over the sampling period; on November 24, major increases in TTHMs were observed for all drinking fountains. On this date, the building was closed due to the fall recess. After Thanksgiving (November 25, 2020), no students but a few faculty and researchers were present in the building who had special permission to access the building. These occupant activities might explain the slight TTHM decreases in the following days after Thanksgiving. Currently, no Maximum Contaminant Level (MCL) is available for TTHM levels at the tap; however, the annual averages of THMs should not exceed 80 ppb at the treatment plant (USEPA, 2016). In the literature, long-term ingestion exposure to TTHMs was associated with increased bladder cancer (≥ 50 µg/L) (King & Marrett, 1996), spontaneous abortion (≥75 µg/L) (Waller et al., 1998), colon cancer (≥50-75 µg/L) (King et al., 2000). High concentrations with potential adverse health effects (e.g., 126.5 µg/L, 80.6 µg/L, 79.0 µg/L) were observed when the building was closed during the fall recess and could be eliminated by conducting building flush-out. For longer breaks (e.g., summer break), flushing procedures that are not tailored for specific plumbing designs might not be effective in reducing some contaminants (e.g., copper) in the drinking water (Ra et al., 2020).

There was a significant difference in TTHM levels between the drinking fountains (p-value <.0001). Further investigation of the data revealed that any comparison combinations except Gre-L2 vs. Gre-L3 (p-value: 0.7963) and Con-L2 vs. Con-L3 (p-value: 0.9985) were statistically significantly different, suggesting that TTHM concentrations were affected by the building type but did not differ based on the building floor in their respective building sides. TTHM levels did not show any statistically significant differences between morning, noon, and evening samplings for each drinking fountain. Although temperatures were colder than the green building side fountains, higher TTHMs were found in the conventional building fountains. This could be due to higher water pH levels. Past studies revealed the relationship between increased TTHM formation at elevated pH levels (Adin et al., 1991; Chowdhury & Champagne, 2008; Salehi et al., 2020). Salehi et al. (2020) found that increasing water pH from 7.8±0.4 to 9 resulted in a 9% to 35% increase in TTHM formation.

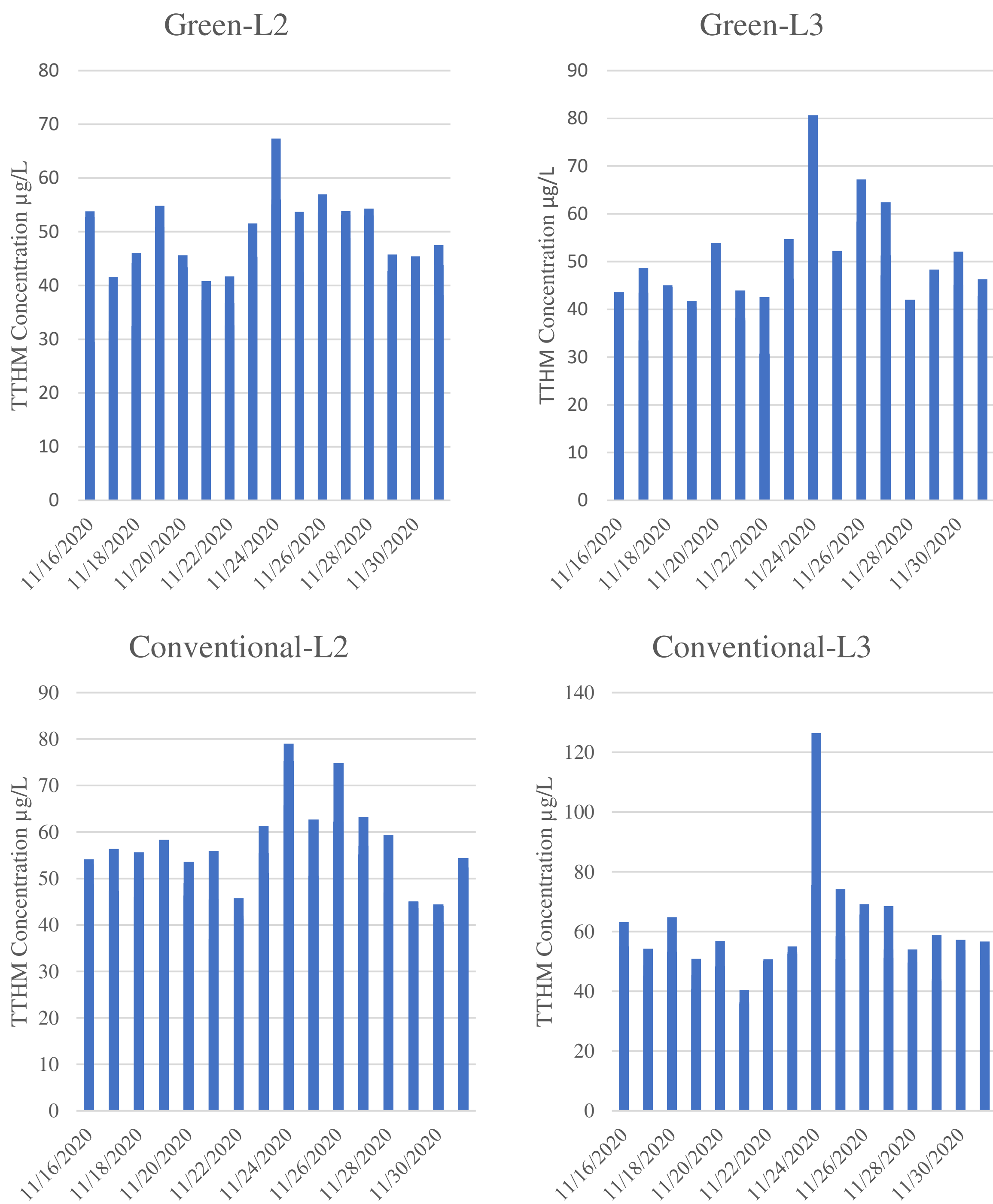

Figure 4. TTHM Concentrations by Drinking Fountains

2.4.1.3. Water Quality When Building In-session and Not-in-session

Water stagnation and water use effects on water quality parameters and TTHMs were investigated by including the building's operation and closure dates. None of the water quality parameters or TTHMs showed statistically significant differences when the building was in-session and not in-session. TTHM concentrations are provided as an example in Table 5. Although higher TTHM concentrations were observed when the building was not occupied (i.e., not in-session), statistically significant differences were not identified.

Table 5. Comparisons of TTHM Concentrations When the Building was in Session vs. Not in Session

Occupancy	Parameter	Green Building Side						Conventional Building Side					
		L2			L3			L2			L3		
		Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
In- Session	TTHM, μg/L	42.6	29.5	54.8	42.1	29.9	53.9	49.9	40.6	58.3	50.9	37.4	64.8
Not In-Session		48.1	32.5	67.4	47.2	30.4	80.6	54.6	37.0	79.0	56.6	35.9	126.5

2.4.1.4. Correlation Analyses Between TTHMs and Water Quality Parameters

Considering the dependency of TTHM formations on the collected water quality parameters, correlation analyses were conducted on the Sampling Event-1 data to answer how water quality parameters affect TTHM generation. The Pearson correlation coefficients and p-values that show the relationship strength and significance probability between TTHMs and water quality parameters are presented in Table 6. A significant negative correlation between TTHMs and temperature (p-value: 0.0350) was observed, while the p-value of 0.1126 did not provide enough evidence to support the negative correlation between TTHMs and chlorine. Other researchers postulate an increase in TTHMs when temperature, pH, free chlorine residuals, and TOC levels increase (Chowdhury & Champagne, 2008). Thus, it is hypothesized that negative correlations might be observed due to the water sampling order (i.e., 40 mL for THMs (first vial), 40 mL for temperature and pH (second vial), 10 mL for chlorine (third vial), and 40 mL for TOC (fourth vial)). These unexpected results might indicate that the sequentially collected water quality parameters do not fully represent the water quality in the first drawn sample for TTHM collections. To the authors' knowledge, negative correlations between TTHMs and selected water quality parameters have not been presented in the literature, and thus, this finding might suggest that sequential sampling should be considered when measuring THMs in stagnant water, especially in drinking fountains. This discovery in the Sampling Event-1 data prompted a further sample collection (i.e., Sampling Event-2) to investigate the reasons for negative correlations.

Table 6. Correlation Coefficients and P-Values Between Water Quality Parameters and TTHM Concentrations

Parameter	TTHMs	pH	Temperature	TOC	Chlorine
TTHMs Correlation Coefficient	1.00000	0.28373	-0.15227	0.16505	-0.11489
p-value		0.0003	0.0350	0.0941	0.1126

2.4.2. Sampling Event-2 Results

2.4.2.1. Temperature and pH Differences Between Three Sequential Sample Collections

In Sampling Event-2, by sequentially collecting 40 mL of water three times a day from the same drinking fountains, temperature and pH variances were evaluated from one sample to another (n= 84). The measurements in sequential samples were treated as paired observations (i.e., Difference-1=First draw-Second draw; Difference-2=First draw-Third draw; Difference-3= Second draw-Third draw) to determine the temperature and pH differences between the draws.

Temperature differences in sequential samples were statistically significantly different from zero (p-value <0.0001 for all comparisons), suggesting that temperature changes occurred from one sample to another for separate drinking fountains. Temperature variations in first and second drawn water were observed in another study conducted in a green institutional building, but as opposed to drinking fountains, the samples were taken from the breakroom faucets; higher temperatures were found in the first draw samples (Richard et al., 2020). Only a few exceptions were observed when comparing pH differences between draws for each drinking fountain. pH differences were statistically significantly different from zero for all paired observations except the green building second-floor drinking fountain (p-value > 0.05 for Difference-2) and the green building third-floor drinking fountain (p-values > 0.05 for Difference-1, Difference-2, Difference-3, individually).

Figure 5 shows the average temperature and pH of each tested sample volume. As seen, a downward trend in temperatures was observed between draws for each drinking fountain, while water pH showed variances. Decreasing temperatures in draw 1 through 3 explain the negative correlation between temperature and TTHMs collected in Sampling Event-1. Thus, it can be concluded that the water temperature was high in TTHM collection vials (i.e., first 40 mL) that coincide with the water volume in the bubbler and continuing piping and decreased in the temperature measurement bottle (i.e., second 40 mL) due to draw water from the evaporator tank. Free chlorine measurements were not further taken in Sampling Event-2 to investigate negative correlations between TTHMs and chlorine; however, it is expected that bubblers, internal piping, and evaporation tanks reacted differently with chlorine resulting in different disinfectant residuals in different sections of the fountains. In the literature, significant bacterial load profiles were also observed between different plumbing sections (e.g., faucet, flexible connection pipe, horizontal riser) (Bédard et al., 2018). This would be an area for future research to determine how bacterial profiles change in different fountains sections and affect the residual chlorine levels.

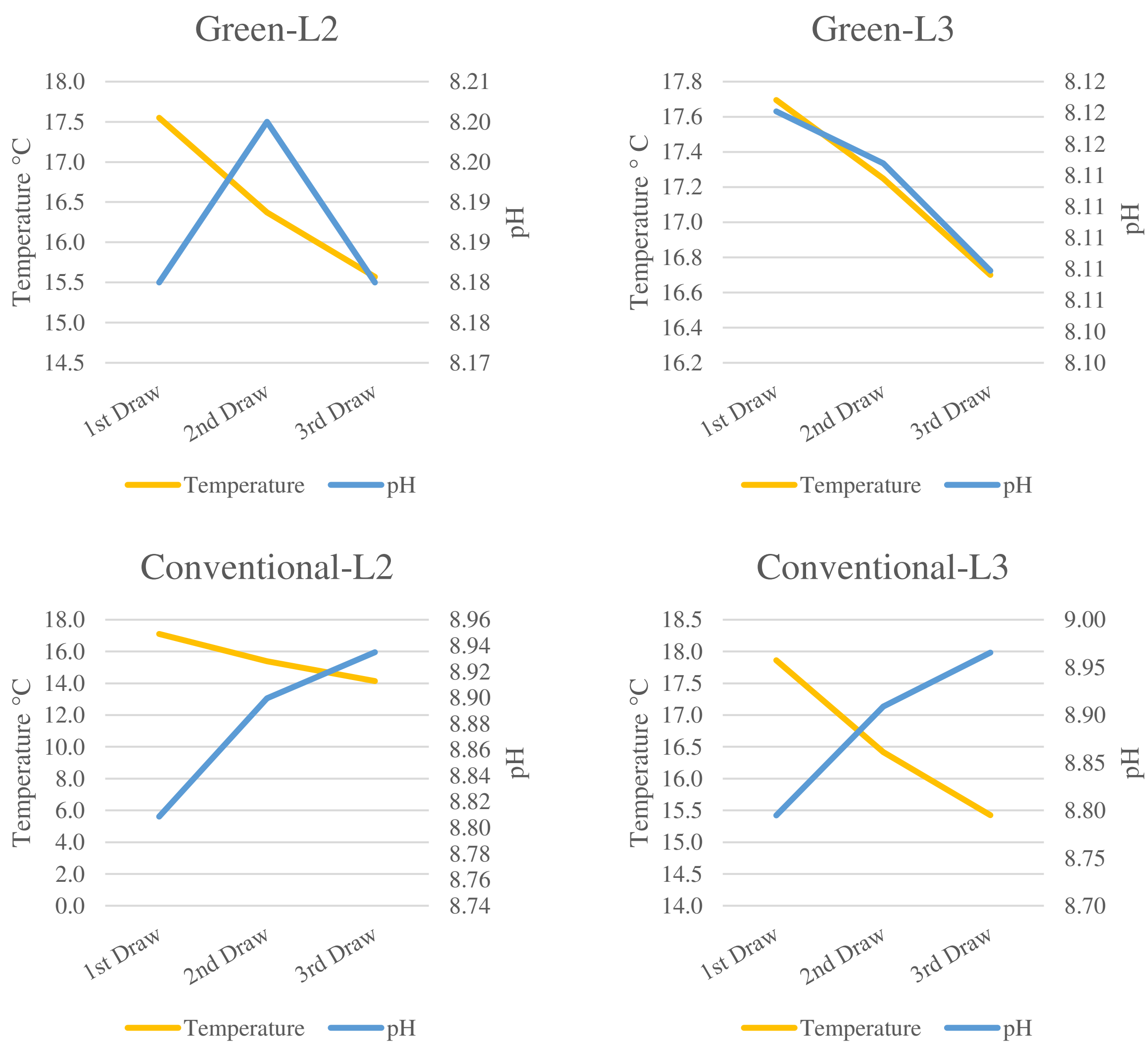

Figure 5. Average Temperature and pH Between 1st, 2nd, and 3rd Collected Samples

2.4.2.2. First Drawn Water Temperature and pH By Building Type, Building Floor

The Kruskal Wallis test was conducted on the first drawn water temperature and pH values of the Sampling Event-2 to explore significant differences between the drinking fountains. This analysis was used to elucidate the temperature variances in the TTHM vials collected during the Sampling Event-1. The p-value of 0.0007 suggested a statistically significant difference in the first drawn water temperatures; variations were observed between Gre-L3 vs. Con-L2 (p-value 0.0149) and Con-L3 vs. Con-L2 (p-value 0.0004) drinking foundations. Similar analyses were conducted for water pH in the first drawn water volume. Statistically significant differences were found for all comparisons except Con-L2 vs. Con-L3 (p-value 0.7919). The comparisons of temperature and water pH between Sampling Event-1 and Sampling Event-2 are presented in Table 7. As shown in the table, the temperatures for all drinking fountains were higher in Sampling Event-2 than Sampling Event-1. On the other hand, similar water pH was observed for both sampling events; Con-L2 and Con-L3 pH measurements were consistently higher than Gre-L2 and Gre-L3 measurements. Assuming temperature measurements taken during Sampling Event-2 represent temperatures in TTHM collection vials (Sampling Event-1, first vial), high temperature and pH variables might explain high TTHM formations in the conventional side second-floor and third-floor drinking fountains. Although water temperatures were high for Gre-L2 and Gre-L3 drinking fountains, lower TTHM levels were likely observed due to lower pH than Con-L2 and Con-L3.

Table 7. Comparisons of Temperature and pH Values Between Sampling Event-1 and Sampling Event-2

Parameter	**Building Type/Floor**	**Sampling Event-1**	**Sampling Event-2 (First Draw)**
Temperature °C	Gre-L2	16.3	17.5
	Gre-L3	17.3	17.7
	Con-L2	14.1	17.1
	Con-L3	15.3	17.9
pH	Gre-L2	8.2	8.2
	Gre-L3	8.1	8.1
	Con-L2	8.7	8.8
	Con-L3	8.8	8.8

Including all drinking fountain measurements for each sampling event, the average temperature was 15.8 °C for the Sample Collection Event-1 data set, while the average was 17.6 °C for the Sample Collection Event-2 (for first draw water results). On the contrary, water pH averages did not change between Sample Collection Event-1 (pH: 8.5) and Sample Collection Event-2 (pH: 8.5).

2.5. Conclusions

This study aimed to identify and compare the impacts of conventional and green building premise plumbing systems on drinking water quality. For this purpose, temperature, pH, free chlorine residuals, TOC, and THMs were sampled from four drinking fountains that are located on the second and third floors of a combined conventional and green building. The building was selected as the sampling location considering its unique structure to eliminate the effects of variables such as distance to the water utility entrance point, water usage rate, variations in distributed water quality to the buildings, and provide a better comparison.

Although the same public utility distributed water to both buildings, differences in some water quality parameters and TTHM formations were identified, as discussed below. These differences could be resulting from plumbing pipe or drinking fountain characteristics such as plumbing piping age and drinking fountain cooler unit settings.

Temperatures were statistically significantly different for all four drinking fountains regardless of their building type or building floor; lower temperatures (1-3 °C) were observed in the conventional side drinking fountains. Water pH values showed statistically significant differences for all comparison combinations except the conventional second and third-floor drinking fountains. High pH was observed in the conventional building fountains than the green building fountains. Overall, 50.6% of the measured pH values exceeded the recommended pH limit of 8.5 in drinking water (USEPA, 2020). Comparisons of chlorine residuals between the drinking fountains on the green and conventional buildings sides did not show any statistically significant differences. The average free chlorine residuals were measured around 0.04-0.05 mg/L-Cl_2 for each drinking fountain; 100% of the samples were under the minimum recommended levels at the point of use (WHO, 2011). These trends have been reported for green-certified buildings (Richard et al., 2020), and similar results were found for the conventional building in this study. Similar average TOC levels ranging from 1.4 to 1.6 mg/L were observed across the green and conventional side drinking fountains; no statistically significant difference was observed. TTHM values were higher in the fountains on the conventional building side than the green building side. Statistically significant differences were found for all comparisons except Con-L2 vs. Con-L3 and Gre-L2 vs. Gre-L3 drinking fountains, showing that building type affected TTHM formations while the building floor was not influential in their respective building sides.

