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Chlorine Conversion: Biological and Water Quality Impact on Activated Carbon Block Point of Use Filters

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Chlorine Conversion: Biological and Water Quality Impact on Activated Carbon Block Point of Use Filters

by

Horace S. Jakpa

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering Department of Civil and Environmental Engineering College of Engineering University of South Florinda

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Keywords: nitrification, drinking water, chloramine, EPA, nitrite

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Dedication

I dedicate this thesis to my parents (Mr. and Mrs. Jakpa), my siblings for allowing me to travel, to make a difference, and for their steadfast love, and encouragement throughout this journey.

To Dr. Abraham Alhassan, Ms. Bonosa Mahama, and Dr. Zenabu Mohamed for their support and for teaching me the value of perseverance as I journey through life.
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Abstract

Point-of-use (POU) activated carbon (AC) filters are ubiquitous in many U.S. households. AC can reduce concentrations of lead, other heavy metals, and mitigate taste and odor issues. However, AC filters also remove residual disinfectants, thus allowing for the proliferation of microbes in the filter. In chloraminated systems, this can lead to localized, filter-induced nitrification. Most notably, high nitrite and nitrate in drinking water can cause methemoglobinemia (blue baby syndrome) in children under the age of three, raising public health concerns.

As a control measure for nitrification within distribution systems, utilities practice periodic, short-term secondary disinfectant switches from chloramine to free chlorine (chlorine conversion/free-chlorine period (FCIP)). This study investigates the impact of chlorine conversions on inline AC-POU filters and the occurrence of nitrification before, during, and after the conversion.

To test these impacts, a laboratory-based filter rig was constructed with three new, commercially available AC-POU filters. The City of Tampa piped water supplied within the laboratory was used as the influent to test impacts of the 7-28 August 2020 (FCIP-1) and the 8-29 March (FCIP-2) chlorine conversion. Filter 1 began operation 34 days before the FCIP-1 Filter 2 started halfway through the FCIP-1 and Filter 3 started once monochloramine concentrations stabilized in tap water samples post-FCIP-1. Monitored influent and effluent water quality parameters included: total ATP, nitrite, nitrate, total chlorine, monochloramine, free-chlorine, pH, temperature, and dissolved oxygen.

Before the FCIP-1, Filter 1 nitrite concentrations exceeded the EPA MCL after only 32 days of operation, implying filters can immediately nitrify after installation in a system expected
to have biofilm and planktonic nitrifiers within the system (immediately before a conversion). During the free-chlorine periods (FCIPs), effluent concentrations of nitrite, nitrate, and total-ATP decreased immediately, signifying microbial inactivation and nitrification reduction in the filters.

Post-conversion nitrification onset depended on filter age and whether the filters previously experienced nitrification. Nitrifiers were reactivated immediately in Filter 1 post-FCIP-1, with observed nitrite and nitrate levels rapidly increasing, with nitrite exceeding 0.5 mg/L-N after only 6 days post chlorine conversion while Filter 2 & 3 delayed nitrification until 4 weeks. Previous incidences of nitrification within the filters had lasting water quality impacts. During FCIP-2, effluent concentrations of nitrite, nitrate, and Total-ATP decreased immediately. However, post-FCIP-2, all three filters re-nitrified immediately within a week, with filter 3 recording the highest concentrations (3.49 mg/L NO₂ as N) and was the fastest to nitrify.

Increasing concentrations of nitrite, nitrate, and total ATP varied based on the filter operation condition. Though there was no statistically significant difference in overnight and weekend stagnation samples, stagnation, in general, resulted in greater concentrations of nitrite, nitrate, and total ATP counts while periodic flush samples recorded the lowest concentration below the USEPA MCLs. This research demonstrates that free chlorine conversions did little to mitigate nitrification in POU AC filters. Based on the results obtained in this study, AC POU in chloraminated water systems practicing periodic free chlorination raises possible public health concerns.
Chapter 1: Introduction

Globally, attention has been drawn to the absolute need for the provision of safe quality drinking water at the point of use (POU). The safety and quality of drinking water can however be influenced by various factors and is intricately linked to the exposure of treated water beyond the treatment plant, through the distribution system, and finally at the tap. Over decades, water utilities have leveraged secondary disinfection (predominantly chloramination and free chlorine) as the key strategy to ensuring and sustaining the safety of treated water. However, this approach is more of a risk trade-off between limiting the formation of disinfection byproducts (DBPs) and the soaring nitrification occurrence potential thus increasing the concentration of nitrogen species in water. Free chlorine is more prone to forming a higher amount of DPBs while limiting nitrification, on the other hand, chloramine limits DPBs formation but promotes nitrification.

Despite the use of this disinfection in the United States, a recent consumer survey report indicates that 48% of respondents have concerns about the safety of tap water (WQA, 2019). To ensure the safety of drinking water beyond the tap at homes, numerous households have therefore embraced the use of POU devices. It is estimated that more than 40% of households in the United States have installed some POU devices in their home water system (WQA, 2019). The use of these point of entry (POE) and point of use (POU) treatment units at homes and public places, however, do come with some disadvantages, and the effectiveness of these devices in ensuring the safety of water is debatable as these filters are not a one size fit all.

Over the years, concerns about the occurrence of nitrification in various water distribution systems have been raised and extensive research has been conducted into clearly understanding
and mitigating this challenge. Nitrification in water systems has been shown to significantly impact water quality, it has been associated with a rapid decrease in residual disinfections and an increase in nitrite and nitrate concentration, raising public health concerns (Wilczak et al., 1996; Alfredo, 2021). Prominent among some mitigating strategies currently utilized include periodic flushing of water systems and temporarily switching between secondary disinfectants (chloramine to free chlorine) at the water treatment plants. The temporary disinfectant switch, which subsequently is referred to as the free chlorine period (FCIP) in this research, is typically practiced twice annually by the City of Tampa in March and August. The FCIP is aimed at eliminating ammonia supplied by chloramine decomposition as an electron donor, thus limiting the occurrence of nitrification and the possible deterioration of water quality. While FCIP is primarily aimed at mitigating nitrification in distribution water systems, it can further be used to reduce biofilm formation, and the potential of developing chloramine resistant bacterial (Odell et al., 1996; Seidel et al., 2005; AWWA M20, 2006; AWWA M56, 2013a; USEPA, 2016) 

Several investigations have been conducted to clearly understand the effectiveness of FCIP and its impact in distribution systems. However, little is known about the effectiveness and impact of FCIP on point-of-use filters. Specifically, knowledge about the effects on filter performance and the risk of consumer exposure to nitrite and nitrate is yet to be fully understood as this subject is currently not fully researched.

1.1 Research Objectives and Goals

Given the lack of research on the use of activated carbon (AC) filters with chloraminated distribution systems and the impact of periodic FCIP could have on installed filters within homes, this research seeks to determine the microbial and chemical risk imposed by using AC POU filters in chloraminated systems, the impact of disinfection switching on microbial behavior, and
nitrification patterns. To investigate this overarching goal, this research is focused on the following objectives:

1. Evaluate how season, use, and stagnation impact filtrate water quality.
   - Hypothesis: Regardless of when a filter was brought online, long periods of stagnation will promote nitrification activity within the filters.

2. Determine the impact of a limited FCIP and filter installation timing on nitrification within filters.
   - Hypothesis: Microbial seeding plays an important role in nitrification onset, thereby delaying the initiation of nitrification for filters seeded during and immediately after an implemented FCIP.

1.2 Organization of Thesis

To satisfy the research objectives, this thesis is organized into 4 main chapters. Chapter 2 presents an overview of relevant literature giving background information to this research and identifying the existing knowledge gaps. Drinking water disinfection practices, nitrification, and the impact on drinking water are further discussed in this chapter.

Chapter 3 presents a detailed description of the research materials, methods, and procedures. In chapter 4, the result, findings, and discussions are presented related to the objective and stated research hypothesis. These results are compared to other findings in the existing literature.

Chapter 5 addresses the overall conclusion, the current research limitations, and possible future works required for further investigations.
Chapter 2: Background and Literature Review

2.1 History of POU Devices in the United States

Addressing growing concerns of water quality and safety at household levels, point-of-use (POU) treatment technology has emerged globally as a prominent option for delivering clean and safe water to households (Taylor et al., 1979). POU treatment devices are typically installed to a fixture (single tap) either directly or under a sink for the sole purposes of minimizing contamination at the tap; thus, improving the water quality and reducing health risk to the water consumers (EPA, 2006; California Code of Regulations, 2017).