Increased water age is anticipated in green-certified buildings due to the utilization of water-efficient plumbing components (Rhoads et al., 2016). In this study, it was expected that higher water stagnation would yield higher TTHM levels on the green building side; however, greater TTHM concentrations were observed in the conventional side drinking fountains. This result was associated with significantly high pH values that were observed in the conventional side drinking fountains. Although the cause of high pH on conventional building plumbing is unclear and requires further research, this result might be related to high water alkalinity and mineral scale build-up in relatively older plumbing pipes of the conventional building. Water age was not measured in this study; however, assuming that water age was high in the green building drinking fountains, it might be concluded that water pH is more influential than water age in

TTHM formation, resulting in high concentrations in the conventional building side drinking fountains.

TTHMs and the water quality parameters did not show any statistically significant differences between sampling time (e.g., morning, noon, evening) comparisons for each drinking fountain. For temperature measurements, it is believed that this result occurred due to the cooling unit presence in the drinking fountains, proving steady water temperatures based on the selected thermostat control settings.

Building operation conditions (such as in-session vs. not in-session) did not affect the water quality parameters and disinfection by-product formation. For several samples, TTHM concentrations exceeding 80.0 μg/L were observed at the drinking fountains when the building was not in-session. Although THMs are not regulated at the tap, these exceeding concentrations could pose a health risk to the public in the long-term exposure; therefore, precautions such as building flush-out should be considered before opening buildings after long water stagnation periods.

Observed negative correlations between TTHMs and water quality parameters in the Sampling Event-1 data prompted another sample collection (i.e., Sampling Event-2) to investigate the cause of negative relationships between the variables. For this purpose, water temperature and pH were consecutively measured in three sample vials from each drinking fountain; the results show that temperatures and water pH changed from one vial to another, underlining the possibility of water quality fluctuations in different sections of the water fountains. Higher temperatures were found in the first drawn samples collected in Sampling Event-2 compared to Sampling Event-1 temperatures measured in the second drawn samples. This finding might explain that the negative correlations between TTHMs and temperatures occurred because of the conducted sampling order in Sampling Event-1. Therefore, it is suggested that sequential order sampling should be taken into account in determining water quality sampling protocols for drinking fountains and THMs testing in the future.

The findings of this study point out the importance of the plumbing pipe age and its impacts on water chemistry. Even though the same quality of water was distributed to the green and conventional building sides, variations in water quality parameters and TTHMs were observed due to the changes in water chemistry in the premise plumbing systems. To better understand the effects of green and conventional buildings design on water quality, more equivalent buildings in the plumbing age aside from already established water quality determinants (e.g., water consumption, piping materials) should be considered for future research. Experimental setups such as Home Plumbing System (HPS), which was used to examine other premise plumbing-related issues (e.g., copper) (Cahalan & Lytle, 2017), could be considered for future research to assess water quality differences between green and conventional building premise plumbing systems. Although laboratory experiments might not reflect water quality in actual buildings, it is believed that controlled experiments that allow testing parameters such as water age could be helpful to capture water quality changes between and within green and conventional buildings. Water chemistry is complex; therefore, more data points, including more water quality parameters, are needed to capture the effects of water conservation strategies (commonly used in green buildings) on water quality.

2.6. References

Adin, A., Katzhendler, J., Alkaslassy, D., and Rav-Acha, C. (1991). "Trihalomethane formation in chlorinated drinking water: a kinetic model". *Water Research,* 25(7), 797-805.

Al-Jasser, A. O. (2007). "Chlorine decay in drinking-water transmission and distribution systems: pipe service age effect". *Water Research,* 41(2), 387-396.

Bédard, E., Céline, L., Déziel, E., and Prévost, M. (2018). "Impact of stagnation and sampling volume on water microbial quality monitoring in large buildings". *PloS One,* 13(6).

Benjamin, H. (2019). Conserving water for all people through LEED v4.1. Retrieved from https://www.usgbc.org/articles/conserving-water-all-people-through-leed-v41

Brown, D., Bridgeman, J., and West, J. R. (2011). "Predicting chlorine decay and THM formation in water supply systems". *Reviews in Environmental Science and Bio/Technology,* 10(1), 79-99.

Cahalan, K., and Lytle, D. (2017). *A simulated household plumbing system to understand water quality and corrosion.* Presented at the American Water Works Association Annual Conference & Exhibition, Denver.

Chambers, B., Pearce, A., Edwards, M., and Dymond, R. (2017). "Experiences of green building professionals with water-related systems". *Journal - American Water Works Association,* 109, 37-46.

Chowdhury, S., and Champagne, P. (2008). "An investigation on parameters for modeling THMs formation". *Global Nest Journal,* 10(1), 80-91.

Chowdhury, S., Champagne, P., and McLellan, P. J. (2009). "Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review". *Science of the Total Environment,* 407(14), 4189-4206.

Chowdhury, S., Rodriguez, M. J., Sadiq, R., and Serodes, J. (2011). "Modeling DBPs formation in drinking water in residential plumbing pipes and hot water tanks". *Water Research,* 45(1), 337-347.

Clark, R. M., Thurnau, R. C., Sivaganesan, M., and Ringhand, P. (2001). "Predicting the formation of chlorinated and brominated by-products". *Journal of Environmental Engineering,* 127(6), 493-501.

DeOreo, W. B., Mayer, P. W., Dziegielewski, B., and Kiefer, J. (2016). *Residential end uses of water, version 2* (1605732354). Retrieved from https://www.waterrf.org/research/projects/residential-end-uses-water-version-2

DeOreo, W. B., Mayer, P. W., Martien, L., Hayden, M., Funk, A., Kramer-Duffield, M., and Davis, R. (2011). *California single-family water use efficiency study*. Boulder, Colorado, USA. Retrieved from https://www.irwd.com/images/pdf/save-water/california_single_family_water_use_efficiency_study.pdf

Dion-Fortier, A., Rodriguez, M. J., Sérodes, J., and Proulx, F. (2009). "Impact of water stagnation in residential cold and hot water plumbing on concentrations of trihalomethanes and haloacetic acids". *Water Research,* 43(12), 3057-3066.

Elkay. (2019). *VRC8TLWS™ series water coolers with EZH2O® bottle filling stations*.

Gallard, H., and von Gunten, U. (2002). "Chlorination of natural organic matter: kinetics of chlorination and of THM formation". *Water Research,* 36(1), 65-74.

Gang, D., Clevenger, T. E., and Banerji, S. K. (2003). "Relationship of chlorine decay and THMs formation to NOM size". *Journal of Hazardous Materials,* 96(1), 1-12.

Gang, D. D., Segar Jr., R. L., Clevenger, T. E., and Banerji, S. K. (2002). "Using chlorine demand to predict TTHM and HAA9 formation". *Journal - American Water Works Association,* 94(10), 76-86.

Gauthier, V., Gérard, B., Portal, J.-M., Block, J.-C., and Gatel, D. (1999). "Organic matter as loose deposits in a drinking water distribution system". *Water Research,* 33(4), 1014-1026.

Golfinopoulos, S. K., Xilourgidis, N. K., Kostopoulou, M. N., and Lekkas, T. D. (1998). "Use of a multiple regression model for predicting trihalomethane formation". *Water Research,* 32(9), 2821-2829.

Gordon, G., and Tachiyashiki, S. (1991). "Kinetics and mechanism of formation of chlorate ion from the hypochlorous acid/chlorite ion reaction at pH 6-10". *Environmental Science & Technology,* 25(3), 468-474.

Haselbach, L. (2008). *Engineering Guide to LEED-New Construction: Sustainable Construction for Engineers*, McGraw-Hill Education.

Hohner, A. K., Cawley, K., Oropeza, J., Summers, R. S., and Rosario-Ortiz, F. L. (2016). "Drinking water treatment response following a Colorado wildfire". *Water Research,* 105, 187-198.

Hong, H., Liang, Y., Han, B., Mazumder, A., and Wong, M. H. (2007). "Modeling of trihalomethane (THM) formation via chlorination of the water from Dongjiang River (source water for Hong Kong's drinking water)". *Science of the Total Environment,* 385(1-3), 48-54.

Hung, Y.-C., Waters, B. W., Yemmireddy, V. K., and Huang, C.-H. (2017). "pH effect on the formation of THM and HAA disinfection byproducts and potential control strategies for food processing". *Journal of Integrative Agriculture,* 16(12), 2914-2923.

Jegatheesan, V., Weragoda, S., and Visvanathan, C. (2008). "Rapid water quality characterization for chlorine demand and THM formation in drinking waters". *Journal of Water Supply: Research and Technology—AQUA,* 57(4), 259-272.

Julien, R., Dreelin, E., Whelton, A. J., Lee, J., Aw, T. G., Dean, K., and Mitchell, J. (2020). "Knowledge gaps and risks associated with premise plumbing drinking water quality". *AWWA Water Science,* 2(3), e1177.

King, W. D., and Marrett, L. D. (1996). "Case-control study of bladder cancer and chlorination by-products in treated water (Ontario, Canada)". *Cancer Causes & Control,* 7(6), 596-604.

King, W. D., Marrett, L. D., and Woolcott, C. G. (2000). "Case-control study of colon and rectal cancers and chlorination by-products in treated water". *Cancer Epidemiology, Biomarkers & Prevention,* 9(8), 813-818.

Liang, L., and Singer, P. C. (2003). "Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water". *Environmental Science & Technology,* 37(13), 2920-2928.

Mutoti, G., Dietz, J. D., Arevalo, J., and Taylor, J. S. (2007). "Combined chlorine dissipation: Pipe material, water quality, and hydraulic effects". *Journal - American Water Works Association,* 99(10), 96-106.

Nguyen, C., Elfland, C., and Edwards, M. (2012). "Impact of advanced water conservation features and new copper pipe on rapid chloramine decay and microbial regrowth". *Water Research,* 46(3), 611-621.

Ra, K., Odimayomi, T., Ley, C., Aw, T. G., Rose, J. B., and Whelton, A. J. (2020). "Finding building water quality challenges in a 7 year old green school: implications for building design, sampling, and remediation". *Environmental Science: Water Research & Technology,* 6(10), 2691-2703.

Rhoads, W. J., Pearce, A., Pruden, A., and Edwards, M. A. (2015). "Anticipating the effects of green buildings on water quality and infrastructure". *Journal - American Water Works Association,* 107(4), 50-61.

Rhoads, W. J., Pruden, A., and Edwards, M. A. (2016). "Survey of green building water systems reveals elevated water age and water quality concerns". *Environmental Science: Water Research & Technology,* 2(1), 164-173.

Richard, R., Hamilton, K. A., Westerhoff, P., and Boyer, T. H. (2020). "Tracking copper, chlorine, and occupancy in a new, multi-story, institutional green building". *Environmental Science: Water Research & Technology,* 6(6), 1672-1680.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., and DeMarini, D. M. (2007). "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research". *Mutation Research,* 636(1), 178-242.

Rook, J. (1974). "Formation of haloforms during chlorination of natural waters". *Water Treatment Exam,* 23, 234–243.

Sadiq, R., and Rodriguez, M. J. (2004). "Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review". *Science of the Total Environment,* 321(1), 21-46.

Salehi, M., Abouali, M., Wang, M., Zhou, Z., Nejadhashemi, A. P., Mitchell, J., Caskey, S., and Whelton, A. J. (2018). "Case study: fixture water use and drinking water quality in a new residential green building". *Chemosphere,* 195, 80-89.

Salehi, M., Odimayomi, T., Ra, K., Ley, C., Julien, R., Nejadhashemi, A. P., Hernandez-Suarez, J. S., Mitchell, J., Shah, A. D., and Whelton, A. (2020). "An investigation of spatial and temporal drinking water quality variation in green residential plumbing". *Building and Environment,* 169, 106566.

SAS Institute Inc. (2015a). *Base SAS 9.4 procedures guide*, SAS Institute Inc., Cary, NC, USA.

SAS Institute Inc. (2015b). *SAS/STAT®14.1 User's Guide The NPAR1WAY Procedure*, SAS Institute Inc., Cary, NC, USA.

Singer, P. C. (1994). "Control of disinfection by-products in drinking water". *Journal of Environmental Engineering,* 120(4), 727-744.

Symons, J. M., Krasner, S. W., Simms, L. A., and Sclimenti, M. (1993). "Measurement of THM and precursor concentrations revisited: the effect of bromide ion". *Journal - American Water Works Association,* 85(1), 51-62.

U.S. Environmental Protection Agency. (2016). Disinfection Byproduct Information. Retrieved from https://archive.epa.gov/enviro/html/icr/web/html/dbp.html#regulatory

U.S. Environmental Protection Agency. (2020). National Primary Drinking Water Regulations (NPDWRs). Retrieved from https://www.epa.gov/sdwa/drinking-water-regulations-and-contaminants#Secondary

U.S. Green Building Council. (2014). *LEED V4 for building design and construction*, U.S. Green Building Council, Washington, DC, USA.

Vasconcelos, J. J., Rossman, L. A., Grayman, W. M., Boulos, P. F., and Clark, R. M. (1997). "Kinetics of chlorine decay". *Journal - American Water Works Association,* 89(7), 54-65.

Waller, K., Swan, S. H., DeLorenze, G., and Hopkins, B. (1998). "Trihalomethanes in drinking water and spontaneous abortion". *Epidemiology,* 9(2), 134-140.

Water Systems Council. (2007). *wellcare® information for you about pH in Drinking Water*. Retrieved from https://www.watersystemscouncil.org/download/wellcare_information_sheets/potential_groundwater_contaminant_information_sheets/9709284pH_Update_September_2007.pdf

World Health Organization. (2011). *Measuring chlorine levels in water supplies*. Retrieved from https://www.who.int/water_sanitation_health/publications/2011/tn11_chlorine_levels_en.pdf

Xu, J., Huang, C., Shi, X., Dong, S., Yuan, B., and Nguyen, T. H. (2018). "Role of drinking water biofilms on residual chlorine decay and trihalomethane formation: An experimental and modeling study". *Science of the Total Environment,* 642, 516-525.

Zheng, M., He, C., and He, Q. (2015). "Fate of free chlorine in drinking water during distribution in premise plumbing". *Ecotoxicology,* 24(10), 2151-2155.

CHAPTER. 3: A State-of-the-Art Review of Contaminant Prediction Models for Premise Plumbing Systems and Indoor Air Environments

3.1. Introduction and Purpose

The novel coronavirus (SARS-CoV-2), known as COVID-19, has resurfaced drinking-water quality problems due to prolonged water stagnation in non-residential buildings (such as workplaces and educational facilities) during the extended "stay-at-home" orders. Early studies estimated water demand reductions in non-residential buildings (35%) and increased water demand in residential water use (8%), causing a $4.7 billion (annualized) loss in water utility revenues in the states (AWWA, 2020). For extreme stagnation conditions, several topics emphasizing the need for recommissioning plans, uniform water quality standards and guidelines, sampling methods (e.g., sampling location, time and frequency, the volume of sampling), and building flush-out procedures (e.g., duration of flush out, flushing flow-rate) have been identified and require immediate research actions (Proctor et al., 2020; Rhoads & Hammes, 2021). Currently, there are knowledge gaps for premise plumbing in residential and non-residential buildings under routine operations, and that has not been fully understood for different building types (e.g., green buildings) and operation scenarios, such as the use of high-efficiency fixtures in conventional buildings (Julien et al., 2020). Recently, Julien et al. (2020) identified five main topics for building premise plumbing that represent the challenges and research needs on such as i) stagnation, ii) water use, iii) standards, iv) risk and disease modeling, and v) safety and sustainability.

Water quality models have been excessively investigated and utilized at the water distribution systems for decades to predict contaminant transfer and fate throughout the piping network systems (Clark, 2015; Grayman, 2018). However, modeling in premise plumbing systems has not been the focus of research and is still lacking (Chowdhury et al., 2018). In a recent study, over 2.4 billion water quality data points were collected using advanced sampling technologies and employed in existing disinfection by-product prediction models. However, none of the existing models (Clark, 1998; Delzer & McKenzie, 2003; Haddad et al., 2014; Roth & Cornwell, 2018) provide accurate results in predicting total trihalomethane (TTHM) concentrations in a premise plumbing system (Salehi et al., 2020).

It is well established that exposure to contaminated water could occur through ingestion, inhalation, and dermal pathways (McKone, 1987). Andelman (1985b) posits that inhalation exposure to toxic chemicals is six times more than ingesting two liters of contaminated water. In the past, water utilities advised emergency response guidelines and protocols, neither considering different exposure routes nor referring to evidence-based decision-making tools (e.g., modeling, pilot studies) in contamination incidents (Casteloes et al., 2015). Whelton and colleagues (2015) were exposed to elevated 4-methylcyclohexane methanol (4-MCHM) levels in indoor air while conducting the recommended premise plumbing flush-out protocol during the West Virginia chemical spill in 2014. Consequently, the research team had to modify the procedure to lessen the symptoms (e.g., eye-burning, dizziness). Therefore, water quality and indoor air quality modeling are crucial for capturing the extent of exposures in accidental or intentional incidents as well as testing the efficiencies of the remediation protocols (Casteloes et al., 2015).

The purpose of this study is to provide a state-of-the-art review of existing contaminant prediction models that could be implemented in residential and non-residential buildings, specifically for premise plumbing systems. Premise plumbing systems differ from water distribution systems with a large surface area to water volume ratio, smaller pipe diameters, lower flow rates, and intermittent and frequent uses resulting in unique flow conditions (Nguyen et al., 2012; Woo et al., 2018; Zheng et al., 2015). The models were categorized as contaminant concentration prediction models in premise plumbing and indoor air with further subcategories under each category. With this review, the authors hope to draw attention to the research needs in modeling approaches and provide a baseline for future research attempts. This is important because prediction models could be very useful in helping design and test immediate and emergency guidelines such as flush-out procedures in unforeseen chemical contaminations or water stagnation problems, as have been recently witnessed due to the COVID-19 pandemic.

3.2. Methodology

3.2.1. Study Search Process

A systematic literature search was conducted in Compendex, Web of Science, IEEE Explore, Science Direct, and PubMed databases (Liberati et al., 2009). No date limitations were implemented, and the last search was initiated on 28 April 2021. The search query was executed in the title, abstract, and keywords using a different set of keywords for premise plumbing and indoor air quality models as the following:

<u>The keywords for premise plumbing models</u>

- *prediction model* AND *premise plumbing*
- *leaching model* AND *premise plumbing*
- *microbial growth model* AND *premise plumbing*
- *corrosion model* AND *premise plumbing*
- *water quality model* AND *premise plumbing*

The keywords for indoor air quality models

- *indoor air quality model* AND *contaminated water*
- *indoor air quality model* AND *shower*
- *indoor air quality model* AND *sink*
- *indoor air quality model* AND *dishwasher*
- *indoor air quality model* AND *washing machine*

Some words, for instance, numerical, forecasting, mathematical, were interchangeably searched instead of the word "prediction" in the "*prediction model* AND *premise plumbing*" keyword set.

3.2.2. Study Inclusion and Exclusion Criteria

The inclusion and exclusion criteria were defined to select the relevant studies for this review (Table 8).