Even though the use of POU devices dates back as early as the 1970s, it was only until the amendments to the Safe Drinking Water Act (SDWA) in 1996 that POU and point-of-entry (POE) treatment units were considered as “compliance technologies” for small water systems. Compliance technologies, as defined by USEPA, may refer to both technology or other means that is affordable and that can achieve compliance with the Maximum Contaminant Level (MCL) and/or can satisfy a treatment technique requirement (Taylor et al., 1979; USEPA, 1998). Tasked with the mandates of protecting water quality and public health, the USEPA therefore, approved the use of POU treatment devices in public water systems (PWS) for the compliance of some MCL requirements set up by the National Primary Drinking Water Regulations under the SDWA (USEPA, 2006a).

In the United States, while federal and state regulations safeguard drinking water at the point of entry to distribution systems, household taps remain susceptible to contamination. To protect and ensure the integrity of drinking water at the consumer end, POU technology is used.
However, the use of POU devices as compliance technologies are highly dependent on state and/or local regulations. For various States that have supported and allowed the use of POU devices to meet the individual State and local water quality regulations, these devices are used primarily to remove taste, odor, heavy metals, organic compounds, and to minimize lead and some radioactive nuclide exposure (USEPA, 1991; Deshommess et al., 2010).

According to the Water Quality Association (WQA) in 2000, in America, it was estimated that about 41% of households used POU devices. Across the USA, as indicated by an NSF International survey, over half of the population surveyed indicated their use of POU filters in their homes (NSF International, n.d.-a). POU treatment devices have further significantly gained prominence in recent years due to concerns of recent lead exposure in drinking water as recorded in Washington, DC in 2005, Flint MI in 2014, and Newark, NJ in 2017. As a temporary solution to these exposures, city authorities recommend the use of POU filters approved for lead and other contaminant removals. For instance, residents in the Pequannock gradient of Newark were provided with over 30,000 POU filters by city authorities to minimize exposure risk (Brown et al., 2017; CDM SMITH, 2019). Homeowners have therefore resorted to the use of POU units as a countermeasure to safeguard their drinking water.

2.2 POU Filter

2.2.1 Type of POU Devices and Filter

POU treatment devices are designed utilizing similar treatment processes used at centralized treatment plants. According to the USEPA guidelines and the National Science Foundation International (NSF Int), a body responsible for the testing and certifying these devices, there are several devices (units) that are considered as POU. Generally, such units include: “plumbed-in units, plumbed-in units with separate faucets for the POU device, faucet connected
countertop units and faucet-attached units” (USEPA, 2006a). The further specific classification of POU includes personal water bottles, pitchers, under-the-sink systems, faucet-mount filters, plumbed-in systems, and refrigerator filters (NSF International, n.d.-b). The guideline focuses, however, on plumbed-in units with separate faucets as shown in Figure 1, these POU units are mostly installed at a single tap or a limited number of taps under a sink to provide water for the sole purpose of consumption either for drinking or cooking (USEPA, 2006a).

![Figure 1 Typical under the sink plumbed-in POU filter unit](image)

2.2.2 POU Treatment Technologies

Plumbed-in POU units rely on various treatment technologies. The USEPA established key POU treatment technologies for regulatory compliance, among these are adsorptive media, ion exchange (IX), granular activated carbon (GAC), and reverse osmosis (RO) (USEPA, 2006a). Though POU units are designed and certified to remove specific contaminants, the effectiveness of these applied technologies is, however, site-specific and highly dependent on water quality, filter operations, and maintenance (USEPA, 2006a). POU devices are therefore approved and listed as Small System Compliance Technologies (SSCTs) based on the various contaminants they are designed and certified to remove. In the United States, POU testing, and certification are carried out by NSF/ANSI, standards 42 and 53 focus on POU devices. NSF 42 certification standard
covers aesthetics and contaminants with no/fewer health effects concerns such as particulate matter and taste and odor compounds. NSF 53 focuses on contaminants with associated health effects such as lead (NSF International, 2011, 2015)

2.3 Activated Carbon (AC) Filters

Activated carbon (AC) based POU devices have gained popularity for their capacity and certification to remove a wide range of contaminants and aesthetic issues, such as volatile organic compounds (VOC), soluble organic compounds (SOC), lead, chlorine, particulates, taste, and odor (USEPA, 2006a; Chaidez & Gerba, 2004; Deshommes et al., 2010). AC POU filters are designed to include three major components from outside-in: (1) a plastic filter housing (2) a prefilter micro-membrane, and (3) a carbon filter media as shown in Figure 2

![Figure 2 Carbon block filter showing plastic housing to the left, prefilter membrane on carbon block, and a cross-sectional view of filter showing activated carbon wrap with membrane prefilter](image)

An AC filter utilizes both the processes of filtration and adsorption in removing contaminants in water. Water is first passed through the micro-membrane where particulates larger than the micro-membrane pores are removed. Next, the water flows through the pores of the carbon
block where the contaminants present are adsorbed onto the AC media, and clean water is collected at the center of the carbon block which later flows out through the filter outlet as illustrated in Figure 3.

![Cross-sectional view of a carbon block filter showing filtration mechanism and water flow pathway](image)

**Figure 3** Cross-sectional view of a carbon block filter showing filtration mechanism and water flow pathway

AC POU filters utilize activated carbon as the primary filter media either in the form of granular activated carbon (GAC), or a solid block activated carbon (SBAC) (USEPA, 2006a). GAC, composed of loose granular carbon particles of high surface area and ununiform porosity while SBAC comprises compressed powdered activated carbon (PAC) particles forming a block of uniform pore sizes thus providing a relatively long contact time between water and carbon (Daniels & Mesner, 2010). Besides, SBAC particle sizes are estimated to be 5-20 times smaller providing SBAC filters a greater surface area and pore sizes of about 0.5-1.0 µm compared to GAC. Furthermore, compacting PAC particles into forming a solid carbon block lowers the available pore sizes, thus reducing flowrate and providing a longer contact time between water and
carbon. SBAC filters are therefore rated with a relatively high purification rate, highly effective at removing smaller particles than GAC filters (Deshommes et al., 2010).

It is worth noting that even though AC filters have been certified to be effective at removing numerous contaminants of health and aesthetic concerns, they are not certified by NSF/ANSI for microbial removal and/or treatment. POU filters under SDWA are therefore not listed as compliance technology for microbial contaminants or an indicator of a microbial contaminant (SDWA section 1412(b)(4)(E)(ii)). The biological stability of AC POU filtrate has recently drawn the attention of several researchers (LeChevallier et al., 1984; Geldreich et al., 1985; Alfredo et al., 2020; Wu et al., 2017). AC filters are not designed to eliminate bacteria and therefore are highly susceptible to microbial colonization and the development of biofilm (USEPA, 2006a).

2.3.1 Microbial Colonization of POU Filters

Maintaining biologically stable water in distribution and connected systems has over the years been a major concern in the water industry. Biologically stable water is characterized by its inability to support microbial growth (NCR, 2007). The proliferation of microorganisms, biofilm growth, and further detachment of bacterial into water systems increasing planktonic cells, heterotrophic bacteria, and other opportunistic pathogens can compromise the integrity of drinking water making it unstable biologically (NCR, 2007). The behavior of these microorganisms in the presence of carbon has been extensively researched in water treatment plants, and distribution systems, but very little is known with connected devices. A wide range of microbes, including bacterial and opportunistic pathogens, have been found in drinking water. Generally, spore-forming microbes, yeast, fungi, acid-fast bacteria, and actinomycetes such as Legionella, Aeromonas spp, Mycobacterium spp, and Nitrospira have been found to evolve and survive bulk
water treatment, while other microorganisms have infiltrated into distribution lines and colonize POU filters through external contamination (Geldreich et al., 1985; NCR, 2007; Wu et al., 2017; Wolfe et al., 1990). Camper et al., 1986 and Wilcox et al., 1983 demonstrated the presence of bacteria in six dominant genera comprising; *Acinetobacter, Aeromonas, Alcaligenes, Corynebacterium, Micrococcus,* and *Pseudomonas* in pilot-scale and full water treatment GAC effluent while Daschner et al., in 1996 reported the same major genera in POU AC filter effluent.

Given that, the USEPA has established a maximum HPC bacterial count of 500 CFU/mL in drinking water, the USEPA does not recommend the use of a POU filter for compliance with microbial contamination as an AC POU filter can rapidly become biologically activated. The health risk associated with the presences of these microflora in water is still highly debated, while some researchers are of the view that the presence of these microorganisms does not pose any health risk, in contrast, other researchers believe that increasing concentration of bacterial and other opportunistic pathogens in water can leave immunocompromised consumers highly susceptible to health risk raising possible health concerns (LeChevallier & McFeters, 1990; Chaidez & Gerba, 2004; Chaidez & Gerba, 2004; Geldreich et al., 1985; Taylor et al., 1979; NCR, 2007).

Heterotrophic plate counts (HPC) have been used as early as the 19th century as an indicator of the presence of bacteria in water and as an index indicator of microbial regrowth in water distribution systems (NCR, 2007). Van der Wende et al., (1989) demonstrated that the development of biofilm on water system surfaces was responsible for the recorded elevated bacteria counts.