Table 8. Study Inclusion and Exclusion Criteria for the Literature Review

Model Categories	Inclusion Criteria	Exclusion Criteria
Premise Plumbing	• Studies that use numerical modeling approaches to predict contaminant concentrations in premise plumbing pipes and/or plumbing components (e.g., water heater). • Studies that are written in English.	• Studies that include water quality models that are designed solely for distribution network systems. • Studies that include ingestion, inhalation and dermal risk exposure assessment models. When studies implement distinctive modeling approaches (e.g., leaching models), they are included, even when they present risk assessment approaches. • Studies that include quantitative microbial risk assessment (QMRA) models. • Studies that include dose-response models. • Duplicate studies that are found in different databases.
Indoor Air Quality	• Studies that use numerical modeling approaches to predict contaminant concentrations in indoor air due to contaminated water use through the sink, shower, washing machine, and dishwasher sources. • Studies that are written in English.	• Studies that include indoor air quality models for other exposure sources (e.g., building and furniture materials, cleaning product use, groundwater volatilization). • Studies that include outdoor air quality models. • Studies that include inhalation risk exposure assessment models. • Studies that include dose-response models. • Duplicate studies that are found in different databases.

3.2.3. Study Selection Process

After removing the duplicates, the literature search resulted in 53 studies for premise plumbing and 246 studies for indoor air quality modeling from all five databases. The study selection for this literature review was completed in three steps: i) title screening, ii) abstract screening, iii) full-text, reference list, and citation screening. In the first step, identified papers' titles were looked at in detail to remove irrelevant studies from the list. As a result of this initial screening, 22 studies from premise plumbing modeling, 183 studies from indoor air quality modeling were removed. Most of the studies removed from indoor quality models were focusing on contaminant predictions from building materials. 31 premise plumbing and 63 indoor air quality modeling studies were selected for the next screening stage. In the next step, the abstracts of the selected publications were reviewed; 7 premise plumbing and 11 indoor air quality modeling studies were found eligible for the full-text screening. The selected articles were thoroughly read in the final screening stage, and the reference lists were further examined. Another literature search in the Web of Science database was conducted to identify other publications citing the selected articles in the full-text screening phase. As a result of these search attempts, a total of 22 contaminant prediction modeling studies for premise plumbing and 12 for indoor air quality were included in this study. Figure 6 provides an overview of the three-step screening process for the study selection.

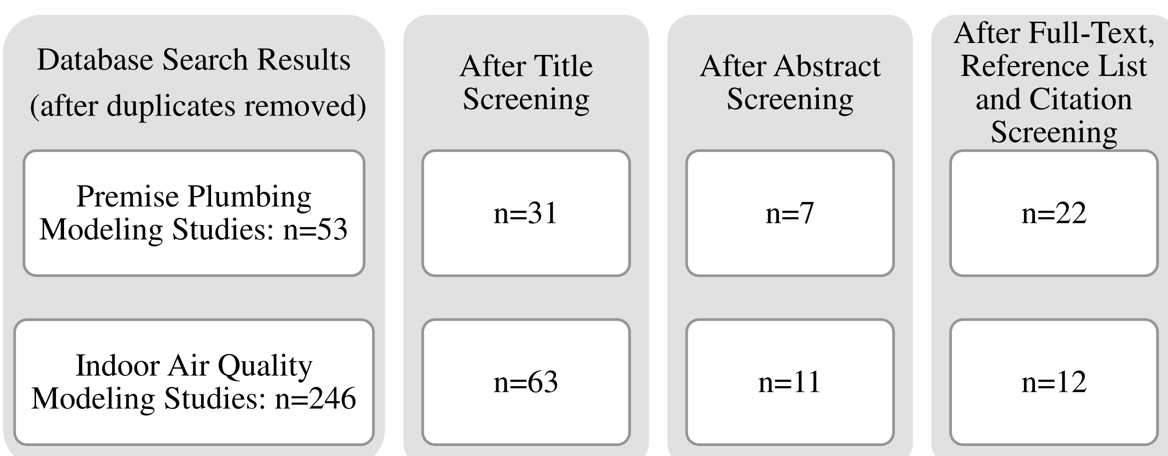

Figure 6. An Overview of Three-Step Screening Process

3.3. Findings

3.3.1. Contaminant Concentration Prediction Models in Premise Plumbing

3.3.1.1. Lead Concentration Prediction Models

Kuch and Wagner (1983) proposed a mass transfer model to predict lead concentrations in a single pipe under flushing and stagnation conditions. The model allowed predicting lead concentrations in pipes with different lengths and diameters, which differed from the early lead prediction models based on stagnation curves combined with probability distributions of lead consumptions for specific water quality (Bailey & Russell, 1981). The Biot number, which is a correction factor for including pipe surface conditions (e.g., depositions on the pipe surface), was used in the models. Later, Lytle and Schock (2000) underlined that the correction factor is necessary for diffusion modeling to provide more precise results. Comparison of the mass transfer calculations to experimental data was in good agreement, and several findings were emphasized in the study: i) during flushing, higher lead concentrations were observed in long pipes with smaller diameters, ii) under stagnation, lead concentration peaks were observed in smaller diameter pipes for a short amount of time. Two normalized lead concentration graphs were provided in the study to demonstrate the mass-transfer model predictions based on pipe diameter (10 mm to 50 mm) and length (2 m to 100 m) under flow conditions and pipe diameter (10 mm to 50 mm) and time (up to 1300 min) under stagnation conditions. When the maximum equilibrium lead concentration is known for specific water, normalized lead concentrations can be determined from these graphs. The model was initially developed to calculate lead concentrations in service lines; however, it was suggested that when maximum equilibrium lead concentration of the distributed water, pipe length and diameter, and water consumption data are known, the model could estimate lead concentrations in households. Lytle and Schock (2000) implemented Kuch and Wagner's (1983) mass diffusion model to develop stagnation curves for lead and copper. Variations were observed in theoretical stagnation curves, and those were associated with the particulate release and water chemistry. The authors explained that the diffusion models could describe the stagnation behavior of experimentally collected data; however, they are insufficient as a prediction tool for determining stagnation behavior. These lacking prediction capabilities of diffusion modeling were associated with the assumption that predictions were made based on the pipes' surface conditions; moreover, the authors suggested that oxidation kinetics of metals should be included in the prediction process.

Using corrosion kinetics, Clement et al. (2000) proposed a model to predict lead concentrations using alkalinity, water pH, temperature, and premise plumbing geometry. Although the model could predict lead exposure concentrations at the tap, the authors suggested that by including the user behavior and local plumbing characteristics, it can be utilized as an operational assessment tool to prioritize high-risk areas. An exponential, an analytical, and a numerical diffusion model in conjunction with three flow models (i.e., plug-flow, laminar, turbulent) were implemented to simulate the lead concentrations in a single pipe (Van Der Leer et al., 2002). These models were combined with a zonal simulation including 2000 properties; three flow models did not show considerable differences when used with the exponential model. Higher failure rates have been observed when the turbulent flow model was implemented in the numerical diffusion model. Associated with the Bessel equation solutions (Watson, 1995), high concentration peaks and loss of conservation of mass problems were observed in predicting lead concentrations in copper pipes using the analytical diffusion model.

Different from mass diffusion models, Chowdhury et al. (2018) developed a lead (Pb) prediction model for hot and cold water faucets by utilizing linear (i.e., linear main factors

(LMF), linear main factors with interactions and high order terms (LMFI), linear logarithmic (LL)), nonlinear (i.e., Three Parameter Logistic (LM-3P), Four Parameter Weibull) and neural network (NN) (i.e., Three-Hidden-Node) models. For the study, water samples were collected from a single housing complex in Saudi Arabia seven times a day over seven months. Galvanized iron pipes were used for both distribution network and premise plumbing systems. Lead prediction models for cold water were ranked based on their performances as LMF, NL, and NN in the given order. For lead predictions in hot water, the NN model showed a better fit.

Burkhardt et al. (2020) utilized Van Der Leer et al.'s (2002) exponential model (i.e., lead dissolution model-LDM). The authors expanded the previous model with the 1D advection-dispersion model (i.e., lead dissolution with an advection-dispersion-reaction model-LDM-ADR) in EPANET to predict lead concentrations in premise plumbing systems. Various experiments (e.g., fixed-duration stagnation, continuous flowing, sequential sampling) were conducted in the Environmental Protection Agency’s (EPA) Home Plumbing Simulator to validate the model findings. The model estimates were in agreement for the fixed-duration experiments; however, the models underpredicted lead concentrations for continuous flowing conditions. Although LDM-ADR model improved the concentration predictions, the sequential sampling results showed that the models overpredicted the peak concentrations (seven times more for some predictions). To improve model prediction abilities, suggestions were made to include other lead-containing fixtures and consider particulate lead in the modeling process. Recently, Chan et al. (2020) applied a 3D computational fluid dynamics (CFD) model to project lead concentrations at the tap resulting from copper pipes equipped with brass plumbing components (e.g., valves, elbows) and leaded solder joints in a high-rise building in Hong Kong. The results were compared with the plug-flow with advection model. The 3D model provided more accurate results when compared with the experimental results, while the plug-flow model overpredicted concentration peaks and was not in line with the experimental data. This result was associated with the shear flow dispersion addition in the 3D model as it smoothes peak lead concentrations by cross-sectional mixing.

3.3.1.2. DBP Concentration Prediction Models

Lin and Hoang (2000) utilized one of the most recognized THM prediction models for distribution systems (Amy et al., 1987) and estimated ingestion (water drinking) and inhalation (shower, pre-post cooking, during cooking) exposures from drinking water by incorporating into the mass balance models. In the study, the model results were not checked against the experimental data, and raw water characteristics were employed to determine THM concentrations at the tap, which could differ from water quality characteristics in households. Chowdhury et al. (2011) implemented three linear (i.e., main factors, main factors with interactions and high order, logarithmic) and two nonlinear (i.e., three parameters Logistic and four parameters Weibull) models to predict trihalomethanes (THMs) and haloacetic acids (HAAs) in plumbing pipes and hot water tanks based on collected water samples from six houses supplied by three different water utilities. The models were structured based on the collected water parameters, including THMs, HAAs, free chlorine residual, total chlorine, temperature, pH, turbidity, conductivity, total organic carbon (TOC), and ultraviolet absorbance (UV_{254}). Overall, linear models showed better prediction capabilities than nonlinear models. The models were validated with randomly selected data from the whole data set, and varying correlation coefficients were observed in models for THMs (R^2=0.58-0.94) and HAAs (R^2=0.72-0.95).

3.3.1.3. Copper Concentration Prediction Models

Vargas et al. (2010) modeled dissolved oxygen depletion (a limiting factor for oxidation of metallic copper in the copper corrosion process) with a first-order kinetic model including pH and temperature parameters. Good agreement (R^2=0.97) between predicted and measured data was observed for pH 5 to 9 during the first 10 hr of the stagnation time. The Copper Tube Release Model (CTRM) was developed to predict copper release by considering dissolution and diffusion kinetics, complexation, adsorption, precipitation, aqueous species equilibrium, inhibition, nucleation, crystal growth, and surface coverage as a function of time (Taxén et al., 2012). Validation of the model was determined by including data sets from other studies and provided a broad range of average error between predicted and measured data points (i.e., -30 to +80%). Being a complex and conclusive model for copper concentration prediction in plumbing pipes, the model was validated to predict accurate results for water parameters ranging for: pH 6.8-8.5; alkalinity 50 mg/L-350 mg/L as $CaCO_3$; TOC < 4.3 mg/L; phosphate < 3 mg/L; sulphate < 300 mg/L; chloride < 250 mg/L; nitrate < 33 mg/L; calcium < 234 mg/L and temperatures 5-25 °C. Pizarro et al. (2014) developed a conceptual and mathematical microbiologically influenced corrosion (MIC) model that combines physical and chemical processes of copper release from copper pipes under stagnation-flow conditions in the presence of a biofilm. The results showed that biofilm presence acts as a copper reservoir in the pipes and liberates copper due to shear stress. Pizarro and Vargas (2016) implemented their MIC model in a premise plumbing system in a later study. The simulation model was verified with the experimental data; however, the accuracy of the model was not provided in the study. High copper mass was observed in the simulation compared with the other models that only considered copper release in the bulk water in the pipe. This finding suggests that biomass presence is an important factor for copper release from the pipes.

3.3.1.4. Decontamination and Leaching Models

Leaching rates of Organotin (OT) compounds (e.g., used as heat stabilizers during polyvinyl chloride (PVC) manufacturing) were modeled based on Fick's second law (Neogi, 1996) as a function of time and pipe surface area and subsequently incorporated into an exposure model. The model predicted the mean leaching rate as $12.26 \pm 3.32\text{x } 10^{-3}$ µg/m^2-day. Considering the most toxic OT, dimethylin (DBT), the average daily dose (ADD) was estimated as $0.034 \pm 2.92\text{x}10^{-4}$ µg/kg as being 120 times lower than World Health Organization-based ADD levels (4.2 µg/kg) (Fristachi et al., 2009). Casteloes et al. (2015) developed a mass balance water heater model and used it to test the efficiency of the flush-out protocol recommended by the water utility as a remediation procedure for the public during the West Virginia chemical spill (Gabriel, 2014; Manuel, 2014; West Virginia American Water, 2014). Several scenarios were considered, including the authorities' recommended guidelines, highest contaminant concentration measured at the water distribution system, typical water heater dimensions, fixture types, and flow rates to determine the effluent concentration of 4-MCHM exiting the heater. The results showed that recommended 15 min of flushing duration was not sufficient to clear contaminants from the water heater, and it was found that in 12% of the simulations, 4-MCHM concentration was not below the Centers for Disease Control and Prevention (CDC) drinking water screening level (1 mg/L). These exceeding concentrations were attributed to different influent concentrations, tank volume, and flow rate scenarios implemented in the models. Hawes et al. (2017) evaluated three mass balance models to predict effluent concentrations leaving water heaters. Continuously stirred tank reactor (CSTR), a combined CSTR and plug-flow reactor (PFR), and variable volume CSTR models were examined. Field and laboratory experiments were conducted to validate model results. For all test conditions (19, 40, 50, 80 gal water heaters), the CSTR model (Casteloes et al., 2015) overestimated effluent concentrations; the best fit was observed for the variable volume CSTR model. It is worth noting that the authors did not consider temperature, sediment deposit, and recirculation effects in the study. Hydraulic and mass transfer models were combined to develop a Legionella pneumophila growth model in a water heater and pipes and corporated into a simulation tool, Modelica (Van Kenhove et al., 2019). The model can estimate short and long-term L. pneumophila growth in bulk water and biofilm. It was suggested that it be expanded easily with an inhalation exposure model in the future.

Haupert and Magnuson (2019) developed a numerical decontamination model to estimate flushing times of toluene leached in permeable cross-linked polyethylene (PEX) pipes. Considering the maximum contaminant level of 1 mg/L of toluene after an overnight stagnation (8h), flushing times up to 48 hr were estimated to decontaminate plumbing pipes. Alternatively, flushing for 30 min every 8 hr was considered; however, this scenario extended the total decontamination time to approximately a week. The authors suggest that 30 min flushing times are not sufficient after 8 hr of contact with PEX pipes when toluene concentration is more than 20 mg/L.

3.3.1.5. EPANET Applications in Premise Plumbing Systems

EPANET (Rossman, 1994; Rossman et al., 1993), which was mainly developed for water quality assessments in water distribution systems, was utilized to determine contaminant concentrations in premise plumbing systems. Grayman and Buchberger (2008) simulated a hypothetical contamination event based on the time-varying movement of a contaminant from the building's street connection to individual fixtures in a residential building. The simulations showed the significant impacts of heater storage tanks on contamination events. The cold water lines decontaminated quickly after the street contamination ended; however, the hot water lines were still contaminated even 48 hr after the street line contamination was cleared. Grayman et al. (2009) expanded their previous research (Grayman & Buchberger, 2008) and simulated a hypothetical contamination movement model in a high-rise building for different contamination scenarios (e.g., contamination enters from the street line, accidental contamination at the feeder tank in the building). Although the results were not supported by the experimental data, the model could track the contaminant movement in the building for various scenarios. The model application requires i) assessing building blueprints and ii) water use patterns of building occupants. Mohamed and Gad (2011) used EPANET to model chlorine concentrations in water storage cisterns placed in a 12-story building over 48 hr simulation period. Although the model predictions and experimental data were matching at the sampling points, the accuracy of the model was not presented in the study. Woo et al. (2018) improved EPANET's prediction capability for premise plumbing systems by including axial dispersion in the contaminant transport mechanism. Three different methods were used to calculate dispersion coefficients; the method of moments (Fischer et al., 1979) and fitting analytical solution methods showed similar results, while Taylor's (1954) dispersion coefficient estimations were significantly different.

3.3.2. Contaminant Concentration Prediction Models in Indoor Air

3.3.2.1. Shower Models

Whitman's (1923) two-film theory has been profoundly applied to determine the volatilizations of toxic compounds in environmental contamination conditions since the 1920s (Mackay, 1981). The two-film theory implies that the diffusion rate drives the absorption rate through the gas and liquid surface films at the gas-liquid boundary (Lewis & Whitman, 1924). Mackay and Paterson (1983) employed two-film theory to determine chemical concentrations in indoor environments and calculated radon evaporation from water, showing that two-film theory is applicable for projections of toxic chemical concentrations from water to indoor air. McKone (1987) implemented Mackay & Paterson's (1983) approach in a three-compartment model and developed mass balance equations between the compartments to predict volatile organic compound concentrations in indoor air due to contaminated water use in the shower, bathroom, and rest of the house. The predicted concentrations in the compartment model were implemented in a risk exposure model in the study; it was predicted that most of the daily inhalation exposure takes place in the shower stall (e.g., half of the exposure) and bathroom area (e.g., two-thirds of the exposure). A practical method to determine transfer efficiencies (the fraction of chemical volatilized from water to air) for unknown chemicals from known transfer efficiencies was also introduced. Radon was used as a surrogate, and chloroform, ethylene dibromide (EDB), dibromochloropropane (DBCP), 1,1,1-trichloroethlynene (TCA), tetrachloroethylene (PCE), trichloroethylene (TCE), and carbon tetrachloride transfer efficiencies were calculated. These chemicals were included in the study based on their presence in California water supplies during that time period. The model predictions for TCE were compared with the measured concentrations from another study (Andelman, 1985a). For a concentration of 3.8 mg/L TCE in the influent, the model predicted 68-100 mg/m^3 of TCE in the shower air, which was experimentally measured as 50-80 mg/m^3 after a 60 min shower event. Later, using a controlled shower stall setup, McKone and Knezovich (1991) measured TCE transfer efficiencies for different shower temperatures (i.e., 22 °C and 37 °C), assuming a 20 min shower event. The experiment results (n=8) showed that the overall TCE transfer efficiency was 61±9.4 percent (mean ± standard deviation); no statistically significant differences were found between the transfer efficiencies for different temperatures nor collected at different time points (i.e., 1, 5, 10, 15, 20 min). The method of determining transfer efficiencies from radon which was previously presented in McKone (1987), was used, and the model predicted the transfer efficiency for TCE as 44 percent. This difference between the predicted and measured efficiencies was attributed to the inaccuracies of water diffusion coefficients used in the model predictions. It was noted that for compounds with high Henry's law constants such as TCE, the transfer efficiency is strongly dependent on diffusion coefficients in water and less dependent on temperature.

Little (1992) applied two-film theory with two transient mass balance models to determine the volatilization of compounds from a shower stall and bathroom area. Liquid and gas mass transfer coefficients for various chemicals (i.e., trichlorofluoromethane, carbon tetrachloride, 1,1,1-trichloroethane-TCA, tetrachloroethylene-PCE, trichloroethylene-TCE, chloroform, 1,2,3-trichloropropane-TCPA, 1,2-dibromo-3-chloropropopane-DBCP) were determined by using experimental data from other studies (Giardino & Andelman, 1991; Hodgson et al., 1988; Jo et al., 1990a, 1990b; McKone & Knezovich, 1991; Tancrede et al., 1992). It was identified that the mass transfer coefficients showed differences between different shower systems; however, they increased with increasing water flow rates. It was also reported that the mass transient balance models could provide more accurate results than steady-state balance models for low volatile compounds used to estimate overall mass-transfer coefficients ($K_{OL}A$). A ratio of 17 between gas-phase mass transfer coefficient (i.e., K_GA) to liquid-phase mass transfer coefficient (i.e., K_LA) was observed for shower-like systems suggesting this value could be used to estimate K_GA from a known K_LA. Since then, Little's (1992) shower model has been excessively used in the literature to calculate various contaminant volatilizations in the shower stall and bathroom area. Several studies that implemented Little's (1992) model are presented in Table 9.

Table 9. Studies Implementing the Shower Model Developed by Little (1992)

Publication	**Predicted Compound in Indoor Air**
Moya et al. (1999)	Acetone, Ethyl Acetate, Toluene, Ethylbenzene, Cyclohexane
Lin and Hoang (2000)	THMs
Xu and Weisel (2003)	HAAs, Haloketones (HKs)
Wang et al. (2007)	THMs
Franco et al. (2007)	TCE, PCE
López et al. (2008)	Benzene, Toluene, Ethylbenzene, Xylene
Chowdhury and Champagne (2009)	THMs
Viana et al. (2009)	THMs
Basu et al. (2011)	THMs
Omur-Ozbek et al. (2011)	Geosmin, 2-Methylisoborneol, (trans,cis)-2,6-Nonadienal , Trichloroethylene
Gan et al. (2013)	THMs, HAAs
Lee et al. (2013)	THMs, HAAs
Uddameri and Venkataraman (2013)	THMs, HAAs
Mishra et al. (2014)	THMs
Sain et al. (2015)	4-MCHM
Babaei et al. (2015)	THMs
Omur-Ozbek et al. (2016)	4-MCHM
Zhang et al. (2018)	THMs, Arsenic
Genisoglu et al. (2019)	THMs
Chowdhury et al. (2020)	THMs
Ahmed et al. (2019)	THMs
Kujlu et al. (2020)	THMs

Kim et al. (2001) extended McKone's (1987) model by including pH-dependent volatilization; comparisons were made between two model predictions for hydrogen cyanide (HCN) and ammonia (NH_3). McKone's (1987) model predicted HCN concentrations in the air four times more than the extended model, while the concentration difference was not presented for NH_3 between the two models in the study. An alternative hybrid-showering model was developed by Chen et al. (2003) that considers "jet" and "spray" showerhead flow patterns from a showerhead to predict contaminant volatilization from water to air during showering events. Two-film theory combined with analogous empirical correlation and penetration theory was employed to estimate mass transfer coefficients. The model predictions were accurate when the results are compared to other study findings (Moya et al., 1999). Several suggestions were made to reduce contaminant exposure via showering, implementing the operation conditions of lower water temperatures, shorter showerhead heights, increased air exchange rates, higher shower stall volumes, and jet-flow type showerheads instead of spray type. Schoen and Ashbolt (2011) developed a shower exposure model to determine the critical densities of infectious Legionella in the air, water, and in-premise plumbing biofilms to achieve the target deposited dose in the lower respiratory tract for possible infection from aspirating shower generated aerosols. Based on 15 minutes of shower event, the critical densities of Legionella were predicted as 3.5×10^1- 3.5×10^3 CFU m^{-3}, 3.5×10^6- 3.5×10^8 CFU L^{-1}, and 7.8×10^5- 7.8×10^8 CFU cm^{-2} for shower air, water, and biofilm, respectively.

3.3.2.2. Sink, Washing Machine, and Dishwasher Models

The volatilization of chemicals from kitchen sinks was also investigated, suggesting stripping efficiencies and mass transfer coefficients were highly sensitive to aerator types used in sink basins (Howard & Corsi, 1996). A comprehensive study of mass-transfer balance models was conducted by Howard (1998); in addition to shower models found in the literature, two-phase dynamic mass transfer models were extended to washing machines, dishwashers, and bathtubs. Howard and Corsi (1998) implemented two-phase mass balance equations for washing machine cycles (i.e., fill, wash, spin, fill, rinse, spin); stripping efficiencies and mass transfer coefficients were calculated for acetone, toluene, ethylbenzene, and cyclohexane. The authors emphasized that these tracers were selected to provide a broad range of Henry's law constants. Based on 26 experiments, increasing stripping efficiencies and overall mass transfer coefficients were observed with increasing Henry's law constants. In the study, the water volume in the basin, detergent, and clothes presence was found as the most influential factors on chemical emissions; however, water temperature and cycle agitation effects were also evident. An example of the model application was presented for 100 µg/L of toluene in the influent water. Over a 30 min total wash cycle, the model predicted a time-weighted average of 55 $\mu g/m^3$ toluene in indoor air in a 20 m^3 room with an air exchange rate of 0.5 per hour, while the peak concentration was estimated as 94 $\mu g/m^3$.

McCready (2013) used the Simulation Tool Kit for Indoor Air Quality and Inhalation Exposure (IAQX) (USEPA, 2000) and the Exposure and Fate Screening Tool (EFAST) Consumer Exposure Model (CEM) (USEPA, 2006) to predict air concentrations in indoor air due to use of toluene contaminated water in washing machines and compared the model predictions. The model predictions were compared with Howard & Corsi's (1998) example model application results. Both models overpredicted (e.g., IAQX ~.1.5 times, EFAST CEM ~ 4 times) the peak concentration of 94 $\mu g/m^3$ in the room.

Two-phase dynamic mass balance models were utilized to predict contaminant emissions in indoor air resulting from dishwasher use (Howard-Reed et al., 1999). The example of model application showed that consideration of 10 µg/L of toluene in influent water resulted in a mass emission of 157µg/L of toluene in indoor, while 117 µg/L of toluene remained in the dishwasher headspace and released as a "puff" effect when the dishwasher door was opened. Relative source strengths (stripping efficiency / 100 x water consumption) based on toluene contamination in different exposure sources were also compared in the study: shower > washing machine (hot water) > washing machine (cold water) > dishwasher > sink. Omur-Ozbek et al. (2016) implemented indoor air quality models to determine 4-MCHM exposures due to dishwasher, washing machine, shower, and kitchen sink use. The results showed that 4-MCHM concentrations in indoor air exceeding EPA's extrapolated short-term inhalation screening level (0.01 ppm) (USEPA, 2014) were observed when the simulations were conducted for washing machine, shower, and kitchen sink models.

3.4. Conclusions and Future Research Directions on Premise Plumbing Water and Air Quality Modeling

Recent research on water quality due to prolonged stagnation times in premise plumbing systems identifies the need for modeling research to develop strategies to improve water quality at the point of use. In the past, the public has been advised to flush out their premise plumbing systems as a remediation action for accidental and intentional contaminant incidents. In most cases, the rationale behind developing such guidelines and protocols has not been clear. Moreover, other exposure routes to contaminated water, such as inhalation or dermal, have not been considered in the decision-making process (Casteloes et al., 2015). Even though water quality models have been developed and utilized at the water distribution system level, modeling in premise plumbing systems has not drawn much attention from researchers (Woo et al., 2018). This study aimed at providing a comprehensive review of contaminant concentration prediction models in premise plumbing and indoor air that could be used in residential and non-residential buildings in case of contamination incidents or unprecedented water stagnations such as caused by COVID-19. The current state of premise plumbing and indoor air quality modeling, research needs, and future research directions were discussed in the following.

3.4.1. Conclusions with respect to the Premise Plumbing Water Quality Modeling

The literature review shows that mass-transfer models have been profoundly used in the premise plumbing modeling studies, while different modeling approaches such as linear and non-linear regression techniques were also implemented. Plumbing system flow conditions (e.g., intermittent, unsteady, low flow rates) are complex due to smaller diameter pipes (Woo et al., 2018). In a few studies, more sophisticated models (e.g., advection-dispersion-reaction) were employed to provide better predictions under premise plumbing flow conditions.

In the literature, lead and copper concentration prediction models have drawn more attention from researchers than any other contaminants. Unexpectedly, only a few DBP prediction models for premise plumbing systems were found in the literature, although more than 100 DBP prediction models are available for water distribution systems (Chowdhury et al., 2009; Sadiq & Rodriguez, 2004). Similarly, modeling decontamination of premise plumbing components and contaminant leaching from pipes has not been a significant topic of research.

Based on the reviewed literature, it can be concluded that there exist knowledge gaps with respect to premise plumbing systems concerning different contaminants as follows:

- According to Pizarro and Vargas (2016), who were identified as the main contributors to the copper corrosion modeling for premise systems in this study, prediction models are needed focusing on hydrodynamics, chemistry, and solid-water interface structures to predict copper corrosion into the water. Detachment of copper nanoparticles due to shear stress, electrochemical reactions at the pipe walls, turbulent flows, biomass-copper sorption kinetics, and copper concentration gradients associated with copper release require further research (Pizarro et al., 2014). Additionally, a better understanding of adsorption kinetics and thermodynamics of organic carbon should be provided for copper corrosion modeling studies (Taxén et al., 2012).

- Including oxygen and chlorine as oxidants, research on the factors affecting the oxidation kinetics of metal pipes and fixture is needed (Lytle & Schock, 2000).
- More research on heater design and its operating conditions as well as influential factors affecting the removal of contaminated water from water heaters is needed (Hawes et al., 2017).
- Dispersion modeling in premise plumbing models is lacking and requires further research (Burkhardt et al., 2020).
- For pipe leaching and decontamination models, practical empirical and mathematical methods to estimate diffusion and partition coefficients are needed (Fristachi et al., 2009; Haupert & Magnuson, 2019).
- Research on host-Legionella interactions, pathogen partitioning, and biofilm detachment rates in the premise plumbing systems is needed (Schoen & Ashbolt, 2011).

3.4.1.1. Premise Plumbing Modeling Future Research Trends

Based on the reviewed literature presented here and building on the findings of Julien et al. (2020) and Persily et al. (2020), it is recommended that future research focuses on premise plumbing modeling as follows:

1. Improving existing tools by expanding hydraulic, chemical, biological, and thermal prediction capabilities (e.g., EPANET, Modelica).
2. Developing new contaminant prediction and decontamination tools using simulation-based data engineering platforms (e.g., Building Information Modelling (BIM), AnyLogic).

3. Implementing advanced scanning technologies that are already used in the construction industry to evaluate as-built conditions of premise plumbing systems in buildings (e.g., Trimble).
4. To validate model predictions, research efforts could focus on providing robust premise plumbing databases, including the parameters below but not limited to:
    - Water quality characteristics (chemical and biological): disinfectant residuals, pH, scaling, biofilm, and pathogen concentrations.
    - Occupant activities: water consumption patterns, number of adults and children in households, and occupant demographics.
    - Physical factors: pressure, plumbing layouts (e.g., manifold, trunk and branch), and piping material characteristics (e.g., length, diameter, age, material).
    - Operational factors: flow rate, velocity, temperature, water age, and stagnation.
5. Categorizing collected data sets based on type (e.g., residential, commercial, institutional) and water-energy efficiency (e.g., conventional, green-certified) characteristics of the buildings.
6. Using alternative modeling approaches such as machine learning techniques to estimate model coefficients and develop new prediction models.
7. Conducting comprehensive field and laboratory-scale experiments to validate models' accuracy. Laboratory-scale experiments could focus on a broad range of source water characteristics to develop more generalizable prediction tools.
8. Developing validation protocols to evaluate models' prediction capabilities that provide clear directions on the minimum data point requirements, boundary conditions, and implementation areas.

9. More studies were found in the full-text, reference list, and citation screening step than the abstract screening step in this study. It is believed that this was caused by the use of different terms in the papers; therefore, fewer studies were found in the database search. For instance, it was found that “residential drinking water systems” and “household drinking water systems” terms were used instead of “premise plumbing systems.” This result shows the need for developing a common terminology for premise plumbing systems. Lacking common language has also been identified in previous studies merely focusing on knowledge gaps and research needs in premise plumbing systems (Julien et al., 2020; Persily et al., 2020). To develop a common language, Julien et al. (2020) suggest collaboration between plumbing designers, code developers, and health risk assessors. In addition to Julien et al.'s (2020) commentary, it is suggested that the plumbing codes could be used as media to establish a common language to provide accurate definitions and generalize their usage among different stakeholders.

3.4.2. Conclusions with respect to the Indoor Air Quality Modeling

The two-film theory underlies the indoor air quality models. The indoor air quality models were constructed using one or multi-compartment mass-balance models. Due to increased exposure levels, shower models have been excessively included in risk exposure studies, while the same trend was not observed for other exposure sources (e.g., dishwashers, washing machines, or sinks). Disinfection by-products, especially THMs, were the most common compounds modeled in showers, coupled with inhalation exposure risk assessments (Table 9).

Based on the reviewed literature, it can be concluded that several research gaps related to indoor air quality models exist in the literature as follows:

- The volume fraction of water flow formed as droplets and size distribution of spray droplets from showerheads require further research (Chen et al., 2003).
- The aqueous chemistry of VOCs is not considered in washing machine models, and future research is needed (McCready, 2013).
- Inhalation exposure studies in non-residential buildings (e.g., schools, hospitals) are lacking and should be further investigated (Kim et al., 2001).
- Experimental studies should be conducted to determine ventilation rates in the different bathroom and shower volumes (Kim et al., 2004)

3.4.2.1. Indoor Air Quality Modeling Future Research Trends

Based on the reviewed literature, it is recommended that future research focuses on air quality modeling as follows:

1. Developing new models using machine learning, data mining, and statistical modeling approaches.
2. Conducting experiments to estimate mass transfer and diffusion coefficients for unknown contaminants.
3. Howard (1998), one of the main contributors to the indoor air quality modeling body of knowledge, suggests replicating headspace air exchange experiments using different dishwashers and washing machines. The literature review shows that there have not been many research attempts in that area; and this requires further research. In addition to Howard's commentary (1998), the research could benefit from conducting experiments with high-efficiency faucet aerators, showerheads, dishwashers, and washing machines that are available today.

4. Future studies could also identify ventilation rates in shower stalls and bathroom areas designed according to the current building codes.
5. Research could identify variations between different professionals' (e.g., janitor, housekeeper, water treatment plant operator) inhalation exposure in different indoor environments.

This study reviewed the literature that focuses on contaminant prediction models in premise plumbing and indoor air. For this purpose, a literature search was conducted in Compendex, Web of Science, IEEE Explore, Science Direct, and PubMed databases; 22 modeling studies for premise plumbing and 12 modeling studies for indoor air quality were reviewed. It is acknowledged that the literature presented here is not extensive, suggesting the need for more modeling studies. Implementation of models could help identify strategies for improving water and air quality in households. A comprehensive decision-making tool that combines water quality models for distribution systems with premise plumbing and indoor air quality models and exposure risk assessment tools could improve public health risk management strategies. With the help of model applications, remediation protocols could be designed for the worst-case scenarios, and the efficiency of those protocols could be tested. Many water quality models were developed for distribution networks in the literature (Grayman, 2018); those models could be adapted to premise plumbing system conditions. Although some models require field sample collections and provide site-specific information, contaminant prediction models in premise plumbing systems and indoor air could be utilized to provide better emergency responses to unprecedented conditions such as those caused by the COVID-19 pandemic.

3.5. References

Ahmed, F., Khan, T. A., Fakhruddin, A. N. M., Rahman, M. M., Mazumdar, R. M., Ahmed, S., Imam, M. T., Kabir, M., and Abdullah, A. M. (2019). "Estimation and exposure concentration of trihalomethanes (THMs) and its human carcinogenic risk in supplied pipeline water of Dhaka City, Bangladesh". *Environmental Science and Pollution Research,* 26(16), 16316-16330.

American Water Works Association and Association of Metropolitan Water Utilities. (2020). *The financial impact of the COVID-19 crisis on U.S. drinking water utilities*. Retrieved from https://www.awwa.org/Portals/0/AWWA/Communications/AWWA-AMWA-COVID-Report_2020-04.pdf

Amy, G. L., Chadik, P. A., and Chowdhury, Z. K. (1987). "Developing models for predicting trihalomethane formation potential and kinetics". *Journal - American Water Works Association,* 79(7), 89-97.

Andelman, J. B. (1985a). "Human exposures to volatile halogenated organic chemicals in indoor and outdoor air". *Environmental Health Perspectives,* 62, 313-318.

Andelman, J. B. (1985b). "Inhalation exposure in the home to volatile organic contaminants of drinking water". *Science of the Total Environment,* 47, 443-460.

Babaei, A. A., Alavi, N., Hassani, G., Yousefian, F., Shirmardi, M., and Atari, L. (2015). "Occurence and related risk assessment of trihalomethanes in drinking water, Ahvaz, Iran". *Fresenius Environmental Bulletin,* 24(12C), 4807-4815.

Bailey, R. J., and Russell, P. F. (1981). "Predicting drinking water lead levels". *Environmental Technology Letters,* 2(2), 57-66.

Basu, M., Gupta, S. K., Singh, G., and Mukhopadhyay, U. (2011). "Multi-route risk assessment from trihalomethanes in drinking water supplies". *Environmental Monitoring and Assessment,* 178(1-4), 121-134.

Burkhardt, J. B., Woo, H., Mason, J., Shang, F., Triantafyllidou, S., Schock, M. R., Lytle, D., and Murray, R. (2020). "Framework for modeling lead in premise plumbing systems using EPANET". *Journal of Water Resources Planning and Management,* 146(12), 04020094.

Casteloes, K. S., Brazeau, R. H., and Whelton, A. J. (2015). "Decontaminating chemically contaminated residential premise plumbing systems by flushing". *Environmental Science: Water Research & Technology,* 1(6), 787-799.

Chan, S. N., Chang, L., Choi, K. W., Lee, J. H. W., Fawell, J. K., and Kwok, K. Y. T. (2020). "Unraveling the causes of excess lead in drinking water supply systems of densely populated high-rise buildings in Hong Kong". *Environmental Science & Technology,* 54(22), 14322-14333.

Chen, M. J., Wu, K. Y., and Chang, L. (2003). "A new approach to estimating the volatilization rates of shower water-contained volatile organic compounds during showering". *Atmospheric Environment,* 37(31), 4325-4333.