Biofilm on carbon can be formed from the increasing accumulation of immobilized biologically active bacterial cells on the media surface. Continuous bacterial growth on carbon is
possible due to the properties of the carbon surface and the interaction between microorganisms and the carbon surface. The ability of microorganisms to colonized and grow on the carbon surface is significantly influenced by the presence of adsorbed matter that contains microbial nutrients, and carbon’s ability to remove disinfection residuals, thus eliminating microbial inactivation and giving rise to a favorable growth environment for bacteria. Furthermore, the presence of some functional groups on carbon surface promotes biofilm growth with the porous carbon’s surface protecting bacteria against fluid shear forces keeping them attached to the carbon surface (Knezev, 2015; Stewart et al., 1990; Weber et al., 1978; LeChevallier & McFeters, 1990). According to some authors, the development of biofilm on carbon follows a three-step process; (1) week physical adsorption of microbes to carbon which is liable to desorption (2) formation of slime matrix (extracellular polymer) that strongly attaches the microorganism to the carbon surface, and (3) the rapid growth of bacterial populations forming a biofilm (Mashall, 1971; Floodgate, 1972; Charakis, 1973; NCR, 2007). However, the continuous creation and attachment of biofilm results in the formation of microcolonies which can be detached and released into water thereby increasing planktonic bacterial counts in the effluent (Fleming, 2004a).

Biologically active carbon filter media have been reported to result in deteriorating water quality due to the release of microorganisms into the filtrate. Taylor et al., (1979) observed elevated bacterial densities in filter effluent in one to two orders of magnitude greater than that of finished treated tap water sampled. Several other investigations have reported similar results of bacteria growth within AC POU filters (Alfredo et al., 2020; Chaidez & Gerba, 2004b; Geldreich et al., 1985; Reasoner et al., 1987; SU et al., 2009; Tobin et al., 1981; LeChevallier & McFeters, 1990).

Using scanning electron microscopy on GAC particles from water filters, varying colonies of microorganisms have been found to exist on and within the crevices and cracks of carbon
particles (Weber et al., 1978; LeChevallier et al., 1984; Camper et al., 1986). While assessing the bacterial quality of a GAC pilot-scale plant effluent, Stewart et al., (1990) observed elevated counts of HPC. Scanning electron microscopy analysis indicated about 77% of the recovered carbon particles were colonized with 1-50 bacterial cells (Stewart et al., 1990). Some concerns have been raised about the effects of carbon on the biological integrity of filtrate, as microbial deposits from within filters can find their way into the filtrate (LeChevallier & McFeters, 1990). Furthermore, according to the NRC (2007), microbial growth and biofilm formation in water systems can result in taste and odor issues, as well as rapid decreases in disinfection residuals. Given that some authors have not associated the presence of HPC bacteria in water with any health concern, in contrast, other authors have established that biofilm in water can harbor and promote opportunistic pathogen growth that can pose possible health threats to immunocompromised consumers (NCR, 2007).

2.3.2 Water Disinfection and Microbial Growth in AC POU Filters

Water treatment plants have resorted to using disinfection technologies such as chlorination, and/or chloramination to safeguard the biological integrity of finished drinking water. Nonetheless, despite disinfection, microbial activity continues to persist in drinking water treatment processes, distribution systems, and connected POU devices (Geldreich et al., 1985; Reasoner et al., 1987; Wingender & Flemming, 2011; Van der Kooij, 2013; Alfredo et al., 2020; Weber et al., 1978).

Using culture-based methods, Chaidez & Gerba, (2004) demonstrated the presence of bacteria at elevated HPC counts in 82.4% of GAC effluent samples of chlorinated water, with HPC bacterial counts as high as $10^7$ CFU/ml. Similarly, SU et al., (2009) monitored the bacterial quality of an AC filter using chlorinated groundwater and observed that, after a third of the filter lifecycle,
bacterial concentrations in the filtrate were greater than the influent, this result was consistent with a similar investigation by Snyder et al., (1995) and Reasoner et al., (1987). However, studies indicate that cultured methods were prone to underestimating cell counts and can be unreliable in events of very high concentrations (Wu et al., 2017).

Similarly, other researchers investigated microbial colonization of AC POU filters while using dechlorinated influent water. These studies typically recorded elevated HPCs in the filter effluent (Tobin et al., 1981; Geldreich et al., 1985; Fiore’ & Babineau, 1977; Reasoner et al., 1987). However, some of these studies did inoculate the influent water with microorganisms representing those found in water systems (Tobin et al., 1981). These investigations did result in the colonization of AC POU, however, they can misrepresent the true existing conditions of drinking water, as published investigations show that dechlorination of filters can increase filtrate HPC counts by 5 logs relative to influent water (Wallis et al., 1974; Wu et al., 2017). Furthermore, microbial inoculum used for seeding can be of a different microbiome from that which naturally exists in drinking water systems biasing results, and conclusions (Alfredo et al., 2020).

At present only a few published investigations have evaluated the impact of microbial colonization of AC POU filters in chloraminated waters. In 2017, Wu et al., though not the focus of their investigation, utilized culture-independent methods of bacterial enumeration to ascertain the microbial growth in AC POU. In their study, after 85% of the manufacturer's filter use volume, effluent HPC counts were observed at concentrations of 2 log units greater than influent levels, indicating that bacteria colonized and grew within the filter. Furthermore, they observed a community diversity change across various sections of the filter. The relative abundance of *Nitrospira* in the filter effluent relative to influent was unexpected and signified an ongoing
biological nitrification process within the filter. Wu et al., therefore concluded that AC POU filters can change the bacterial composition and their relative abundance in AC filters (Wu et al., 2017).

Similarly, an investigation was done by Alfredo et al., (2020), aimed at evaluating the impact of AC POU filters in chloraminated water systems. This study used available methods (ATP, HPC, and flow cytometry) in enumerating bacterial cell (live and dead) counts as compared to other researchers. Alfredo et al., (2020) observed elevated cell counts in effluent samples, which they associated with the reduced disinfection residual in the filters due to decomposition of chloramine by AC carbon. They indicated that reduction in disinfection residuals can promote microbial growth and increase planktonic cell concentrations in the filter effluent. Notably, Alfredo et al., (2020) measured elevated concentrations of nitrite (mean NO\textsubscript{2} = 0.03 mg/L N) in the filtrate despite the concentration of influent disinfection residuals, signifying ongoing nitrification within the filters. Using flow cytometry, they further showed a change in microbial composition in the filter effluent relative to the influent which is consistent with Wu et al., 2017 findings (Alfredo et al., 2020; Wu et al., 2017). Given the limited available studies on the impact of AC on the microbiological quality of chloraminated water and the possible occurrence of nitrification, it is important to conduct further investigations into understanding the impact of chloraminated water on AC filtrate with the focus on nitrite and nitrate production.

2.4 Water Disinfection

Water disinfection involves the use of specialized methods to destroy and inactivate objectionable microorganisms that otherwise can cause various water-borne diseases. The disinfection of drinking water and maintenance of disinfection residuals in water systems started as early as the 1900s with the sole aim of destroying microbial pathogens and preventing water-related diseases such as cholera, typhoid, and dysentery. Disinfection focuses on destroying and/or
inactivating pathogenic microorganisms and minimizing their regrowth in water systems. It is done to eliminate microbial contamination in water, and thus ensures safety and potability throughout the distribution process and to the consumer (AWWA, 2006; Crittenden et al. 2012).

There are numerous available disinfection methods, from non-chemical methods such as the use of Ultraviolet light (UV) radiation to chemical-based processes such as ozonation (O₃), and chlorination (chlorine dioxide, hypochlorite, and chloramine). However, ozone and chlorine dioxide are highly reactive and have a low residual persistence, they are therefore usually applied as primary disinfectants during the treatment process before the secondary disinfectant. Secondary disinfection is typically applied before entry into the distribution system.

A current survey by the AWWA Disinfection system committee indicates that chlorination is the most widely used disinfection method (Malley, 2008). Free chlorine and chloramine can persistently maintain their residuals and are predominantly used. (AWWA, 2013; AWWA, 2002; Komorita & Snoeyink, 1985). Even though free chlorine has a better germicidal efficacy as a disinfection agent than chloramine, it is associated with several drawbacks such as taste, odor, and the formation of disinfection by-products (DBPs). Chloramine is often preferred because it is more stable, less reactive, persists longer in water, and is effective at minimizing the formation of DBPs relative to free chlorine; however higher concentration doses are required to achieve similar bacterial inactivation as free-chlorine (Komorita & Snoeyink, 1985; AWWA, 2013; Malley, 2008; AWWA, 2005, Water Stewardship, 2005)

Over the years, pathogen resistance to inactivation and disinfection has led to the adoption of alternative disinfectants in a multi-stage disinfection scheme. The efficacy of each disinfectant is dependent on the existing condition within the water system such as pH, temperature, and water quality as well as the type of pathogen to be inactivated (Earth Tech (Canada), 2005). Many water
treatment facilities have resorted to a two-stage disinfection process to meet the required objectives of microbial inactivation and maintaining disinfectant residuals within water systems. Treatment plants implement a combination of primary and secondary disinfection in a sequential process ("interactive disinfection") in treating water (Earth Tech (Canada), 2005). The first stage, primary disinfection, is the main disinfection process required to meet bacterial reduction through microbial inactivation of targeted pathogens. Secondary disinfection is applied to finished water to sustain microbial stability by providing persistent disinfection residual throughout the water system, especially at dead ends within the distribution system. The process of secondary disinfection helps prevent the proliferation of microbial pathogens and biofilms, and minimizes the impact of external contaminants within distribution systems (AWWA, 2013; Water Stewardship, 2005). It is generally required that water distribution systems maintain a detectable disinfectant residual. Chloraminated water systems are required to maintain 1.0 - 4.0 mg/L of disinfectant residual and a typically accepted range of 1.5-2 mg/L to minimize the risk of nitrification (AWWA, 2013).

A major criterion for secondary disinfectant selection is a long-lasting residual. Even though ozone, UV, and chlorine dioxide are efficacious disinfectants, they offer poor persistent residuals. Monochloramine is the most common chloramine species used as a secondary disinfectant because it significantly reduces taste and odor issues, is more stable, and it persists longer as a residual. Monochloramine has further been demonstrated to be better at penetrating biofilm and inactivating attached organisms as compared to free-chlorine (LeChevallier & McFeters, 1990). However, monochloramine is unable to control sudden surges of contamination and is associated with the occurrence of nitrification in water systems (Wilczak et al., 1996). Given
that no one disinfection strategy can solve all water quality issues, more efficient strategies are therefore required.

The most prominent disinfection strategy is the use of chlorine as the primary disinfectant and chloramine as a residual disinfectant (AWWA M20, 2006). This combination significantly minimizes the formation of chlorine disinfection by-products and meets microbial water quality requirements. However, an improper dosage of chlorine and ammonia during chloramination can lead to excess ammonia and increase nitrification potential within water systems. Nitrification can further impact water quality, by diminishing residual disinfectants and leaving water susceptible to microbial growth (Alfredo et al., 2020).

2.4.1 Chlorination

Chlorine exists in the gaseous state as greenish yellow with a pungent smell. Chlorine (Cl\textsubscript{2}) exists only as a diatomic molecule with a molecular weight of 70.92. It is a strong oxidant and highly reactive, thus enabling it to react with many substances. Chlorine is commercially produced by electrolysis of sodium chloride brine according to equation 2-1 (AWWA M20, 2006).

\begin{align*}
2NaCl + 2H_2O + \text{electric current} & \rightarrow 2NaOH + Cl_2 + H_2 \\
\end{align*}

The process of chlorination involves the addition of chlorine to water either as chlorine gas (Cl\textsubscript{2}) or sodium or calcium hypochlorite (NaOCl or Ca (OCl)\textsubscript{2}). Chlorine gas once added to water, hydrolyzes rapidly to form hypochlorous acid (HOCl), an active form of chlorine as indicated in equation 2-2. Sodium and calcium hypochlorite reacts with water according to equations 2-3 and 2-4 releasing hypochlorite ions which later combine with available hydronium ions (H\textsuperscript{+}) to further produce hypochlorous acid (HOCl) (Judd, 1999; AWWA, 2006).

\begin{align*}
Cl_2 + H_2O & \leftrightarrow HOCl + H^+ + Cl^- \\
NaOCl + H_2O & \rightarrow +Na^{2+} + HOCl + OH^- \\
\end{align*}
\[ Ca(OCl)^2 + 2H_2O \rightarrow +Ca^{2+} + 2HOCl + 2OH^- \quad 2 - 4 \]

The literature indicates that hypochlorous acid is a weak acid that undergoes partial dissociation, establishing equilibrium in water to produce hydronium (H\(^+\)) and hypochlorite ion (OCl\(^-\)) according to equation 2-5.

\[ HOCl \leftrightarrow H^+ + OCl^- \quad 2 - 5 \]

Generally, in water treatment, the sum of hypochlorous acid and hypochlorite ion species commonly called “free available chlorine” exist in water (Judd, 1999; Harp, 2002; AWWA, 2006). However, the dominant chlorine species present depends on other factors such as pH and temperature. The durability and persistence of a disinfection residual are therefore greatly influenced by the pH of the disinfection water. As pH decreases with a corresponding increase in temperature, HOCl dominates as free chlorine (Judd, 1999; AWWA, 2006). Chlorine disinfection has been used for decades and investigations show that, even though hypochlorous acid is significantly more effective as a germicidal agent compared to hypochlorite ions during water disinfection, hypochlorous acid is more rapidly consumed (AWWA M20, 2006). The existence of other compounds in water can exert an increasing chlorine demand, resulting in the loss of residual chlorine. A reaction of great significance is the reaction of chlorine with nitrogenous compounds leading to the formation of chloramine an alternative disinfectant.

2.4.2 Chloramination

Chloramination is often used as a secondary disinfectant and an alternative disinfection method in water treatment to free chlorine. Chloramination involves the use of chloramine (combined chlorine) which is comprised of three chemicals that are formed from the reaction of chlorine and ammonia. Chloramine speciation depends on the chlorine-to-ammonia ratio (Cl\(_2\)::NH\(_3\)) and the existing conditions. Typically, monochloramine (NH\(_2\)Cl), dichloramine
(NHCl₂), and trichloramine (nitrogen trichloride (NCl₃)) are the chloramine species formed according to the generalized chloramine formation reaction according to equations 2-6, 2-7, and 2-8 respectively.

Monochloramine
\[ NH_3 + HOCl \rightarrow NH_2Cl + H_2O \]  \hspace{1cm} 2 – 6

Dichloramine
\[ NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \]  \hspace{1cm} 2 – 7

Trichloramine
\[ NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \]  \hspace{1cm} 2 – 8

The relative percentages of each chloramine present are dependent on factors such as temperature, pH, Cl₂: NH₃ -N ratio, and contact time. Typically monochloramine is formed in the weight ratios of 3:1 to 5:1 (Cl₂: NH₃-N) at pH >7.5 and temperature of 25°C (Wolfe et al., 1984; Bauer & Snoeyink, 1973; Kirmeyer et al., 2004; Chowdhury, 2007; AWWA M56, 2013). Preferentially, water treatment plants use monochloramine as it is comparatively more effective in disinfection and has minimal taste and odor issues as compared to dichloramine and trichloramine (Kirmeyer et al 2004). Jafvert and Valentine indicated that monochloramine hydrolyses in water and forms HOCl for disinfection purposes according to the equation 2-9 (Valentine & Jafvert, 1992).

\[ NH_2Cl + H_2O \rightarrow HOCl + NH_3 \]  \hspace{1cm} 2 – 9

During chloramination, chlorine is dosed to water as a gas, as sodium hypochlorite in a solution, or in solid form as calcium hypochlorite. Ammonia is added to water as dry ammonium sulfate solid, liquid ammonium hydroxide, or ammonium gas. Post chloramine formation,
ammonia is present in water as either free-available ammonia, combined available ammonia, or total ammonia (Tokuno, 1997).

### 2.4.2.1 Chloramine Demand and Decay

Maintaining disinfection residuals post water treatment is important in ensuring sustained delivery of safe water to consumers. Even though chloramines are relatively more stable than free-chlorine, the demand and subsequent loss of disinfectant residuals can occur due to several existing water quality and infrastructure factors such as system piping material, pH, temperature, presence of biofilm, and natural organic matter (Kirmeyer et al. 2004; Chowdhury, 2007). Jafvert and Valentine (1992), demonstrated that monochloramine is unstable at neutral pH and a series of reactions involving the oxidation of ammonia and loss of chlorine can trigger auto decomposition of chloramine, resulting in the release of ammonia (free ammonia) as represented in equation 2-10, for every mole of monochloramine, one mole of free ammonia is released (Valentine & Jafvert, 1992; AWWA, 2013a).

\[
\text{Demand equation} (\text{NOM}, NO_2, \text{bromide}) + NH_2Cl \rightarrow NH_3 + Cl^- + \text{product} \quad 2-10
\]

Further research has established that oxidation-reduction reaction between nitrite and chloramine can accelerate the decay of chloramine resulting in the formation of ammonia and potentially initiating nitrification represented in equation 2-11 which indicates 3 moles of ammonia is released for every 4 moles of monochloramine (Vikesland et al., 2001; Carrico et al., 2008). Nitrification is a resulting consequence of chloramine decomposition and decay and can immensely deteriorate the quality of water.

\[
4NH_2Cl + 3 H_2O \rightarrow 3NH_3 + NO_3^- + 5H^+ + 4Cl^- \quad 2-11
\]
2.4.3 Chlorine Reaction with Carbon

Whereas maintaining residual disinfectant concentration is important to ensure the potability of drinking water, chlorine has been reported to rapidly react with carbon, thus limiting its ability to persist in water systems. Bauer and Snoeyink, (1973) used a series of batch reactors to monitor the dechlorination ability of activated carbon, demonstrating fresh activated carbon can chemically reduce chlorine to chloride ion following the reaction equation 2-12, where $C^*$ represents activated carbon and $CO^*$ represents surface oxides on carbon.

\[
C^* + HOCl \rightarrow CO^* + H^* + Cl^- 
\]

Atkins et al. (1975) used a pilot-scale study to monitor the dechlorination by GAC for the removal of ammonia-nitrogen. They reported a complete removal of all forms of free- and combined chlorine using GAC leaving no residual chlorine, consistent with Zhang et al. (2008) results.