Chowdhury, I. R., Chowdhury, S., and Al-Suwaiyan, M. S. (2020). "Human exposure and risk of trihalomethanes during continuous showering events". *Science of the Total Environment,* 701, 134521.

Chowdhury, S., and Champagne, P. (2009). "Risk from exposure to trihalomethanes during shower: Probabilistic assessment and control". *Science of the Total Environment,* 407(5), 1570-1578.

Chowdhury, S., Champagne, P., and McLellan, P. J. (2009). "Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review". *Science of the Total Environment,* 407(14), 4189-4206.

Chowdhury, S., Kabir, F., Mazumder, M. A. J., and Zahir, M. H. (2018). "Modeling lead concentration in drinking water of residential plumbing pipes and hot water tanks". *Science of the Total Environment,* 635, 35-44.

Chowdhury, S., Rodriguez, M. J., Sadiq, R., and Serodes, J. (2011). "Modeling DBPs formation in drinking water in residential plumbing pipes and hot water tanks". *Water Research,* 45(1), 337-347.

Clark, R. M. (1998). "Chlorine demand and TTHM formation kinetics: a second-order model". *Journal of Environmental Engineering,* 124(1), 16-24.

Clark, R. M. (2015). "The USEPA's distribution system water quality modelling program: a historical perspective". *Water and Environment Journal,* 29(3), 320-330.

Clement, M., Seux, R., and Rabarot, S. (2000). "A practical model for estimating total lead intake from drinking water". *Water Research,* 34(5), 1533-1542.

Delzer, G. C., and McKenzie, S. W. (2003). *Chapter A7. Section 7.0. Five-Day Biochemical Oxygen Demand* (09-A7.0). Reston, VA. Retrieved from http://pubs.er.usgs.gov/publication/twri09A7.0

Fischer, H. B., List, J. E., Koh, C. R., Imberger, J., and Brooks, N. H. (1979). *Mixing in inland and coastal waters*, Academic press.

Franco, A., Costoya, M. A., and Roca, E. (2007). "Estimating risk during showering exposure to VOCs of workers in a metal-degreasing facility". *Journal of Toxicology and Environmental Health, Part A,* 70(7), 627-637.

Fristachi, A., Xu, Y., Rice, G., Impellitteri, C. A., Carlson-Lynch, H., and Little, J. C. (2009). "Using probabilistic modeling to evaluate human exposure to organotin in drinking water transported by polyvinyl chloride pipe". *Risk Analysis,* 29(11), 1615-1628.

Gabriel, T. (2014). Thousands without water after spill in West Virginia. Retrieved from https://www.nytimes.com/2014/01/11/us/west-virginia-chemical-spill.html

Gan, W., Guo, W., Mo, J., He, Y., Liu, Y., Liu, W., Liang, Y., and Yang, X. (2013). "The occurrence of disinfection by-products in municipal drinking water in China's Pearl River Delta and a multipathway cancer risk assessment". *Science of the Total Environment,* 447, 108-115.

Genisoglu, M., Ergi-Kaytmaz, C., and Sofuoglu, S. C. (2019). "Multi-route – Multi-pathway exposure to trihalomethanes and associated cumulative health risks with response and dose addition". *Journal of Environmental Management,* 233, 823-831.

Giardino, N., and Andelman, J. (1991). Presented at the Annual Conference of the American Water Works Association., Philadelphia, PA.

Grayman, W. M. (2018). "*History of water quality modeling in distribution systems"*. Presented at the 1st International WDSA / CCWI 2018 Joint Conference, Kingston, Ontario, Canada

Grayman, W. M., Buchberger, S., and Samuels, W. (2009). Hydraulic models of buildings for use in contamination studies. In *Water Distribution Systems Analysis 2008* (pp. 1-10).

Grayman, W. M., and Buchberger, S. G. (2008). Fixture-level human exposure calculation model. In *Water Distribution Systems Analysis Symposium 2006* (pp. 1-13).

Haddad, M., McNeil, L., and Omar, N. (2014). "Model for predicting disinfection by-product (DBP) formation and occurrence in intermittent water supply systems: Palestine as a case study". *Arabian Journal for Science and Engineering,* 39(8), 5883-5893.

Haupert, L. M., and Magnuson, M. L. (2019). "Numerical model for decontamination of organic contaminants in polyethylene drinking water pipes in premise plumbing by flushing". *Journal of Environmental Engineering,* 145(7), 04019034.

Hawes, J. K., Conkling, E. A., Casteloes, K. S., Brazeau, R. H., Salehi, M., and Whelton, A. J. (2017). "Predicting contaminated water removal from residential water heaters under various flushing scenarios". *Journal - American Water Works Association,* 109(8), E332-E342.

Hodgson, A. T., Garbesi, K., Sextro, R. G., and Daisey, J. M. (1988). *Evaluation of soil-gas transport of organic chemicals into residential buildings: Final report* (LBL-25465). CA, USA. Retrieved from https://www.osti.gov/servlets/purl/6006558

Howard-Reed, C., Corsi, R. L., and Moya, J. (1999). "Mass transfer of volatile organic compounds from drinking water to indoor air: the role of residential dishwashers". *Environmental Science & Technology,* 33(13), 2266-2272.

Howard, C., and Corsi, R. (1998). "Volatilization of chemicals from drinking water to indoor air: the role of residential washing machines". *Journal of the Air & Waste Management Association,* 48 10, 907-914.

Howard, C., and Corsi, R. L. (1996). "Volatilization of chemicals from drinking water to indoor air: role of the kitchen sink". *Journal of the Air & Waste Management Association,* 46(9), 830-837.

Howard, C. L. (1998). Volatilization rates of chemicals from drinking water to indoor air. In: ProQuest Dissertations Publishing.

Jo, W. K., Weisel, C. P., and Lioy, P. J. (1990a). "Chloroform exposure and the health risk associated with multiple uses of chlorinated tap water". *Risk Analysis,* 10(4), 581-585.

Jo, W. K., Weisel, C. P., and Lioy, P. J. (1990b). "Routes of chloroform exposure and body burden from showering with chlorinated tap water". *Risk Analysis,* 10(4), 575-580.

Julien, R., Dreelin, E., Whelton, A. J., Lee, J., Aw, T. G., Dean, K., and Mitchell, J. (2020). "Knowledge gaps and risks associated with premise plumbing drinking water quality". *AWWA Water Science,* 2(3), e1177.

Kim, E., Little, J. C., and Chiu, N. (2004). "Estimating exposure to chemical contaminants in drinking water". *Environmental Science & Technology,* 38(6), 1799-1806.

Kim, E., Little, J. C., Chiu, N., and Chiu, A. (2001). "Inhalation exposure to volatile chemicals in drinking water". *Journal of Environmental Science and Health Part C-Environmental Carcinogenesis & Ecotoxicology Reviews,* 19(2), 387-413.

Kuch, A., and Wagner, I. (1983). "A mass transfer model to describe lead concentrations in drinking water". *Water Research,* 17(10), 1303-1307.

Kujlu, R., Mahdavianpour, M., and Ghanbari, F. (2020). "Multi-route human health risk assessment from trihalomethanes in drinking and non-drinking water in Abadan, Iran". *Environmental Science and Pollution Research,* 27(34), 42621-42630.

Lee, J., Kim, E., Roh, B., Eom, S., and Zoh, K. (2013). "Occurrence of disinfection by-products in tap water distribution systems and their associated health risk". *Environmental Monitoring and Assessment,* 185(9), 7675-7691.

Lewis, W. K., and Whitman, W. G. (1924). "Principles of gas absorption". *Industrial and Engineering Chemistry,* 16(12), 1215-1220.

Liberati, A., Altman, D. G., Tetzlaff, J., Mulrow, C., Gøtzsche, P. C., Ioannidis, J. P. A., Clarke, M., Devereaux, P. J., Kleijnen, J., and Moher, D. (2009). "The PRISMA statement for reporting systematic reviews and meta-analyses of studies that evaluate health care interventions: explanation and elaboration". *PLoS Medicine,* 6(7), e1000100.

Lin, T. F., and Hoang, S. W. (2000). "Inhalation exposure to THMs from drinking water in south Taiwan". *Science of the Total Environment,* 246(1), 41-49.

Little, J. C. (1992). "Applying the two-resistance theory to contaminant volatilization in showers". *Environmental Science & Technology,* 26(7), 1341-1349.

López, E., Schuhmacher, M., and Domingo, J. L. (2008). "Human health risks of petroleum-contaminated groundwater". *Environmental Science and Pollution Research International,* 15(3), 278-288.

Lytle, D. A., and Schock, M. R. (2000). "Impact of stagnation time on metal dissolution from plumbing materials in drinking water". *Aqua,* 49(5), 243-257.

Mackay, D. (1981). "Environmental and laboratory rates of volatilization of toxic chemicals from water". *Hazard Assessment of Chemicals: Current Developments,* 1.

Mackay, D., and Paterson, S. (1983). "Fugacity models of indoor exposure to volatile chemicals". *Chemosphere,* 12(2), 143-154.

Manuel, J. (2014). "Crisis and emergency risk communication: lessons from the Elk River spill". *Environmental Health Perspectives,* 122(8), A214-A219.

McCready, D. (2013). "A comparison of screening and refined exposure models for evaluating toluene air emissions from a washing machine". *Human and Ecological Risk Assessment: An International Journal,* 19(4), 972-988.

McKone, T. E. (1987). "Human exposure to volatile organic compounds in household tap water: the indoor inhalation pathway". *Environmental Science & Technology,* 21(12), 1194-1201.

McKone, T. E., and Knezovich, J. P. (1991). "The transfer of trichloroethylene (TCE) from a shower to indoor air: experimental measurements and their implications". *Journal of the Air & Waste Management Association,* 41(3), 282-286.

Mishra, B. K., Gupta, S. K., and Sinha, A. (2014). "Human health risk analysis from disinfection by-products (DBPs) in drinking and bathing water of some Indian cities". *Journal of Environmental Health Science & Engineering,* 12, 1-19.

Mohamed, H. I., and Gad, A. A. M. (2011). "Effect of cold-water storage cisterns on drinking-water quality". *Journal of Water Resources Planning and Management,* 137(5), 448-455.

Moya, J., Howard-Reed, C., and Corsi, R. L. (1999). "Volatilization of chemicals from tap water to indoor air from contaminated water used for showering". *Environmental Science & Technology,* 33(14), 2321-2327.

Neogi, P. (1996). *Diffusion in polymers*,(Vol. 32), CRC Press.

Nguyen, C., Elfland, C., and Edwards, M. (2012). "Impact of advanced water conservation features and new copper pipe on rapid chloramine decay and microbial regrowth". *Water Research,* 46(3), 611-621.

Omur-Ozbek, P., Akalp, D., and Whelton, A. (2016). "*Tap water and indoor air contamination due to an unintentional chemical spill in source water"*. Presented at the Proceedings of International Structural Engineering and Construction, Istanbul, Turkey.

Omur-Ozbek, P., Gallagher, D. L., and Dietrich, A. M. (2011). "Determining human exposure and sensory detection of odorous compounds released during showering". *Environmental Science & Technology,* 45(2), 468-473.

Persily, A., Yashar, D., Ferretti, N. M., Ullah, T., and Healy, W. (2020). *Measurement science research needs for premise plumbing systems* (NIST Technical Note 2088). Retrieved from https://nvlpubs.nist.gov/nistpubs/TechnicalNotes/NIST.TN.2088.pdf

Pizarro, G. E., and Vargas, I. T. (2016). "Biocorrosion in drinking water pipes". *Water Science and Technology-Water Supply,* 16(4), 881-887.

Pizarro, G. E., Vargas, I. T., Pasten, P. A., and Calle, G. R. (2014). "Modeling MIC copper release from drinking water pipes". *Bioelectrochemistry (Amsterdam, Netherlands),* 97, 23-33.

Proctor, C. R., Rhoads, W. J., Keane, T., Salehi, M., Hamilton, K., Pieper, K. J., Cwiertny, D. M., Prévost, M., and Whelton, A. J. (2020). "Considerations for large building water quality after extended stagnation". *AWWA Water Science,* 2(4).

Rhoads, W. J., and Hammes, F. (2021). "Growth of Legionella during COVID-19 lockdown stagnation". *Environmental Science: Water Research & Technology,* 7(1), 10-15.

Rossman, L. A. (1994). *EPANET users manual*. Cincinati, OH, USA. Retrieved from https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=124908&simpleSearch=1&searchAll=epanet

Rossman, L. A., Boulos, P. F., and Altman, T. (1993). "Discrete volume-element method for network water-quality models". *Journal of Water Resources Planning and Management,* 119(5), 505-517.

Roth, D. K., and Cornwell, D. A. (2018). "DBP impacts from increased chlorine residual requirements". *Journal - American Water Works Association,* 110(2), 13-28.

Sadiq, R., and Rodriguez, M. J. (2004). "Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review". *Science of the Total Environment,* 321(1), 21-46.

Sain, A. E., Dietrich, A. M., Smiley, E., and Gallagher, D. L. (2015). "Assessing human exposure and odor detection during showering with crude 4-(methylcyclohexyl)methanol (MCHM) contaminated drinking water". *Science of the Total Environment,* 538, 298-305.

Salehi, M., Odimayomi, T., Ra, K., Ley, C., Julien, R., Nejadhashemi, A. P., Hernandez-Suarez, J. S., Mitchell, J., Shah, A. D., and Whelton, A. (2020). "An investigation of spatial and temporal drinking water quality variation in green residential plumbing". *Building and Environment,* 169, 106566.

Schoen, M. E., and Ashbolt, N. J. (2011). "An in-premise model for Legionella exposure during showering events". *Water Research,* 45(18), 5826-5836.

Tancrede, M., Yanagisawa, Y., and Wilson, R. (1992). "Volatilization of volatile organic compounds from showers—I. Analytical method and quantitative assessment". *Atmospheric Environment. Part A. General Topics,* 26(6), 1103-1111.

Taxén, C., Letelier, M. V., and Lagos, G. (2012). "Model for estimation of copper release to drinking water from copper pipes". *Corrosion Science,* 58, 267-277.

Taylor, G. (1954). "The dispersion of matter in turbulent flow through a pipe". *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences,* 223(1155), 446-468.

U.S. Environmental Protection Agency. (2000). *Simulation tool kit for indoor air quality and inhalation exposure (IAQX) version 1.0 user's guide.* Retrieved from https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=63471

U.S. Environmental Protection Agency. (2006). *Exposure and fate assessment screening tool (E-FAST) version 2.0 documentation manual*. Retrieved from https://www.epa.gov/tsca-screening-tools/e-fast-exposure-and-fate-assessment-screening-tool-version-2014

U.S. Environmental Protection Agency. (2014). *Derivation of an extrapolated short-term inhalation screening level for 4-Methylcyclohexanemethanol (MCHM – CAS# 34885-03-5)*. Retrieved from http://media.wvgazette.com/static/watchdog/EPA%20MCHM%20Air%20Screening%20Level.pdf

Uddameri, V., and Venkataraman, K. (2013). "Assessing the effect of initial vapor-phase concentrations on inhalation risks of disinfection-by-products (DBP) in multi-use shower facilities". *Clean Technologies and Environmental Policy,* 15(4), 591-606.

Van Der Leer, D., Weatherill, N. P., Sharp, R. J., and Hayes, C. R. (2002). "Modelling the diffusion of lead into drinking water". *Applied Mathematical Modelling,* 26(6), 681-699.

Van Kenhove, E., De Backer, L., Janssens, A., and Laverge, J. (2019). "Simulation of Legionella concentration in domestic hot water: comparison of pipe and boiler models". *Journal of Building Performance Simulation,* 12(5), 595-619.

Vargas, I. T., Pasten, P. A., and Pizarro, G. E. (2010). "Empirical model for dissolved oxygen depletion during corrosion of drinking water copper pipes". *Corrosion Science,* 52(7), 2250-2257.

Viana, R. B., Cavalcante, R. M., Braga, F. M., Viana, A. B., de Araujo, J. C., Nascimento, R. F., and Pimentel, A. S. (2009). "Risk assessment of trihalomethanes from tap water in Fortaleza, Brazil". *Environmental Monitoring and Assessment,* 151(1-4), 317-325.

Wang, G. S., Deng, Y. C., and Lin, T. F. (2007). "Cancer risk assessment from trihalomethanes in drinking water". *Science of the Total Environment,* 387(1-3), 86-95.

Watson, G. N. (1995). *A treatise on the theory of Bessel functions*, Cambridge University Press.

West Virginia American Water. (2014). How to flush your plumbing system and how to flush plumbing faucets and appliances. Retrieved from https://www.wvdhhr.org/HowFlushPlumbingSystem.pdf

Whelton, A. J., McMillan, L., Connell, M., Kelley, K. M., Gill, J. P., White, K. D., Gupta, R., Dey, R., and Novy, C. (2015). "Residential tap water contamination following the Freedom Industries chemical spill: perceptions, water quality, and health impacts". *Environmental Science & Technology,* 49(2), 813-823.

Whitman, W. G. (1923). "The two-film theory of gas absorption". *Chemical and Metallurgical Engineering* 29, 146-148.

Woo, H., Burkhardt, J., and Rossman, L. (2018). *Modeling of dispersion effect for intermittent flow in premise plumbing systems.* Presented at the WDSA/CCWI Joint Conference Proceedings.

Xu, and Weisel, C. P. (2003). "Inhalation exposure to haloacetic acids and haloketones during showering". *Environmental Science & Technology,* 37(3), 569-576.

Zhang, H., Chang, S., Wang, L., and Wang, W. (2018). "Estimating and comparing the cancer risks from THMs and low-level arsenic in drinking water based on disability-adjusted life years". *Water Research,* 145, 83-93.

Zheng, M., He, C., and He, Q. (2015). "Fate of free chlorine in drinking water during distribution in premise plumbing". *Ecotoxicology,* 24(10), 2151-2155.

CHAPTER. 4: Development of a Disinfection By-product Prediction Simulation Model in a Premise Plumbing System

4.1. Introduction and Purpose

While the novel coronavirus (SARS-CoV-2) known as COVID-19 has confined millions of people to their homes due to stay-at-home orders across the globe, many commercial buildings, including schools, government offices, and factories faced building closures ranging from weeks to months (Lee et al., 2020). The sudden and unprecedented water consumption reductions in buildings have induced other health concerns such as Legionnaires' disease, prompting many public health agencies to provide guidelines for reopening buildings after a prolonged water stagnation (CDC, 2020; OSHA, 2020; WHO, 2020). Although the standards and guidelines are lacking uniformity, several precautions are commonly mentioned, including: i) conducting building flush-out to bring disinfectant residual levels up for remediating chemical and microbial problems, ii) identifying and monitoring problematic locations in the system, and iii) temperature management for bacterial growth (Proctor et al., 2020; Van Kenhove et al., 2019).

Chlorine is the most commonly used disinfectant in the US and the world and is a prerequisite to provide microbiologically safe drinking water quality. Most of the microbial problems could be solved by increasing chlorine dose; however, reactions between chlorine and organic/inorganic matter could result in disinfection by-products (DBPs) known to be harmful to humans (Richardson et al., 2007). Currently, more than hundreds of halogenated DBPs have been identified in drinking water (e.g., trihalomethanes (THMs), haloacetic acids (HAAs), halo ketones (HKs), haloacetonitriles (HANs), cyanogen chloride, chloral hydrate, and chloropicrin (CP)) (Singer, 1994). THMs, namely chloroform, bromodichloromethane, dibromochloromethane, and bromoform, represent the most ubiquitous DBPs in drinking water. Although water quality models that seek answers to optimal chlorine doses that yield minimal DBP formations have been excessively implemented at the distribution level, the final water quality at the point of use (POU) still relies on predictions made at the treatment plant outlet. Research on water quality due to the coronavirus lockdown has pointed out the importance of water stagnation at the point of use, addressing the need for water decision-making tools for premise plumbing systems (Proctor et al., 2020).

This study aims to implement a first-order chlorine decay model, to predict chloroform concentration within a premise plumbing system for eight hours of stagnation. For this purpose, bench-scale experiments were conducted to determine prediction model coefficients considering the water quality parameter ranges reported for premise plumbing systems. The fitted model coefficients were incorporated into simulation software, AnyLogic. Chloroform concentrations were tested in a two-story townhouse; experimental and model prediction results were compared. This study contributes to the body of knowledge by developing a chloroform prediction tool for premise plumbing systems integrated with a simple user simulation interface.

4.2. Literature Review

4.2.1. Factors Affecting Chlorine Decay Kinetics and DBP Formations

Chlorine is the most common disinfection method due to its effortless application, stable residual levels, efficacy in pathogen inactivation, and cost (Al-Jasser, 2007). According to the American Water Works Association (AWWA) 2017 survey results, more than 80 percent of the water utilities they surveyed (i.e., 239 out of 277 survey respondents) in the US use chlorine as a primary disinfectant (AWWA, 2018). When chlorine gas dissolves in water, hypochlorous acid (HOCl) is formed, which dissociates into hypochlorite ion (OCl^-) depending on water temperature and pH (Brown et al., 2011; Clark & Sivaganesan, 2002). Chlorine reacts with organic and inorganic constituents in water, and these reactions exert chlorine demand. Several concurrent reactions were identified in the literature that drive chlorine demand in engineered water systems. Those are: i) reactions with organic and inorganic (e.g., ammonium ion, nitrite, sulfide, ferrous iron, and manganous manganese) constituents in the bulk flow, ii) reactions on the pipe wall (e.g., biofilm, pipe material, sediments), iii) consumption due to corrosion spots, and iv) mass transport of chlorine between the pipe wall and bulk water (Clark, 1998; Taras et al., 1950; Vasconcelos et al., 1997). Disinfectant dose, pH, reaction time, water quality, and treated microorganism characteristics, temperature, and residuals maintained over a period of time are the factors that impact chlorine disinfection efficacy (Brown et al., 2011; Clark & Sivaganesan, 2002). Despite its operational advantages, chlorine dosing should be done with caution at the drinking water treatment plants. Low chlorine doses might not be sufficient to control pathogen regrowth, and in contrast, excess chlorine might react with organic and inorganic constituents in water, forming DBPs, which are known to be harmful to humans (Richardson et al., 2007).

Currently, two main groups of DBPs, total THMs (TTHMs), and HAAs are regulated under Stage 1 and Stage 2 Disinfectants and Disinfection By-products Rules (DBPRs) at the water treatment plant level. The maximum allowable annual average levels of 80 parts per billion (ppb) and 60 parts per billion (ppb) were established for TTHMs and HAAs, respectively, by the Environmental Protection Agency (EPA) (2016). Similar parameters that affect chlorine are also influential on THM formation; disinfectant dose, nature and concentration of natural organic matter (NOM), contact time, pH, water temperature and season, and bromide ion presence are the most significant factors (Brown et al., 2011; Chowdhury & Champagne, 2008). Higher THM levels are anticipated at the higher levels of the abovementioned parameters (Al-Omari et al., 2005; Sadiq & Rodriguez, 2004).

Although some unsophisticated water quality models can be traced back to the 1930s, water quality modeling at the distribution systems gained popularity in the 1980s; their prevalence predominantly escalated by the passage of The Safe Drinking Water Act (SDWA) in 1974 (Grayman, 2018). During the 1980s, technological advancements in computer science have contributed to the broader applicability of the water quality models (Clark, 2015). Since the 1980s, many modeling studies have dealt with the unique research question of predicting chlorine decay and disinfection by-product formations in complex water distribution systems (Clark, 2015; Grayman, 2018).

4.2.2. Chlorine Decay Prediction Models

Haas and Karra (1984) compared various chlorine decay models, including first-order decay, power-law decay (n^{th} order), first-order decay with stable component, power-law decay with stable component (n^{th} order), and parallel first-order decay. They found that the parallel first-order decay equation gave the best fit among other models considering fast and slow chlorine reactions in wastewater effluents. While the feasibility of the models for drinking water has raised questions, the first-order decay model has also been criticized for its limited prediction capabilities for re-chlorination conditions (Brown et al., 2011; Jadas-Hécart et al., 1992). In a relatively recent study, a comprehensive water sampling effort (n=2000) was undertaken over a broad range of water sources (n=4); and chlorine decay kinetic models (i.e., first order, second order with respect to chlorine, second-order with respect to chlorine, and another reactant, n^{th}

order, limited first order, and parallel first order) were compared in their predictive performances. The results proved that other models' prediction capabilities were minimal compared to the first-order decay model results for potable water systems (Powell et al., 2000). In Table 10, various chlorine decay kinetic models are presented.

Table 10. Bulk Chlorine Decay Kinetic Models (Brown et al., 2011; Haas & Karra, 1984; Powell et al., 2000)

Kinetic Model	**Equation**	**Adjusted Parameters**
First-order	$C_0 \exp(-k_b t)$	k_b
Second-order (chlorine)	$\dfrac{C_0}{1 + C_0 k_b t}$	k_b
Second-order (chlorine and another reactant)	$\dfrac{U - C_0}{\frac{U}{C_0} \exp[W(U - C_0)t - 1]}$	U, W
Power-law decay (n^{th} order)	$[k_b^{"}(n-1) + (1/C_0)^{(n-1)}]^{-(1/n-1)}$	$k_b^{"}, n$
First-order decay with stable component	$C^* + (C_0 - C^*)\exp(-k_b t)$	k_b, C^*
Power-law decay with stable component (n^{th} order)	$C^* + (k"_b t(n-1) + (1/(C_0 - C^*)^{(n-1)})^{(1/n-1)}$	$k"_b, n, C^*$
Parallel first-order decay	$C_0 x \exp(-k_1 t) + C_0(1-x)\exp(-k_2 t)$	k_1, k_2, x

C_0= initial chlorine concentration (mg/L); n= order of reaction (dimensionless); k_b= bulk decay constant; $k"_b$=n^{th} order bulk decay constant (L/[h(mg/L)$^{(n-1)}$]); C*=limiting chlorine concentration (mg/L); U= reactant concentration parameter; W= decay rate parameter; k_1=bulk decay constant for fast reactions (L/h); k_2= bulk decay constant for slow reactions (L/h); x= fast to slow reactions ratio (dimensionless)

More advanced models (e.g., dynamic hydraulic models) that assess the transport and fate of contaminants have been proposed to provide better simulations of chlorine reactions throughout complex pipe networks. Biswas et al. (1993) developed a two-dimensional (2D) model for single pipes that incorporates bulk flow reaction, radial diffusion, and wall decay reactions under steady-state flow conditions. Rossman et al. (1994) proposed one-dimensional conservation of mass-equation model that considers chlorine reaction in the bulk flow, on the pipe wall, and the mass transfer of chlorine from the bulk water to the pipe wall that is suitable for non-steady flow conditions for turbulent and laminar flow. Vasconcelos et al. (1997) used a dynamic water quality simulation model called EPANET (Rossman et al., 1994) over a broad range of field measurements to test different decay kinetic models (e.g., first-order bulk decay kinetics, first-order, mass transfer limited wall decay kinetics, zero-order, mass transfer-limited wall decay kinetics). The study findings showed that a first-order kinetic model could define chlorine decay in bulk water while first-order or zero-order kinetic models could characterize pipe wall reactions.

Clark (1998) used a second-order reaction model to predict chlorine decay and TTHMs formation in water distribution systems. First-order, n^{th} order, limited first-order, parallel first-order, and second-order decay kinetic model performances were compared, and a better fit was observed for the second-order model estimates. Clark and Sivaganesan (1998) proposed a model that predicts chlorine decay and THM formation in water distribution systems. The model was structured based on bench-scale experiments to provide generalizable results and tested using various field data sets. The model parameters were determined by regression analyses as the functions of initial chlorine concentration, total organic carbon (TOC), pH, and water temperature. The second-order model has also been modified to incorporate bromide ion contribution to TTHM formation (Clark et al., 2001) and include fast and slow reacting components in the decay process (Clark & Sivaganesan, 2002).

Ozdemir and Ger (1998) proposed a numerical mass transport model suitable for low flow conditions. In the study, the model predictions were compared with Biswas's (1993) and Rossman's (1994) findings and found that the proposed model provides better results for smaller

Reynold numbers than the other two models. Ozdemir and Ucak (2002) developed a computer program referred to as DYNAQ that computes chlorine decay using a time-driven method. The study results were compared with EPANET (Rossman et al., 1994), and accurate results were observed. Yeh et al. (2008) proposed a new approximate solution to Biswas' (1993) 2D steady-state chlorine transport model under turbulent conditions. The model was implemented in two case studies; the results provided good accuracy and easy application when the wall decay rate was higher than 0.1.

Jonkergouw et al. (2009) developed a semiempirical chlorine forecast model referred to as the variable-rate coefficient (VRC) to provide better predictions for re-chlorination conditions. However, the VRC model has been commented on its limited ability to incorporate temperature variations on chlorine decay. For this purpose, temperature effects were included in the augmented two-reactant (2RA) model. The VRC and 2RA model performances were compared; although the VRC model provided more accurate results than the 2RA, the differences were minimal considering the 2RA's capability of describing the effects of initial chlorine concentration, temperature, and re-chlorination dose and timing (Fisher et al., 2017).

4.2.3. DBP Prediction Models

4.2.3.1. DBP Prediction Models in Water Distribution Systems

Since monitoring DBPs can be time-consuming and often requires expensive and sensitive techniques, predictive modeling has gained importance in quantifying DBP formation (Sadiq & Rodriguez, 2004). More than 100 DBP formation prediction models have been identified in the literature (Chowdhury et al., 2009), and most models utilize statistical methods such as non-linear regression models using one or more field and laboratory samples in the prediction process (Brown et al., 2011; Sadiq & Rodriguez, 2004). Chowdhury and Champagne

(2008) reported that 3 to 8 water quality parameters were utilized in individual THM prediction models.

Amy et al. (1987) developed a TTHM prediction model using nine raw water characteristics collected in the US to provide a wide range of model applicability. Although the authors developed a model including all data points (n=1090), better fitting models were observed when the data sets were analyzed for short-term (≤ 8-h) and long-term (≥ 24-h) reaction times. Segar et al. (2003) implemented a first-order chlorine decay reaction model to predict THM and HAA formation using eight surface water characteristics. The model was able to predict concentrations accurately in the given boundary conditions. The authors emphasized that the model may not be applicable for predictions for groundwater. Under controlled laboratory experiments, Li and Zhao (2006) found that THM formation is both first-order with respect to chlorine and humic acid precursor levels, suggesting an overall second-order formation reaction. Rodrigues et al. (2007) developed regression models for individual THMs based on laboratory experiments utilizing factorial experiment designs. Detailed information on these models can be found in Chowdhury et al. (2009) and Sadiq and Rodriguez (2004).

4.2.3.2. DBP Prediction Models in Premise Plumbing Systems

Most water quality models have been developed based on the samples taken from distribution systems; however, premise plumbing systems differ from water distribution networks for many reasons such as: A large surface area to water volume ratio, regular and intermittent stagnation conditions, variable and elevated temperature, longer residence times, redox potentials, deposit accumulations and, reduced flow rates (Nguyen et al., 2012; Zheng et al., 2015).

Along with other prediction models, Lin and Hoang (2000) employed a model developed by Amy et al. (1987) to predict inhalation exposure of THMs due to cooking and showering activities in households. In that study, the water quality parameters were measured at the treatment plant and incorporated into Amy's (1987) model, which was developed for water distribution systems and calculated based on the untreated natural water quality characteristics. Thus, the reported results at the households might show differences due to the distinct characteristics of premise plumbing systems mentioned above. Chowdhury et al. (2011) implemented linear and non-linear statistical models to predict DBPs in premise plumbing systems; the models were constructed using the water quality parameters from six houses in Canada. The coefficient of determination values (R^2) of the models were reported to be between 0.77 and 0.96. In several studies, the first-order decay kinetic model has been used for premise plumbing systems. However, the model was applied to experimental pipe loops to simulate premise plumbing conditions (Xu et al., 2018; Zheng et al., 2015). Salehi et al. (2020) applied three TTHM prediction models from the literature (Clark, 1998; Haddad et al., 2014; Roth & Cornwell, 2018) for premise plumbing conditions and reported that the models were insufficient to predict TTHMs at the studied fixture.

Kalan, Ozbek, and Omur-Ozbek (Unpublished work) conducted a comprehensive literature review to identify water quality models that are used to predict contaminant concentrations in premise plumbing systems. In that study, more than 20 modeling studies that focus on different contaminants were identified; however, only two of those (Chowdhury et al., 2011; Lin & Hoang, 2000) included DBP prediction models for premise plumbing systems. This study differs from Lin and Hoang (2000) by using regression model coefficients based on the water quality parameters that can be seen in premise plumbing systems and validating the model predictions by conducting house experiments. This study differs from Chowdhury et al. (2011) by conducting laboratory-controlled experiments in developing a more generalizable model.

This study aimed to predict chloroform concentrations in premise plumbing systems after eight hours of stagnation. This stagnation time was selected as most THM formation occurred in 7 hours (Chowdhury & Champagne, 2008). A first-order reaction model was used to fit chlorine decay and combined with the chloroform yield coefficient equation to predict chloroform concentrations. Several parameters, including TOC, pH, initial chlorine, and reaction time, were included in determining the chloroform formation yield coefficient. For the model simplicity, bromide ion effects were not considered, and brominated THMs were excluded from the model development process. Three sampling events were conducted in a two-story townhouse, and the model's prediction ability was tested, comparing the model results with the experimental findings.

4.3. Materials and Methods

4.3.1. Bench-Scale Experiments

This study aimed to adopt a DBP prediction tool, which was developed for water distribution systems, and adapt it to premise plumbing systems. To test the model's applicability and evaluate its prediction capability in premise plumbing conditions, the ranges of water quality parameters for the bench-scale experiments were selected based on the water quality tests from a townhouse and an accompanying study's (Kalan, Ozbek, Omur-Ozbek, et al., Unpublished work) experiment results as discussed below.

Synthetic water samples of various TOC, pH, and chlorine levels were prepared to propagate chloroform concentrations under controlled laboratory conditions (Table 11). TOC (0.4, 0.8, and 1.5 mg/L) and pH (7, 8, and 9) levels were selected based on the mean and frequency of the observed concentrations in an accompanying study (Kalan, Ozbek, Omur-Ozbek, et al., Unpublished work). In that study, TOC and pH levels were collected for 16 days from an institutional building, which uses the water distributed from the same public utility as the townhouse. Free chlorine levels were selected based on the observed chlorine levels in the townhouse; on three different days, the kitchen faucet (cold water tap) was thoroughly purged until the water temperature was stabilized, and free chlorine residuals were measured (0.5 and 0.8 mg/L).

Table 11. Initial Conditions for Bench-Scale Experiments

Data Set	**Initial Chlorine Concentration (mg/L)**	**TOC (mg/L)**	**pH**	**Temperature (°C)**	**Reaction Time (h)**
1	0.5±0.04	0.4	7±0.03	20	1, 5, 8
2	0.5±0.04	0.4	8±0.04	20	1, 5, 8
3	0.5±0.04	0.4	9±0.04	20	1, 5, 8
4	0.5±0.04	0.8	7±0.03	20	1, 5, 8
5	0.5±0.04	0.8	8±0.04	20	1, 5, 8
6	0.5±0.04	0.8	9±0.04	20	1, 5, 8
7	0.5±0.04	1.5	7±0.03	20	1, 5, 8
8	0.5±0.04	1.5	8±0.04	20	1, 5, 8
9	0.5±0.04	1.5	9±0.04	20	1, 5, 8
10	0.8±0.14	0.4	7±0.03	20	1, 5, 8
11	0.8±0.14	0.4	8±0.04	20	1, 5, 8
12	0.8±0.14	0.4	9±0.04	20	1, 5, 8
13	0.8±0.14	0.8	7±0.03	20	1, 5, 8
14	0.8±0.14	0.8	8±0.04	20	1, 5, 8
15	0.8±0.14	0.8	9±0.04	20	1, 5, 8
16	0.8±0.14	1.5	7±0.03	20	1, 5, 8
17	0.8±0.14	1.5	8±0.04	20	1, 5, 8
18	0.8±0.14	1.5	9±0.04	20	1, 5, 8

Samples were prepared using de-ionized, organic-free ultra-filtered water (Barnstead™ Nanopure™ Model D11901, Thermo Fisher Scientific, Waltham MA). The desired pH levels were obtained with borate and sodium hydroxide (Fisher Scientific, Waltham MA) buffer solutions prepared in de-ionized water. The humic acid (HA) stock solution was prepared by dissolving 0.5 g of commercial HA (Sigma Aldrich, St. Louis, MO) in 500 mL de-ionized water. The solution's pH was adjusted to 10 with sodium hydroxide and stirred for 24 h (Li & Zhao, 2006). The filtered solution (0.45 µm membrane filter, Whatman, United Kingdom) was stored at 4 °C during the experiments. Commercial chlorine stock solution was purchased from HACH® to adjust free chlorine concentrations in samples.

Chlorine demand-free glassware was prepared according to the procedure described by Summers et al. (1996): the incubation bottles and flasks were: i) soaked in a detergent bath overnight, ii) rinsed four times with hot tap water, iii) rinsed two times with distilled water, iv) soaked in a 20 mg/L chlorine solution for at least 24 h, v) rinsed four times with distilled water, vi) rinsed two times with laboratory clean water and vii) dried at 140 °C in the oven overnight.