However, very little is understood about the reactions between activated carbon and chloramine. The available research, however, indicates that while the reaction between monochloramine and carbon is relatively slow compared to that of free-chlorine, the rate of such a reaction is yet to be understood (Komorita & Snoeyink, 1985). Komori & Snoeyink, (1985) showed that carbon can catalytically reduce monochloramine resulting in the formation of free ammonia. Even though further reactions in the presence of some surface oxides can partially oxidize monochloramine to nitrogen gas, as indicated in equations (2-13) and (2-14). However, as a steady-state condition is approached, it is speculated that the rate of the reaction is reduced (Komorita & Snoeyink, 1985; Bauer & Snoeyink, 1973).

\[
2NH_2Cl + H_2O + C^* \rightarrow NH_3 + H^* + Cl^- + CO^* 
\]

\[
2NH_2Cl + CO^* \rightarrow N_2 + C^* + 2H^* + 2Cl^- + H_2O 
\]
Shin-ichi Tokuno, (1997) further observed that monochloramine in tap water was converted to free-ammonia within 30 min of contact with 5 g of GAC/100 ml, signifying some degree of conversion. Similarly, (Fairey et al., 2007) concluded that irrespective of the type of activated carbon used, monochloramine was reduced, substantiating the established results of other researchers indicating carbon’s ability to catalytically convert chloramine to free ammonia.

2.5 Nitrification

The abundance of nitrogen in nature and its ability to transform from one form to the other through the nitrogen cycle makes it an indispensable element in most biological processes (Sawyer et al., 2003). Microorganisms, such as nitrifiers, have the capacity under different environmental conditions to utilize a wide range of nitrogenous compounds in carrying out cellular processes such as nitrification. Nitrifiers can fix and reduce inorganic carbon and can also slowly carry out nitrification heterotrophically relative to autotrophs. (Wolfe et al., 1988).

Nitrifying bacteria are described as chemolithotrophs (use inorganic chemicals as an energy source), or obligate aerobes (use oxygen for respiration-electron acceptor) depending on the existing environmental conditions (Rittmann and McCarty, 2001). Nitrifiers are further classified based on their ability to oxidize either ammonia or nitrite. Ammonia oxidizing bacteria (AOB) convert available ammonia to nitrite whereas nitrogen oxidizing bacteria (NOB) convert nitrite to nitrate. Recent studies have identified a third class of microorganisms, ammonia-oxidizing archaea (AOA) in the Archaea domain (AWWA M56, 2013b). Regan et al. (2003), reported that *Nitrosomonas oligotroph* is currently the commonly encountered AOB in distribution systems while *Nitrospira* genus and *Nitrobacter* species are often the most detected NOB. Nitrifiers are predominantly associated with nitrification processes in water systems, where they use oxygen as a terminal electron acceptor and ammonia or nitrite as substrate (Fleming, 2004b).
2.5.1 Nitrification Chemistry

Nitrification is generally considered as a two-step microbiological reaction process carried out by nitrifying microorganisms in which nitrogen compounds are oxidized to nitrite and then nitrate. The first step is carried out by ammonia-oxidizing microbes (AOM) which comprise ammonia-oxidizing bacterial (AOB) and ammonia-oxidizing archaea (AOA) which involve the catalyzed oxidization of available ammonia to nitrite known as “incomplete nitrification” as represented in equation 2-15. The nitrite produced is then further oxidized to nitrate by nitrite-oxidizing bacteria (NOB), completing the nitrification process as shown in Equations 2-16 (Rittmann and McCarty, 2001; Wang et al., 2014; Madigan, 2018; AWWA M56, 2013). Recent investigation has demonstrated the existence of complete ammonia oxidizer (commamox), a type of nitrifier that is capable of completely oxidizing ammonia to nitrate (Wang et al., 2017, Van Kessel et al., 2015, Daims et al., 2015) The overall complete nitrification reaction process is represented in equation 2-17 adopted from Grady et al.(1999). Besides the formation of $NO_3^-$, the overall stochiometric equation indicates a major oxygen demand and produces a strong acid equivalent.

Nitrosomonas reaction (AOB):

$$2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 2H^+ \quad 2-15$$

Nitrobacter reaction (NOB):

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad 2-16$$

Commamox

$$NH_4^+ + O_2 \rightarrow 2NO_3^- + H_2O + H^+ \quad 2-17$$

Complete nitrification stoichiometry equation

$$NH_4^+ + 3.3 \ O_2 + 6.708HCO_3^- \rightarrow 0.129 \ C_5H_7O_2N + 3.373 \ NO_3^- + 1.041 \ H_2O + 6.463 \ H_2CO_3 \quad 2-18$$
2.5.2 Nitrification in Chloraminated Water DWS and POU Devices

While biological water treatment processes utilize nitrification in making water biologically stable by eliminating biodegradable electron donors and chlorine demand, nitrification can otherwise result in chemical and biological deterioration of finished drinking water quality. Nitrification has emerged to be a major challenge faced by many water distribution systems. Recorded episodes of nitrification in distribution systems date back to the 1930s (Hulbert, 1933). Globally, nitrification incidence in chloraminated waters has been reported across the United States, Canada, Finland, and Australia (Cunliffe, 1991; Lipponen et al., 2002; AWWA, 2013). Wilczak et al., (1996) estimated 63% of surveyed utilities in the United States practicing chloramination had undergone some extent of nitrification (Wilczak et al., 1996). Various incidences of nitrification have been recorded at different locations of water distribution systems, with dead-ends, poorly cycled areas, and storage facilities as the prominent areas (AWWA M56, 2013b). Wolfe et al., (1988) associated the occurrence of nitrification with the proliferation of AOBs in two covered water reservoirs. Further studies of 5 chloraminated water systems in South Australia showed that 64% of 1184 samples collected and analyzed contained nitrifying bacteria (Cunliffe, 1991). Nitrification in water distribution systems has been extensively researched; however, beyond the distribution system, there exist limited research. In the United States, the SDWA regulatory MCLs only apply to the point of entry to distribution systems, limiting our knowledge of nitrification beyond distribution systems. (AWWA, 2013).

Nitrification can occur in water systems containing ammonia, for instance in chloraminated water, as the water flows through distribution systems, gradually decomposing the residual chloramine due to various water reactions and releasing ammonia. The presence of ammonia in water systems can serve as a substrate to nitrifiers and studies have associated this with increased
biological activities resulting in increased nitrite and nitrate concentrations (Alfredo et al., 2020; Wu et al., 2017; Zhang et al., 2009a). Various authors have extensively studied the occurrence and impact of nitrification in distribution water systems and have associated nitrification with the reduction of disinfection residual and degradation of water quality integrity. Many studies have also associated the consequences of nitrification with bacterial proliferation in distribution water systems and possible health risks (Wolfe et al., 1990; Wilczak et al., 1996; Other researchers have further stated that nitrification can result in lead and copper leaching from water fixtures and copper-lead rigs (Zhang et al., 2008). While the presence of microbial communities and activities in POU units have been extensively studied, only Alfredo et al., 2020 and Wu et al., 2017 investigations talked about the presence of nitrifiers activities and increased nitrite concentrations in the filtrate indicating ongoing nitrification within the filter.

Extensive research and investigation have been conducted to better understand nitrification in DWS (Wilczak et al., 1996; AWWA M56, 2013; Alfredo, 2021). Both bulk water and pilot-scale experiments have been carried out evaluating the occurrence and contributing factors influencing the occurrence of nitrification.