For each sample batch, humic acid stock solution was added to 300 mL of blank water in a flask to prepare samples at selected TOC levels. The pH of the solution was adjusted to the closest desired level, and then the flask was filled up to 500 mL. Chlorine stock solution was added to the flask to reach desired disinfectant level, and the mixture was mixed thoroughly using a magnetic stirrer. The free chlorine and pH levels were measured and recorded before dividing samples into 125 mL amber glass vials. The samples were sealed headspace-free and placed in a temperature-controlled water bath at 20±0.5 °C. After one, five, and eight hours of incubation periods, sample aliquots were transferred into 40 mL vials containing phosphate buffer and sodium sulfite (Mallinckrodt Pharmaceuticals, Ireland) to adjust pH and quench further chloroform formation, respectively. The remaining aliquots in 125 mL bottles were used to measure free chlorine concentrations for each incubation period. Bench-scale experiments and chloroform analyses were performed in the same laboratory; the chloroform collection vials were immediately stored at 4 °C and analyzed within 24 hours. A total of 54 samples were collected and analyzed for chloroform concentrations.

4.3.2. Experimental Methods for the House Samplings

A two-story townhouse single-family house located in Northern Colorado was selected to test the model prediction results. The water is distributed to the house by a public utility that uses chlorine as the primary disinfectant. The building blueprints were not accessible; however, further discussions with the building management revealed that copper pipes were installed. Three sampling events were conducted on different days between February 2021 and March 2021, and all experiments started in the evening and ended in the morning. The following procedure was followed for the samplings:

The kitchen faucet (cold water tap) was purged thoroughly until the water temperature was stabilized. At the beginning of the experiments, 500 mL of water collected in a glass flask. 125 mL of water was decanted into a chlorine demand-free amber glass bottle, sealed headspace-free, and placed in the temperature-controlled water bath at 20 °C for eight hours of incubation. 40 mL of water was taken into a chloroform collection vial that contains phosphate buffer and sodium sulfite, and another 40 mL of water was collected for TOC measurement. Free chlorine residual, pH and temperature were also measured at the beginning of the experiments. After eight hours of stagnation, 10 mL of water was directly collected from the faucet for free chlorine measurement. Immediately, 40 mL of water was sampled from the faucet to determine chloroform concentrations after the stagnation. Free chlorine level was measured from the 125 mL bottle that was incubated in the water bath. Chloroform and TOC collection vials were stored in the fridge and transported to the laboratory in a cooler; the analyses were completed within 24 hours of the sample collections.

4.3.3. Analytical Methods

The USEPA 551.1 method was utilized to analyze chloroform concentrations with gas chromatography equipped with an electron capture detector (Hewlett Packard HP 6890 Series). Calibration curves were created with chloroform concentrations at 1 µg/L, 5 µg/L, 10 µg/L, 50 µg/L, 100 µg/L, 200 µg/L, and 500 µg/L, and run at the beginning of every sample set analysis. TOC measurements were performed using a HACH® DR/2500 spectrophotometer according to HACH® Method 10129. DPD (*N, N-diethyl-p-phenylenediamine*) method 8021 was followed to measure free chlorine residuals using a HACH® Pocket Colorimeter. Temperature and pH measurements were carried out with a pH meter (PH838, Dr. Meter) and calibrated with three-point calibration before the experiments.

4.3.4. Data Analysis

All statistical analyses were performed using SAS Institute Inc. (2015). Linear regression analysis assumptions were examined for statistical adequacy, and due to the non-normal distribution of the data, data transformations were considered.

4.4. Model Development

In this study, existing models in the literature that were mainly developed for water distribution systems were adapted to premise plumbing systems. These models were selected due to their simplicity, adaptability to the premise plumbing conditions, and high prediction capabilities observed in a previous study (Gang et al., 2002). The general structure of the models with slight modifications was used as it is; the premise plumbing conditions were incorporated into the models utilizing coefficients and constants that reflect water quality parameter ranges that can be found in premise plumbing systems based on the townhouse and accompanying study experiment results as discussed earlier.

Generally, chlorine decay is described by the first-order kinetics (Clark, 1998):

$$dc/dt=-kt \tag{1}$$

where c is chlorine concentration (mg/L), k is first-order decay constant rate (min^{-1}), and t is time in minutes.

Integrating equation (1) yields the following equation:

$$C(t)=C_0\, e^{-kt} \tag{2}$$

where C(t) is chlorine concentration (mg/L) at time t, C_0 is initial chlorine concentration (mg/L) and t is time of reaction.

It is well established in the literature that chlorine demand is exerted due to reactions with the constituents in bulk water and reactions on the pipe wall (Wable et al., 1991). Therefore, the overall decay constant is separately modeled as bulk and pipe wall decay constants to represent water quality of source water and plumbing pipe:

$$k=k_b+k_w \tag{3}$$

where k (hr^{-1}) is the overall decay constant, k_b (hr^{-1}) is the bulk decay constant, and k_w (hr^{-1}) is the pipe wall decay constant.

In the literature, it was assumed that DBP formation is directly proportional to the consumed chlorine, and it could be modeled as follows (Clark & Sivaganesan, 1998; Gang et al., 2002):

$$DBP=D\,(C_0-C_t) \tag{4}$$

where DBP represents chloroform concentration (µg/L), *D* is the chloroform yield coefficient (µg Chloroform/mg Cl_2 consumed), C_0 is the initial chlorine concentration (mg/L), C_t is chlorine concentration (mg/L) at time t. *D* could be defined as the ratio of the generated chloroform concentration (µg/L) per the concentration of chlorine consumed (mg/L) (Gang et al., 2002).

By incorporating equations (2) and (3) in equation (4), the chloroform formation model could be expressed as follows:

$$CHCl_3 = D\ (C_0 - C_0\ e^{-(kb+kw)t}) \quad (5)$$

Temperature adjustments were integrated into the model by the following equation (Fisher et al., 2012):

$$k_T = k_{20} * exp\left[\frac{-E/R(20-T)}{(273+20)(273+T)}\right] \quad (6)$$

where k_T is the reaction coefficient at temperature T, k_{20} is the reaction coefficient at 20 °C, E is the activation energy (J), R is the universal gas constant (J K^{-1}). The E/R (activation coefficient) value of 11,800 K was used in the model, which was estimated based on the initial chlorine concentration (1-4 mg/L) and temperature (10-25 °C) ranges (Fisher et al., 2012). Other E/R values (e.g., 5440 and 8720) were reported in the literature (Fisher et al., 2012). Considering the effects of water quality and treatment characteristics (e.g., treated water, raw water), initial chlorine concentrations, and temperature ranges on the estimated E/R values, the value of 11,800 K was identified as the most appropriate E/R for this study.

4.5. Results and Discussion

4.5.1. Development of the Predictive Equation

Equation (2) was used to fit the chlorine decay data; the first-order chlorine decay constants (k) were estimated for each data set given in Table 11. Chloroform yield coefficients (*D*) were calculated from equation (5) by implementing chlorine decay constants and experimentally determined chloroform concentrations for the data sets in Table 11. As chlorine demand-free glassware was used in the experiments, the chlorine decay in bottles was treated as bulk decay, and k_w was not used in equation (5) to determine chloroform yield coefficients. The regression equation was developed for the parameter *D* by defining initial chlorine concentration, TOC, pH, and reaction time as the predictor variables. The estimation of *D* differs from Gang et al. (2002) with the inclusion of reaction time as the predictor variable in the regression equation.

The data set was explored for linear regression assumptions; non-normal distribution of the residuals was observed. The best-fitting model transformation was selected using TRANSREG procedure in SAS; a better fit was found with the quadratic model. One outlier was identified and omitted from the data set. One of the samples was lost during the sample collection; therefore, 52 observations were used for the regression analyses. A backward variable selection procedure in SAS was employed to identify the best-fitting parameters; the procedure suggested excluding the initial chlorine concentration parameter from the regression model due to the high p-value (>0.5670). This result might be associated with including a narrow range of chlorine concentrations in the study. Given that chlorine concentration is a prerequisite for chloroform formation, this important parameter was ultimately decided to be kept in the model. Other parameters were significant at the 0.05 significance level. The estimated model R^2 was 0.47 (p-value <.0001) for the following equation:

$$\mathrm{SQRT}(D) = -2.52761 + (\mathrm{pH} * 0.40452) + (\mathrm{TOC} * 1.27163) + (\mathrm{Time} * 0.12916) + (\mathrm{Chlorine} * 0.32069) \quad (7)$$

where *D* is the chloroform yield coefficient (µg Chloroform/mg Cl_2 consumed), pH of the sample, TOC is total organic carbon (mg/L), time is the reaction time (hr), and chlorine is initial chlorine concentration (mg/L). The yield coefficient ranged from 0.03 to 24.22 µg Chloroform/mg Cl_2 consumed. Statistically significant positive correlations were observed between the yield coefficient and pH (p-value: 0.03), TOC (p-value: <.0001), and reaction time (p-value: 0.02).

4.5.2. AnyLogic Simulation Model

Equations (2), (3), (5), (6), and (7) were incorporated in AnyLogic simulation software using the modeling elements (e.g., parameter, link, dynamic variable) built in the System Dynamics palette in AnyLogic (Grigoryev, 2018). In the simulation model, initial chlorine concentration, TOC, pH, temperature, bulk, and wall decay constants were linked to edit boxes to allow users to implement their site-specific conditions. A data set tracker and time plot were added to simulate chlorine decay and chloroform formation over eight hours.

4.5.3. Comparison of House Sampling and Model Simulation Results and Discussion

Collected water quality parameters from the townhouse and estimated chlorine decay constants are provided in Table 12.

Table 12. Measured Water Quality Parameters and Estimated Bulk Water and Pipe Wall Decay Constants in the House

Parameter	**House Sampling-1**				**House Sampling-2**				**House Sampling-3**			
	Time-0 hr		**Time-8 hr**		**Time-0 hr**		**Time-8 hr**		**Time-0 hr**		**Time-8 hr**	
	Faucet	**Bottle**	**Faucet**	**Bottle**	**Faucet**	**Bottle**	**Faucet**	**Bottle**	**Faucet**	**Bottle**	**Faucet**	**Bottle**
Free-Chlorine Concentration (mg/L)	0.78	0.78	0.03	0.54	0.77	0.77	0.07	0.58	0.80	0.80	0.07	0.44
TOC (mg/L)	1.4	-	-	-	1.4	-	-	-	1.6	-	-	-
pH	8.17	-	7.89	-	8.15	-	-	-	8.35	-	-	-
Temperature (°C)	12.3	-	26.9	-	9.6	-	-	-	12.2	-	-	-
Bulk Water Decay Constant (hr^{-1})	0.05				0.04				0.07			
Pipe Wall Decay Constant (hr^{-1})	0.36				0.26				0.23			

The bulk water (k_b) and pipe wall (k_w) chlorine decay constants were estimated based on the samples taken from the faucet and incubation bottle. Equation (2) was used to fit the chlorine decay constants for each sampling day at the house. The decay rates estimated from the faucet include both bulk and pipe wall decay constants; therefore, the bulk decay constant was subtracted from the estimated value to find the wall pipe decay constant. k_b ranged from 0.04 to 0.07 hr^{-1} , while k_w ranged from 0.23 to 0.36 hr^{-1}. Smaller bulk decay constants were observed than the wall pipe decay constants, and the results were consistent with the literature (Brown et al., 2011, Table 2).

Experimentally determined chloroform concentrations from the house samplings and simulation model predictions are shown in Table 13. For house sampling 1, at time 0 hr, the chloroform concentration was found 16.8 µg/L at the faucet; this value represents the existing chloroform concentration in the distribution system. After eight hours of stagnation, the chloroform concentration level was found 34.2 µg/L at the faucet. The concentration difference during the stagnation shows that 17.4 µg/L of chloroform was generated within the household. For house samplings 2 and 3, 14.2 µg/L and 16.6 µg/L of chloroform formations were observed at the faucet, respectively. Initial chlorine concentration, TOC, and pH levels were similar except for temperatures between house sampling events 1 and 2. As expected, higher chloroform concentrations were observed during house sampling 1, when the water temperature was higher. A comparison was also made between house sampling 1 and 3; in house sampling 3, initial chlorine concentration, TOC, pH levels were higher than house sampling 1, and the temperature measurements were close to each other. Unexpectedly, a relatively lower chloroform concentration was observed in house sampling 3 compared with house sampling 1. The reason for this finding is unclear; however, it is suspected that it could occur due to the effects of other factors (e.g., bromide ion) that were not collected in this study or might point out an instrumentation error.

Table 13. Chloroform Concentrations from House Samplings and Model Predictions

Parameter	**Sampling Number**	**Time-0 hr Faucet (A)**	**Time-8 hr Faucet (B)**	**Chloroform Formation at the Faucet (B-A)**	**Model Prediction**	**Difference (%)**
Chloroform Concentration (µg/L)	House Sampling-1	16.8	34.2	17.4	10.9	-37
	House Sampling -2	16.9	31.1	14.2	10	-30
	House Sampling -3	13.6	30.2	16.6	12.1	-27

Initial chlorine concentration, TOC, pH, temperature, bulk water, and pipe wall decay constants from the house samplings (Table 12) were entered into the AnyLogic software user interface. Chloroform concentrations of 10.9 µg/L, 10 µg/L, and 12.1 µg/L were predicted by the model for house sampling 1, house sampling 2, and house sampling 3, respectively. For all cases, the simulation model underpredicted the chloroform levels by 27-37% after eight hours. In previous studies, model tendencies to underpredict TTHMs (by 10-30% and 20-30%) and chloroform levels were observed when linear regression equations were utilized for predictions (Greiner et al., 1992; Harrington et al., 1992). Biofilm deposition could be an important contributor to the chloroform formation at the tap (Xu et al., 2018), and its effects were not included in the model. It is important to emphasize that the model estimates the chloroform levels based on fixed temperature, pH, and TOC levels; therefore, the changes in water quality parameters at the tap over the stagnation period could influence the results. In several studies, temperature increases in the premise plumbing were observed compared to the water temperature in the distribution system (Dion-Fortier et al., 2009; Salehi et al., 2020). For instance, for house sampling 1, pH decreased from 8.17 to 7.89, while temperature increased from 12.3 °C to 26.9 °C after eight hours. The increase in temperature in premise plumbing possibly increased chloroform concentrations at the faucet.

In this study, underpredicted chloroform levels might result from the moderate R^2 value (0.47) of the *D* chloroform yield coefficient equation, pointing out unexplained variations by the model. In general, the water's NOM content is explained by different surrogate parameters such as TOC, dissolved organic carbon (DOC), or UV absorbance capacity (UV_{254}) (Chowdhury & Champagne, 2008; Edzwald et al., 1985). Chowdhury and Champagne (2008) suggest that DOC or UV_{254} could be used for THM formation modeling. Therefore, the inclusion of other parameters could improve the model's precision and provide better estimates. Besides the yield coefficient regression model, the temperature adjustment model could affect the results. Here, equation 6 was used to adjust the bulk decay constant at different temperatures based on the constants estimated at 20 °C. The E/R value of 11,800 K was selected, which was determined for chlorine concentrations of 1-4 mg/L; however, a different E/R value is expected for the chlorine ranges used in this study and requires future assessments.

Several peculiarities were observed during the bench-scale experiments, and it was suspected that those might have effects on the model's prediction ability. Higher chlorine residuals were found for some data sets after 8 hours of stagnation than the measured residuals at 5 hours, which is believed to affect the yield coefficient equation estimation. These results might occur from differing reactions between the sample aliquots and the chlorine demand-free glass bottles. Considering the study's small sample size, these data points were kept in the regression analysis. Other factors such as variations between added chlorine and TOC content might also be influential on the results. In the present study, chlorine stock solutions were purchased in 10 mL ampules, and between the ampules, concentration differences were observed in added doses. For future research attempts, it is suggested to decant chlorine ampules in the same bottle or prepare chlorine stock solutions in bulk using aqueous sodium hypochlorite solutions to eliminate variations in added concentrations (Summers et al., 1996). In this study, the sample batches were not analyzed for TOC during the bench-scale experiments due to some restrictions. It was assumed that the added doses of humic acid yielded the desired TOC levels in the samples. Performed duplicative analyses of the same doses showed that variations (±0.1) occurred between the added TOC concentrations.

4.6. Conclusions and Future Research

To date, many predictive models have been developed to determine disinfection by-product concentrations at the water distribution system level. This study aimed to predict the chloroform concentrations in premise plumbing. One of the THM species, chloroform, was examined in this study to simplify the model development process, and brominated THMs were excluded. Bench-scale experiments were conducted with typical water quality parameter levels that can be observed at the tap. TOC, pH, initial chlorine concentration, and reaction time variables were utilized to determine the chloroform yield coefficient and implemented in AnyLogic simulation software with the first-order chlorine decay and temperature adjustment models. A two-story townhouse was selected to test the model's predictive abilities, and three house sampling results were compared with the model predictions. The chloroform prediction model underpredicted chloroform concentrations by 27-37% compared with the house measurements. It is assumed that implementation of fixed water quality parameters in the model, temperature adjustments, varying reactions of sample aliquots with the incubation bottles, and differences in added TOC and chlorine doses could cause underpredicted chloroform concentrations. One of the limitations of this study is that, as seen in any other prediction model studies based on regression analysis, the model might not provide accurate results if used outside of the boundary conditions. However, this study represents an important initial attempt in developing a simulation-based water quality prediction model, which can be implemented in premise plumbing systems. The simulation-based model presented herein can further be improved and be used by building and facility managers as a decision-making tool to identify the most problematic water outlets under normal operations and unprecedented water stagnation conditions such as the ones caused by the building shutdowns due to COVID-19.

The chloroform concentration prediction model can be expanded in the future by including more data points, longer stagnation times, and other disinfection by-products. AnyLogic is a powerful simulation tool in which the chlorine decay model is extendable to higher-order disinfection by-product prediction models and applicable to other water-related risk exposure assessment studies in the future. The model in AnyLogic provides a simple user interface by eliminating the complexity of the model equations and allows variable adjustments. Making prediction models available in the public domain could also encourage models' adoption by practitioners such as building and facility managers. The chloroform prediction tool discussed in this paper is available from the corresponding author by request.

4.7. References

Al-Jasser, A. O. (2007). "Chlorine decay in drinking-water transmission and distribution systems: pipe service age effect". *Water Research,* 41(2), 387-396.

Al-Omari, A., Fayyad, M., and Qader, A. A. (2005). "Modeling trihalomethane formation for Jabal Amman water supply in Jordan". *Environmental Modeling & Assessment,* 9(4), 245.

American Water Works Association. (2018). *2017 Water utility disinfection survey report*. Denver, Colorado.

Amy, G. L., Chadik, P. A., and Chowdhury, Z. K. (1987). "Developing models for predicting trihalomethane formation potential and kinetics". *Journal - American Water Works Association,* 79(7), 89-97.

Biswas, P., Lu, C., and Clark, R. M. (1993). "A model for chlorine concentration decay in pipes". *Water Research,* 27(12), 1715-1724.

Brown, D., Bridgeman, J., and West, J. R. (2011). "Predicting chlorine decay and THM formation in water supply systems". *Reviews in Environmental Science and Bio/Technology,* 10(1), 79-99.

Centers for Disease Control and Prevention. (2020). Guidance for reopening buildings after prolonged shutdown or reduced operation. Retrieved from https://www.cdc.gov/coronavirus/2019-ncov/php/building-water-system.html

Chowdhury, S., and Champagne, P. (2008). "An investigation on parameters for modeling THMs formation". *Global Nest Journal,* 10(1), 80-91.