Seasonal temperature variations in distribution water systems can range between 0 to 30°C which can greatly influence the growth rate of nitrifiers. Various authors have established that nitrification is temperature-dependent, and it can occur over a wide range of temperatures, (5°C to 34°C), with the optimum temperature reported varies over 15°C to 28°C. But, elevated incidence of nitrification has been reported to occur during warmer temperatures (summer season) with a reported increase in chloramine decay (Skadsen, 1993b; Wilczak et al., 1996; Zhang et al., 2009; AWWA, 2013a; Lieu et al., 1993).
Nitrifying bacteria are highly sensitive to pH changes, resulting in changes in growth patterns and biological activities. Though a wide range of pH has been reported for each nitrifier species, the optimum pH range of 7 to 8 is favorable for nitrification (Wilczak et al., 1996).

Nitrifying bacteria utilize ammonia as their source of energy to carry out biological activities. In drinking water systems, sources of ammonia include the decomposition of chloramine from existing water reactions while in AC systems the carbon catalytically converts chloramine into free available ammonia. Research has indicated at low ratios of Cl₂:NH₃ excess free-ammonia is readily available for nitrifiers to utilize, thus resulting in nitrification (Fleming, 2004, 2008; Skadsen, 1993a; Feben, 1935)

Nitrifiers are obligate aerobes and thus utilizes oxygen as an electron acceptor in the oxidation of ammonia to nitrate during nitrification. According to Grady et al., 1999, for every mg-N of ammonia, 4.33 mg O₂ is required to oxidize it to nitrate. However, several published studies have indicated that nitrification can be inhibited at DO levels less than 2.5 mg/L. At such low DO levels, nitrifiers can utilize nitrate or nitrite as a substitute for oxygen (Zhang et al., 2009a; AWWA M56, 2013).

Wolfe et al., (1990) indicated that free-chlorine was relatively effective at inactivating nitrifiers and thus controlling nitrification. Fleming et al., 2008 based on a pilot study demonstrated that a total chlorine residual of 1.6 mg/L was capable of inhibiting nitrification occurrence (Fleming et al., 2008). However, in chloraminated water, the influence of monochloramine on the occurrence of nitrification is quite debatable. Monochloramine confers a biocidal effect for inactivating nitrifiers and can double as a source of a substrate to nitrifiers it is unclear which effect dominates the other. While Wolfe et al.( 1990) and Feben (1935) observed the survival of AOB in 1 – 2 mg/L monochloraminated water, Skadsen( 1993) and Cunliffe (1991) indicated that
nitrification was observed in waters at 5-6 mg/L monochloramine. Skadsen (1993) established that at higher doses of 8 mg/L monochloramine, once nitrification was initiated, nitrifiers were unable to be inactivated by chloramine residual.

Long stagnation time can significantly influence the occurrence of nitrification. In the absence of continuous exchange of water at dead ends, longer water detention time can allow nitrifiers to acclimatize to water conditions and thus promote biofilm growth and nitrification. Developed biofilm and settled sediment in water systems at dead ends can further impose a disinfection demand, and thus rapidly decreasing residual disinfection given way to increased bacterial actives and nitrification (Skadsen, 1993a; Wilczak et al., 1996; Roy L Wolfe et al., 1988).

2.5.3 Nitrification Concerns

2.5.3.1 Regulatory Concerns

Nitrification in DWS has been associated with the violation of various SDWA regulations and statutes. Published research indicates that in distribution water systems, nitrite and nitrate concentrations typically increase on the order of 0.05-0.5 mg/L-N. Waters with longer detention time can increase to as high as 1 mg/L (Wilczak et al., 1996). Some authors have recommended 0.05 mg/L nitrate-nitrogen as a potential indicator of ongoing severe nitrification (Wilczak et al., 1996), lower concentration of 0.025 mg/L nitrite-nitrogen action level has been proposed by Fleming et al.( 2008) as the action level for the onset of nitrification. At increasing nitrite and nitrate concentrations, the SWDA MCLs of 1 mg/L and 10 mg/L for nitrite and nitrate compliance respectively can be violated. The violation of the Total Coliform Rule is possible as nitrification is associated with bacterial growth and elevated HPC counts (Wilczak et al., 1996). During nitrification control, the disinfection byproduct rule can be violated as changing the ratios of chlorine to ammonia can result in the formation DBPs while the decrease and loss of residual
disinfection during nitrification impact surface water treatment rule compliance. Continuous nitrification can decrease alkalinity, pH, and DO. At these reduced conditions, it is possible to trigger lead and copper release in water systems made of lead service lines and copper materials thus resulting in the violation of LCR (AWWA, 2013a; Deshommes et al., 2010; Zhang et al., 2009a; NCR, 2007).

2.5.3.2 Health Concerns

The health risk associated with nitrification is linked to the consumption of elevated concentrations of nitrite and nitrate in water. Published reports by Bouchard et al., (1992), indicate that nitrite and nitrate can cause methemoglobinemia, otherwise known as “blue baby syndrome”. This is a condition where nitrite and nitrate in the human bloodstream prevent the binding of oxygen to blood cells thus blocking oxygen transport. This affects predominantly infants below the ages of six months old (Bouchard et al., 1992). Some authors have shown a weak association of nitrate to cancer in immunocompromised populations as nitrate is a precursor for N-nitroso (NOC) a potent animal carcinogen; however, this is still a matter of debate as much research is required to further understand the association (Bouchard et al., 1992; De Roos et al., 2003; Ward et al., 2003).

2.5.4 Nitrification Mitigation

Nitrifiers are sensitive to a wide range of chemical inhibitions, which to a large extent impacts their activities and growth. Researchers have leverage these inhibitions to develop strategies used in biologically stabilizing water, thus controlling and limiting the occurrence of nitrification. Among the major nitrification control strategies include (1) the mechanism of breakpoint chlorination (otherwise known as instituting a free chlorine period or FCIP). This involves increasing chlorine to ammonia ratio thus limiting the availability of ammonia while
increasing residual free chlorine concentration to facilitate microbial inactivation and reduced microbial activities, (2) changing pH to reduce nitrifier growth and disinfection decay, (3) decreasing the concentration of organic matter to reduce disinfection demand, and bacterial nitrifiers growth, and (4) regular flushing of water systems (Skadsen, 1993b; Zhang et al., 2009a; Wolfe et al., 1988; Seidel et al., 2005; Odell et al., 1996; AWWA M56, 2013). Though some strategies are relatively more effective than others depending on the nitrification episode and site water conditions, breakpoint chlorination is however more an effective control strategy that can be employed irrespective of site conditions (Odell et al., 1996; Skadsen, 1993).

2.5.4.1 Disinfection Switch (Breakpoint Chlorination)

Some water treatment plants have resorted to periodic disinfection switching as a short-term nitrification mitigation measure. This switch is referred to as “disinfectant switching, “breakpoint chlorination”, and as the “free chlorine conversion period” or FCIP. Colloquially it is referred to as a “chlorine burn. “A survey by Seidel et al.,( 2005 ) reported that out of a total of 23 utilities surveyed, 20 indicated they periodically switch disinfection, with about half the utilities practicing disinfection switch twice a year mostly during March and August.

Breakpoint chlorination theoretically involves the addition of chlorine to water until all available ammonia materials have been oxidized to nitrogen, leaving free chlorine residual as represented in Figure 4 (adapted from Alley, 2007)). The breakpoint curve is a graph of available residual chlorine (mg/L) plotted against applied chlorine dose in mg/L. The plot is divided into three sections; point A, point B, and breakpoint. Point A begins the formation of chloro-organic compounds and chloramine. Between points A and B, chloramine is formed at a typical Cl2: N ratio of 3:1 and 5:1. Predominantly monochloramine is the most formed chloramine species at neutral pH within this zone. However, at a very low pH (< 5) dichloramine can be formed. At point
B, a free chlorine residual begins to form coupled with the destruction (oxidation) of chloramine resulting in a formation of nitrogenous compounds thus increasing chlorine demand. The chlorine demand subsequently reduces the concentrations of the formed free available chlorine residual till the breakpoint is reached. At the breakpoint, all available chloramines are oxidized, and no chlorine demand is exerted. Beyond this point, a continuous increase in chlorine dosage results in an excess available free chlorine residual known as the breakpoint chlorination (Alley, 2007).

At the treatment plant level, breakpoint chlorination is achieved through switching disinfectants from chloramine to free chlorine by cutting the ammonia feed, thus limiting the formation of chloramine while increasing free chlorine doses. The main objective of breakpoint chlorination is to (1) eliminate ammonia from the water source, thus depriving nitrifiers of their main substrate to facilitate growth and nitrification, (2) ensure the inactivation of nitrifiers by free chlorination, limiting biological activities and thus nitrification, and (3) reduce disinfection demand and decay by oxidizing available nitrite (AWWA M56, 2013b).

Water plants routinely switch from chloramine to free chlorine once or twice a year over varying durations to facilitate nitrification control, even though some utilities have reported recurring nitrification events even after switching back to chloramine disinfection (Alfredo, 2021). In the short term, disinfection switching was highly effective at controlling nitrification by eliminating ammonia within the distribution system. The consequences after this temporary FCIP is not fully understood, but it has been associated with the rapid proliferation and growth of HPC bacterial, increase in planktonic cell counts due to washing off (sloughing) of biofilm into bulk water have been observed (Odell et al., 1996; Wang et al., 2014) and the potential for chlorinous taste and odor occurring is highly very likely (AWWA M56, 2013; Carrico et al., 2008).
An extended free-chlorination period has the potential of increasing the formation of DBPs (Odell et al., 1996). Skadsen, (1993a) reported that simply a change from 6.5 mg/L monochloramine to 2.5 mg/L free chlorine was effective at controlling nitrification; however, it resulted in a 0.8 log increase in HPC counts at non-nitrifying parts of the distribution system. While investigating the impact of periodic FCIP in distribution systems, Alfredo, 2021 and Wang et al., 2014 both demonstrated a reduction in nitrification as nitrifying populations greatly reduced. However, after several weeks post-FCIP, nitrification reoccurred increasing nitrate and microbial counts.

Given the rise of household POU filters (WQA, 2019) and the limited research on their use within chloraminated systems, it is important to investigate and understand the possible impact of FCIPs on the performance of AC POU filters. This research seeks to monitor and understand the impact of a limited FCIP on the biological water quality of POU filtrate before, during, and after periodic FCIP. It further seeks to investigate the effect of filter operation conditions and seasonal...
variation on the occurrence of nitrification and filtrate water quality in AC POU filters. Research findings from this study are intended to contribute to public health policy and water quality regulation formulation that reaches beyond the point of entry to/and the distribution system to protect and sustain the quality of water consumed at the household tap.
Chapter 3: Method and Materials

3.1 Study Site and Water Source

The study was carried out at a research laboratory at the University of South Florida, Tampa campus. The City of Tampa Water Facility supplies chloraminated water to the laboratory and was used as the influent throughout the study. Each year, the water facility carries out two, 3-week periodic annual disinfection switches (Tampa.Gov, 2021). One occurs around March and the second around August or September. For the year 2020, the second FCIP occurred on 7th – 28th August 2020 (representing FCIP-1 in this study), while in 2021 the first occurred on the 8th – 29th of March (denoted here as the second FCIP-2). The study began in July 2020 before the FCIP-1 in 2020 until FCIP-2 in 2021. The study was conducted in three phases, using a laboratory-based filter rig constructed using three new, commercially available AC-POU filters from a prominent manufacturer.

3.1.1 Source Water Characteristics

The City of Tampa primarily treats surface water from the Hillsborough River, and periodically augments the supply with finished water stored within underground aquifers. The City’s David L. Tipping Water Treatment facility, with an average treatment capacity of 80 million gallons per day, uses a multi-step treatment process in delivering potable water to its users. It utilizes two stages of disinfection using ozonation as the primary step and chloramination or chlorine as secondary disinfection. At the time of this study, available information from the 2019 water quality report indicates finished water has an average pH of 7.86, monochloramine
application averaged 3.3 mg/L, and measured total chlorine ranged between 3.5 and 4 mg/L (Water Department City of Tampa, 2019).

3.2 Filter Properties

The Elkay EWF300 POU filter was used in this study. The filter is predominantly available for use in water bottle filling stations and fountains. All filters used have been tested and certified according to NSF/ANSI 42 and 53 for chlorine reduction, taste, odor, lead, and particulate class 1 removal. The filters are made of a prefilter membrane, and an activated carbon base filter media as shown in Figure 5. The manufacturer’s recommend a once a year or after a maximum use capacity of 11,356 L use condition for filter replacement, at a flow rate not greater than 5.7 L/min.

Figure 5 Carbon block filter and cross-sectional cut, showing membrane prefilter and solid carbon block

3.3 Experimental Setup

The experiment was conducted in three phases as shown in Figure 6, with corresponding three carbon filters installed, operated, and monitored in parallel at these respective phases. A pre-FCIP experiment was conducted in phase I beginning on 7/1/2020. During this phase, filter 1 was installed and monitored 37 days before the FCIP-1 and subsequently monitored throughout all
three phases of the experimental period. Phase II was conducted during the FCIP-1. Filter 2 was installed and operated starting on 8/14/2020, halfway through the FCIP-1. This was done to ensure that there were no influent traces of chloramine introduced into Filter 2 and all influent water was treated with free chlorine. The third filter was installed on 9/4/2020, after the FCIP-1 once it was observed that monochloramine concentrations stabilized in tap water samples post-FCIP-1. It is worth noting that the FCIP-2 (in 2021) occurred during the third phase of the study.

![Figure 6 Experimental setup showing the various experimental phases and corresponding filters](image)

For quality control, all tubing of the experimental setup was duct-taped to prevent the interference of sunlight as light can induce growth inhibition of nitrifiers limiting the occurrence of nitrification and promote algae growth within lines (Alleman et al., 1987). To purge air and remove carbon particles, each filter was also allowed to run for an average period of a week before the first samples were collected post-installation. A detailed schematic of the installation of each filter is presented in Figure 7.
To simulate home usage of the filters, solenoid valves were attached to a programmable controller (Rain Bird®). Flushes were automated Monday to Friday for each filter, at 10:00 am, 12 pm, 2:00 pm, and 4:00 pm for 5 min at an average 3.9 ±1 L/min flow rate. A water flow meter was installed before each filter to enable the recording of the total filtered water volumes as shown in the schematics in Figure 7. Each filter processed approximately 20 L of water per flush and 100 L per day. Flushing of each filter did not occur on Saturday and Sunday to simulate long periods of stagnation as most of these filters were operated in schools and at the workplace where they are often left stagnating during the weekends.

### 3.4 Sample Collection

The monitoring period extends to about nine months (at the time of this writing) after filter installation. Grab water samples were collected four times each week and a total of 10 water samples were collected per day from all filters. Each water quality test sample had a corresponding microbial sample for analysis. Microbial samples comprise 50 mL of water collected in sterile centrifuge tubes filled to zero headspace and 100 mL water samples were collected in 250 mL covered plastic bottles for water quality analysis.
There were three main types of filtrate sampling events: stagnation samples, first flow samples, and post flush samples. In addition, microbiological and water quality samples were collected directly from the tap (unfiltered) to monitor influent water conditions following an unfiltered control sample from the tap directly. Stagnation samples consisted of stagnant water within the filter for a period of either 1080 min or 3960 min representing overnight or two-day stagnation periods, respectively. Stagnation samples were collected after wasting about 140ml of stagnant tubing water. The 140ml wasted volume was obtained by calculating the volume of water stagnating in tubing connecting the filter to the sampling port. It is, however, an average for all three filters as they were approximately equal. First flow samples represent the first draw of water from the filters. These samples consisted of the first flowing fresh filtrate samples after a stagnation event. First flow samples were obtained by allowing an estimated 1.6 times the filter volume to exchange before sampling. Post flush water samples consisted of filtrate collected after a 5-minute flush.

Preceding each sampling process, the exteriors of all sampling ports were sanitized using a Kim wipe soaked in 70% ethanol to prevent external contamination of samples. Each microbial sample was collected in a sterile, autoclaved, high-density polyethylene centrifuge tube and analyzed immediately (within 3hr).

3.5 Sampling Protocol

- Tap Sample (Unfiltered)
  1. The tap was manually flushed for 20min to stabilize the residual disinfectant concentration and to draw freshwater into the tap.
  2. The tap port is sanitized with Kim wipe soaked in 70% ethanol.
3. The required tap sample was collected according to sample collection protocol into the respective bottles.

- Stagnation, First Flow, and Post Flush Samples

1. Record the initial volume on the flow meter before sampling.
2. The collection port of the faucet was sanitized,
3. Wasted required volume for the filter.
4. A stagnant water sample is collected.
5. The cumulative volume reading on the flow meter is recorded.
6. 600 mL water is wasted representing approximately 1.6 times of filter exchange
7. Collect first flow samples.
8. Record cumulative flow meter reading.
9. Allow for automated 5 min flush.
10. Waste required volume for the filter.
11. Post flush samples are collected after wasting the 140mL, for quality control, these samples are collected immediately or within 2 min after automatic flushing.

3.5.1 Flush Profile and Stagnation Profile

Flush profile sampling was conducted manually by maintaining a consistent flow rate of 0.5 L/min, while samples were collected periodically after a predetermined volume of water was wasted.