Chowdhury, S., Champagne, P., and McLellan, P. J. (2009). "Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review". *Science of the Total Environment,* 407(14), 4189-4206.

Chowdhury, S., Rodriguez, M. J., Sadiq, R., and Serodes, J. (2011). "Modeling DBPs formation in drinking water in residential plumbing pipes and hot water tanks". *Water Research,* 45(1), 337-347.

Clark, R. M. (1998). "Chlorine demand and TTHM formation kinetics: a second-order model". *Journal of Environmental Engineering,* 124(1), 16-24.

Clark, R. M. (2015). "The USEPA's distribution system water quality modelling program: a historical perspective". *Water and Environment Journal,* 29(3), 320-330.

Clark, R. M., and Sivaganesan, M. (1998). "Predicting chlorine residuals and formation of TTHMs in drinking water". *Journal of Environmental Engineering,* 124(12), 1203-1210.

Clark, R. M., and Sivaganesan, M. (2002). "Predicting chlorine residuals in drinking water: second order model". *Journal of Water Resources Planning and Management,* 128(2), 152-161.

Clark, R. M., Thurnau, R. C., Sivaganesan, M., and Ringhand, P. (2001). "Predicting the formation of chlorinated and brominated by-products". *Journal of Environmental Engineering,* 127(6), 493-501.

Dion-Fortier, A., Rodriguez, M. J., Sérodes, J., and Proulx, F. (2009). "Impact of water stagnation in residential cold and hot water plumbing on concentrations of trihalomethanes and haloacetic acids". *Water Research,* 43(12), 3057-3066.

Edzwald, J. K., Becker, W. C., and Wattier, K. L. (1985). "Surrogate parameters for monitoring organic matter and THM precursors". *Journal - American Water Works Association,* 77(4), 122-132.

Fisher, I., Kastl, G., and Sathasivan, A. (2012). "A suitable model of combined effects of temperature and initial condition on chlorine bulk decay in water distribution systems". *Water Research,* 46(10), 3293-3303.

Fisher, I., Kastl, G., and Sathasivan, A. (2017). "A comprehensive bulk chlorine decay model for simulating residuals in water distribution systems". *Urban Water Journal,* 14(4), 361-368.

Gang, D. D., Segar Jr., R. L., Clevenger, T. E., and Banerji, S. K. (2002). "Using chlorine demand to predict TTHM and HAA9 formation". *Journal - American Water Works Association,* 94(10), 76-86.

Grayman, W. M. (2018). "*History of water quality modeling in distribution systems"*. Presented at the 1st International WDSA / CCWI 2018 Joint Conference, Kingston, Ontario, Canada

Greiner, A. D., Obolensky, A., and Singer, P. C. (1992). "Technical note: comparing predicted and observed concentrations of DBPs". *Journal - American Water Works Association,* 84(11), 99-102.

Grigoryev, I. (2018). *AnyLogic in Three Days*.

Haas, C. N., and Karra, S. B. (1984). "Kinetics of wastewater chlorine demand exertion". *Water Pollution Control Federation,* 56(2), 170-173.

Haddad, M., McNeil, L., and Omar, N. (2014). "Model for predicting disinfection by-product (DBP) formation and occurrence in intermittent water supply systems: Palestine as a case study". *Arabian Journal for Science and Engineering,* 39(8), 5883-5893.

Harrington, G. W., Chowdhury, Z. K., and Owen, D. M. (1992). "Developing a computer model to simulate DBP formation during water treatment". *Journal - American Water Works Association,* 84(11), 78-87.

Jadas-Hécart, A., El Morer, A., Stitou, M., Bouillot, P., and Legube, B. (1992). "Chlorine demand of a treated water[Modelisation de la demande en chlore d'une eau traitee]". *Water Research,* 26(8), 1073-1084.

Jonkergouw, P. M. R., Khu, S.-T., Savic, D. A., Zhong, D., Hou, X. Q., and Zhao, H.-B. (2009). "A variable rate coefficient chlorine decay model". *Environmental Science & Technology,* 43(2), 408-414.

Kalan, D., Ozbek, M., and Omur-Ozbek, P. (Unpublished work). *A state-of-the-art review of contaminant prediction models for premise plumbing systems and indoor air environments*.

Kalan, D., Ozbek, M., Omur-Ozbek, P., and Dooley, G. (Unpublished work). *A case study: comparison of disinfection by-product formations between green and conventional buildings*.

Lee, J., Mervosh, S., Avila, Y., Harvey, B., and Matthews, A. (2020). See how all 50 states are reopening (and closing again). *The New York Times.* Retrieved from https://www.nytimes.com/interactive/2020/us/states-reopen-map-coronavirus.html

Li, X., and Zhao, H.-b. (2006). "Development of a model for predicting trihalomethanes propagation in water distribution systems". *Chemosphere,* 62(6), 1028-1032.

Lin, T. F., and Hoang, S. W. (2000). "Inhalation exposure to THMs from drinking water in south Taiwan". *Science of the Total Environment,* 246(1), 41-49.

Nguyen, C., Elfland, C., and Edwards, M. (2012). "Impact of advanced water conservation features and new copper pipe on rapid chloramine decay and microbial regrowth". *Water Research,* 46(3), 611-621.

Ozdemir, O. N., and Ger, A. M. (1998). "Realistic numerical simulation of chlorine decay in pipes". *Water Research,* 32(11), 3307-3312.

Ozdemir, O. N., and Ucak, A. (2002). "Simulation of chlorine decay in drinking-water distribution systems". *Journal of Environmental Engineering,* 128(1), 31-39.

Powell, J. C., West, J. R., Hallam, N. B., Forster, C. F., and Simms, J. (2000). "Performance of various kinetic models for chlorine decay". *Journal of Water Resources Planning and Management,* 126(1), 13-20.

Proctor, C. R., Rhoads, W. J., Keane, T., Salehi, M., Hamilton, K., Pieper, K. J., Cwiertny, D. M., Prévost, M., and Whelton, A. J. (2020). "Considerations for large building water quality after extended stagnation". *AWWA Water Science,* 2(4).

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., and DeMarini, D. M. (2007). "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research". *Mutation Research,* 636(1), 178-242.

Rodrigues, P. M. S. M., Esteves da Silva, J. C. G., and Antunes, M. C. G. (2007). "Factorial analysis of the trihalomethanes formation in water disinfection using chlorine". *Analytica Chimica Acta,* 595(1), 266-274.

Rossman, L. A., Clark, R. M., and Grayman, W. M. (1994). "Modeling chlorine residuals in drinking-water distribution systems". *Journal of Environmental Engineering,* 120(4), 803-820.

Roth, D. K., and Cornwell, D. A. (2018). "DBP impacts from increased chlorine residual requirements". *Journal - American Water Works Association,* 110(2), 13-28.

Sadiq, R., and Rodriguez, M. J. (2004). "Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review". *Science of the Total Environment,* 321(1), 21-46.

Salehi, M., Odimayomi, T., Ra, K., Ley, C., Julien, R., Nejadhashemi, A. P., Hernandez-Suarez, J. S., Mitchell, J., Shah, A. D., and Whelton, A. (2020). "An investigation of spatial and temporal drinking water quality variation in green residential plumbing". *Building and Environment,* 169, 106566.

SAS Institute Inc. (2015). *Base SAS 9.4 procedures guide*, SAS Institute Inc., Cary, NC, USA.

Segar, R., Clevenger, T., and Banerji, S. (2003). "Using chlorine demand to predict TTHM and HAA9 formation". *Journal - American Water Works Association,* 94, 76-86.

Singer, P. C. (1994). "Control of disinfection by-products in drinking water". *Journal of Environmental Engineering,* 120(4), 727-744.

Summers, R. S., Hooper, S. M., Shukairy, H. M., Solarik, G., and Owen, D. (1996). "Assessing DBP yield: uniform formation conditions". *Journal - American Water Works Association,* 88(6), 80-93.

Taras, M. J., Hedgepeth, L. L., and Faber, H. A. (1950). "Preliminary studies on the chlorine demand of specific chemical compounds [with discussion]". *Journal - American Water Works Association,* 42(5), 462-474.

U.S. Department of Labor Occupational Safety and Health Administration. (2020). *Guidance on preparing workplaces for COVID-19* (OSHA 3990-03 2020). Retrieved from https://www.osha.gov/sites/default/files/publications/OSHA3990.pdf

U.S. Environmental Protection Agency. (2016). Disinfection Byproduct Information. Retrieved from https://archive.epa.gov/enviro/html/icr/web/html/dbp.html#regulatory

Van Kenhove, E., Dinne, K., Janssens, A., and Laverge, J. (2019). "Overview and comparison of Legionella regulations worldwide". *American Journal of Infection Control,* 47(8), 968-978.

Vasconcelos, J. J., Rossman, L. A., Grayman, W. M., Boulos, P. F., and Clark, R. M. (1997). "Kinetics of chlorine decay". *Journal - American Water Works Association,* 89(7), 54-65.

Wable, O., Dumoutier, N., Duguet, J., Jarrige, P., Gelas, G., and Depierre, J. (1991). "Modeling chlorine concentrations in a network and applications to Paris distribution network". *Proc. Water Quality Modeling in Distribution Systems. AWWA Research Foundation, US EPA, Cincinnati, OH*.

World Health Organization. (2020). *Water, sanitation, hygiene, and waste management for SARS-CoV-2, the virus that causes COVID-19*. Retrieved from https://www.who.int/publications/i/item/WHO-2019-nCoV-IPC-WASH-2020.4

Xu, J., Huang, C., Shi, X., Dong, S., Yuan, B., and Nguyen, T. H. (2018). "Role of drinking water biofilms on residual chlorine decay and trihalomethane formation: An experimental and modeling study". *Science of the Total Environment,* 642, 516-525.

Yeh, H.-D., Wen, S.-B., Chang, Y.-C., and Lu, C.-S. (2008). "A new approximate solution for chlorine concentration decay in pipes". *Water Research,* 42 10-11, 2787-2795.

Zheng, M., He, C., and He, Q. (2015). "Fate of free chlorine in drinking water during distribution in premise plumbing". *Ecotoxicology,* 24(10), 2151-2155.

CHAPTER. 5: Conclusions, Research Contributions, and Future Research Directions

5.1. Summary and Conclusions

This dissertation includes three independent but complementary articles that focus on essential aspects of water quality in premise plumbing systems. With the primary objective of addressing the knowledge gaps in the literature, the articles provide a better insight into i) the effects of conventional and green-certified building premise plumbing systems on water quality, ii) the current state of numerical modeling research for water quality in premise plumbing systems, and iii) the implementation of a chloroform prediction and simulation tool that is developed for premise plumbing systems. The significant findings of the three articles are summarized in this chapter, followed by the research contributions and future research directions.

The first study aimed to identify and compare the effects of conventional and green-certified premise plumbing on drinking water quality. For this purpose, TTHMs and temperature, pH, free chlorine residuals, and TOC were collected from the four drinking fountains of a combined conventional and green-certified building. Two sampling events were conducted for the first study: Sampling Event-1 and Sampling Event-2. The statistical analysis of Sampling Event-1 data revealed that there were statistically significant differences in temperature, pH, and TTHM formations between some of the drinking fountains, while no statistically significant difference was found for the free chlorine residual and TOC comparisons. Water temperatures were higher on the green building side; these trends were associated with the cooling unit settings in the drinking fountains. High pH levels were observed in the conventional building fountains compared to the green building fountains. Overall, 50.6% of the measured pH values exceeded the recommended pH limit of 8.5 in drinking water (USEPA, 2020). Although the reasons for high water pH are not clear and require further research, high water alkalinity, and mineral scale build-up may increase water pH in relatively older plumbing pipes of the conventional building. The average free chlorine residuals were measured at around 0.04-0.05 mg/L-Cl_2 for each drinking fountain; 100% of the samples were under the minimum recommended levels at the point of use (WHO, 2011). TTHM values were higher in the fountains on the conventional building side than the green building side. This finding might result from significantly high pH values that were observed in the conventional side drinking fountains. Building operation conditions (such as semester in-session vs. not in-session) did not affect the water quality parameters and TTHM formations. For several samples, TTHM concentrations exceeding 80 μg/L were observed at the drinking fountains when the building was not in-session. These concentration levels could pose a health risk to the public in the long-term exposure (King & Marrett, 1996; King et al., 2000; USEPA, 2016). Even though the distributed water quality to the green and conventional building sides was the same, variations in water quality parameters and TTHMs were observed due to the changes in water chemistry in the premise plumbing systems. The study findings point out the importance of the plumbing pipe age and its impacts on water chemistry.

Observed negative correlations between TTHMs and water quality parameters in the Sampling Event-1 data prompted Sampling Event-2 to investigate the cause of negative relationships between the variables. Statistically significant differences were observed from one vial to another for most of the temperature and pH comparisons for each drinking fountain. This finding underlines the possibility of water quality fluctuations in different sections of the water fountains and pipes and highlights the importance of sequential order sampling. Therefore, it is suggested that sequential order sampling should be taken into account in determining water quality sampling protocols for drinking fountains and THMs testing in the future.

The second study provides a state-of-the-art review of existing premise plumbing and indoor air quality contaminant prediction models that could be implemented in residential and non-residential buildings. A systematic literature search was conducted for the second study in the Compendex, Web of Science, IEEE Explore, Science Direct, and PubMed databases. The search query was executed in the title, abstract, and keywords using a set of keywords for premise plumbing and indoor air quality models. As a result of the three-step screening process (i.e., 1-title screening, 2-abstract screening, 3-full-text, reference list, and citation screening), a total of 22 contaminant prediction modeling studies for premise plumbing and 12 for indoor air quality were reviewed in this study.

The mass-transfer models have been predominantly used in the premise plumbing modeling studies, while other modeling approaches (e.g., statistical modeling) were implemented in a few studies. Among the premise plumbing models, lead and copper prediction models have drawn more attention from researchers than any other contaminants. The literature review shows that the two-film theory underlies the indoor air quality models. Although the shower models were excessively used for risk exposure assessments, the model applications were limited for a sink, dishwasher, and washing machine. This section of the dissertation is important for providing a clear insight into the current modeling efforts for premise plumbing and indoor air quality and future research directions. Implementing the models could help identify strategies to improve water and air quality in buildings and assist decision-makers in their public health risk management decisions.

The third study aimed to predict the chloroform concentrations in premise plumbing systems. An existing model in the literature that was mainly developed for water distribution systems was adopted and then adapted to premise plumbing systems. TOC, pH, initial chlorine concentration, and reaction time variables were utilized to determine the chloroform yield coefficient and implemented in a simulation software with the first-order chlorine decay and temperature adjustment models. A two-story townhouse was selected to test the model's predictive abilities, and three sets of house sampling results were compared with the model predictions. The chloroform prediction model underpredicted chloroform concentrations by 27-37% compared with the house measurements. Implementation of fixed water quality parameters in the model, temperature adjustments, varying reactions of sample aliquots with the incubation bottles, and differences in added TOC and chlorine doses could cause underpredicted chloroform concentrations. The simulation provides a simple user interface by eliminating the complexity of the model equations and allows variable adjustments. The simulation-based model presented here can be used by building and facility managers as a decision-making tool to identify the most problematic water outlets under normal operations and unprecedented water stagnation conditions such as the ones caused by the building shutdowns due to COVID-19.

5.2. Research Contributions

Based on the findings of the three articles, this dissertation contributes to the body of knowledge as follows:

1. Emphasizing the consideration of piping age as a factor in water quality comparisons between conventional and green buildings.
2. Promoting the attention to and inclusion of sequential order sampling in drinking fountain sampling protocols.

3. Presenting the current state of premise plumbing and indoor air quality modeling and highlighting the future research needs.
4. Developing a DBP prediction and simulation tool to assist decision-makers in improving water quality at the point of use.

5.3. Future Research Directions

Future research directions for each article were presented in their respective chapters to promote the research efforts on water quality in premise plumbing systems. A summary of future research directions is presented in the following paragraphs resulting from this dissertation.

In the first study, higher water pH was observed in the conventional building fountains than the green building side fountains. The reason for this finding is unclear and might stem from mineral build-up in the relatively older plumbing pipes of the conventional building. Future research is needed to investigate the effects of system age on water chemistry. By including more data points and other water quality parameters, longitudinal-experimental studies might reveal water quality changes due to system aging over time. The sequential sampling findings suggested that water temperature and pH changes between different piping sections of the drinking fountains. More research is required on how residual chlorine levels, pathogen loads, and metal concentrations change in different sections of drinking fountains. The literature reporting the premise plumbing effects on water quality for conventional and green-certified buildings is limited and requires further research. Additionally, future studies could focus on plumbing simulation systems controlled under laboratory conditions to investigate the impacts of water conservation strategies on water quality.

Based on the reviewed literature in the second study, it is recommended that existing contaminant prediction models for both premise plumbing and indoor air quality be expanded by including multi-disciplinary approaches to improve their prediction capabilities. Further research could focus on developing new prediction tools using alternative modeling methods and simulation-based engineering platforms, and consequently, validating model predictions. Innovative tools and technologies such as building scanners that are already used in other engineering disciplines could be utilized to solve water quality problems in premise plumbing systems in future studies. Experimental studies are vital for model input estimation and validation purposes; future studies could investigate contaminant transport and volatilization characteristics of high-efficiency premise plumbing components (e.g., faucet aerators, showerheads). Developing model validation protocols could be another future research area to provide clear directions on the minimum data point requirements, boundary conditions, and model application areas. In addition, robust databases are needed to categorize water and air quality parameters for different types of buildings with different water-air-energy performance characteristics.

The prediction capability of the chloroform prediction tool was tested using only three sets of data from a single house. Future studies could implement the tool by including more data points and buildings with different characteristics. The model can be expanded in the future by including other disinfection by-products and longer stagnation times. In addition, the model predictions could be improved by modeling the inconstant nature of the water quality parameters in plumbing pipes during stagnation. The chlorine decay model is extendable to higher-order disinfection by-product prediction models and can be applied to other water-related risk exposure assessment studies in the future.

5.4. References

King, W. D., and Marrett, L. D. (1996). "Case-control study of bladder cancer and chlorination by-products in treated water (Ontario, Canada)". *Cancer Causes & Control,* 7(6), 596-604.

King, W. D., Marrett, L. D., and Woolcott, C. G. (2000). "Case-control study of colon and rectal cancers and chlorination by-products in treated water". *Cancer Epidemiology, Biomarkers & Prevention,* 9(8), 813-818.

U.S. Environmental Protection Agency. (2016). Disinfection Byproduct Information. Retrieved from https://archive.epa.gov/enviro/html/icr/web/html/dbp.html#regulatory

U.S. Environmental Protection Agency. (2020). National Primary Drinking Water Regulations (NPDWRs). Retrieved from https://www.epa.gov/sdwa/drinking-water-regulations-and-contaminants#Secondary

World Health Organization. (2011). *Measuring chlorine levels in water supplies*. Retrieved from https://www.who.int/water_sanitation_health/publications/2011/tn11_chlorine_levels_en.pdf