1. Record initial cumulative volume on the flow meter.
2. Waste the required volume for the filter.
3. Leave the filter sampling port open throughout the flush profile sampling process.
4. Collect and waste samples as stipulated by the protocol.
5. At the end of the sampling period, record the cumulative volume reading on the flow meter. Stagnation profile samples were collected after a manual 5 min flush at a predetermined stagnation length ranging between 120 min to 0 min. After every collected sample, the filter was manually flushed for 5 min and allowed to stagnate before the next sample collection. For each sample, flowmeter readings were recorded, and the process was repeated.

1. Turn off all pre-programmed automatic flushes for the filter of interest.

2. The initial cumulative flow meter of the associated filter is recorded.

3. The waste volume associated with the filter is wasted.

4. Stagnation and fist flow samples are collected respectively as per the protocol mentioned previously.

5. Record cumulative volume for each sample taken.

6. Manually flush the filter for 5 min.

7. Allow the filter to stagnate for the required duration.

8. Repeat steps 2-4 above for each stagnation length.

3.6 Physio-Chemical Analysis

The physiochemical analysis was performed per Standard Method for the Examination of Water and Wastewater, and the USEPA approved methods for water quality testing as compiled in Table 1. PH and temperature were determined using the Thermo Scientific Orion Star A100. Dissolved oxygen was measured using the Thermo Scientific Orion Star A123 DO meter star A123 and DO probe 081010MD.

Nitrite, nitrate, monochloramine, and free ammonia were tested using the HACH DR 890 colorimeter (HACH, Loveland CO) with USEPA approved methods for testing. The HACH DR 890 has a wavelength ranging between 420 nm to 610 nm and varying detection limits ranged
depending on the chemical to be tested (HACH Company, 2013). Various methods and detection limits utilized are summarized in Table 1.

Nitrite was measured by reacting HACH Nitri Ver 3 pillow packet (cat no. 2107169) with Sulfanilic acid that forms diazonium salt and further reacts with Chromotropic acid forming a pink color solution.

Nitrate concentration was determined by reacting a pillow packet containing HACH Nitra Ver 5 (contains cadmium metal Cat No. 2106169) this reduces the nitrate present to nitrite. The nitrite ion then reacts in an acidic medium to form diazonium salt and later forms an amber-colored solution.

Monochloramine (NH₂Cl) and free-ammonia (NH₃-N and NH₄⁺-N) concentrations were determined by reacting Monochlor F powder (Cat No. 2802299) with a water sample. In the presence of a cyanoferrate catalyst, a phenol produced reacts to form a green color indophenol solution. Free ammonia can react with added hypochlorite to form monochloramine. Free-ammonia concentration is determined by comparing the color intensities of the sample with and without hypochlorite. The HACH DR 890, is then used to measure the various light intensities developed by the various reaction and correlates the light intensity to their corresponding concentrations (HACH Company, 2013); HACH Company, 2018).

The HACH Pocket Colorimeter II (Cat. No. 58700-00) was used in testing for total and free chlorine. The instrument has a wavelength of ±2 nm, a filter bandwidth of 15 nm, and an absorbance range of 0 to 2.5 Abs (Pathlength, 2014). With a total and free-chlorine low range detection limit occurring within 0.02-0.2 mg/L- Cl₂ and a high range between 0 to 10 mg/L- Cl₂. The colorimeter uses USEPA DPD method 3305 (method 10069 and method 10070) equivalent to standard method 4500-Cl G (DPD colorimetric method) to measure total and free-
chlorine respectively in the water samples. To determine total and free-chlorine, DPD pillow packets are added to water samples, this oxidizes chlorine to form a magenta color in the water sample. The color intensity was measured using the PC II colorimeter, the concentration of Chlorine present is proportional to the color intensity.

3.7 Microbial Analysis

Hygiena\textsuperscript{©} ATP (Camarillo, CA, USA) tests with a detection limit as low as 1 femtomole of ATP were used due to their accuracy, ease to use, and affordability compared to conventional microbiological test methods. Using the Aqua Snap-liquid ATP test swap and the system plus luminometer, total-ATP was measured for each water sample. This method leverages the use of bioluminescence technology in evaluating the number of viable micro-organisms present in water which indicates the presence of biological matter and the extent of microbial activity (microbial load)(Delahaye et al., 2003). Through the enzymatic reaction between Luciferase and ATP, bioluminescence (light) is produced. The light generated is measured and is directly proportional to the amount of ATP measured in units of Relative Light Units (RLU). This method is limiting; since it only serves as an operational guide, it does not report in units of CFU/mL as it is not a culturable method.

\[ ATP + Luciferase = Light \]

3.8 Statistical Analysis

Statistical analysis was performed using an open-source software RStudio, version 1.2.5033 (RStudio Inc, Boston, USA). Various packages were used in data processing, cleaning, and data virtualization and analysis. Summary statistics including the mean, median, and standard deviation of each parameter measured was generated for each sample type.
Spearman’s rank correlation coefficient, a distribution-free (non-parametric) method, was used to determine the existence and strength of an association between paired measured parameters (Zar, 1972; Hauke & Kossowski, 2011). Spearman’s rank correlation method was used since the collected data was not normally distributed compared to the Pearson product-moment correlation method which requires the data to be normally distributed. Spearman correlations range between -1 and 1, with the strength of association between variables corresponding to the larger absolute value of the correlation coefficient (Lehman et al. 2005).

Mann-Whitney Wilcoxon (MWW) and Kruskal-Wallis tests were used in testing null hypotheses. This was done to determine the probability (p-value) of the null hypothesis within an acceptable confidence level. Using a cutoff of 5% for rejecting the null hypothesis, where p-values less than 0.05 correspond to the absence of a relationship between paired variables (A. Lehman, 2005). In an event where more than two groups were to be compared, the Kruskal-Wallis tests non-parametric tests by ranks were used to establish a general p-value among the groups while MWW was used to perform pairwise p-value comparisons.
<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>Method</th>
<th>Test Reagent</th>
<th>Instrument (Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Chlorine</td>
<td>USEPA DPD Method 10070</td>
<td>DPD Total Chlorine Reagent</td>
<td>Pocket Colorimeter II (0-10 mg/L-Cl&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>Indophenol Method 10171</td>
<td>HACH: Monochlor F</td>
<td>Hach DR 890 (0-4.5 mg/L Cl&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Free Ammonia</td>
<td>Indophenol Method 10200</td>
<td>Hach: Free Ammonia Reagent Solution + Monochlor F</td>
<td>Hach DR 890 (0-0.50mg/l NH&lt;sub&gt;3&lt;/sub&gt;-N)</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Diazotization Method 8507</td>
<td>HACH: Nitri Ver 3 Nitrite Reagent</td>
<td>Hach DR 890 (0-0.35 mg/L NO&lt;sub&gt;2&lt;/sub&gt;-N)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Cadmium Reduction Method 8171</td>
<td>HACH: Nitra Ver 5 Nitrate Reagent</td>
<td>Hach DR 890 (0-5 mg/L NO&lt;sub&gt;3&lt;/sub&gt;-N)</td>
</tr>
</tbody>
</table>
Chapter 4: Results and Discussions

This chapter presents the results and discussion of the research objectives and hypothesis. The results are presented in five main sections following the outlined objectives of the investigation. The characteristics of the influent and filtrate water are presented in section 4.1; it is important to note that this section focuses only on filtrate water quality of samples collected immediately after a 5 min flush---thus representing a flow-through model with no stagnation impacts. The results of the effect of filter use, season, and stagnation length have on filtrate quality are discussed in section 4.2. Section 4.3 presents AC filters and their nitrification potential; section 4.4 discusses the results of stagnation length effect on nitrification. The results of the impact of the limited FCIP and the filter installation period on the extent of nitrification are presented in section 4.5. Finally, the results of the role of microbial seeding and filter installation timing on the occurrence of nitrification in carbon filter block are presented in the final section 4.6 of this chapter.

Results and findings presented in this chapter reflect data collected between July 2020 and April 2021. It is worth noting that in all analyses, data points representing the transition phase between the immediate change from chloramine to free chlorine were eliminated (similar to methods used by Alfredo (2021)). As these transition data points could greatly skew the calculated averages results.
4.1 Water Chemistry of Filter Influent and Flushed Filtrate

4.1.1 Physiochemical Characteristics

The study monitored influent water quality throughout the 9 months of sampling. The mean and Standard deviation (SD) of various physiochemical characteristics of the influent water chloramine period (CP) and FCIP are summarized by disinfection residual in Table 2.

Throughout the investigation, there was little variation in the physical characteristics of the influent water. The mean influent pH remained unchanged during both FCIPs, increasing generally from 7.92 ± 0.06 during the FCIP to 8.01 ± 0.09 during CP. As shown in Figure 8-A, filtrate pH was lower compared to influent during both the FCIP (represented on the plot as a grey rectangle) and CP possibly due to the water-carbon interaction and/or due to ongoing biological processes. A continuous increase in influent pH measurement relative to effluent is observed during CP. In all three filters and influent samples, a constant pH is observed during the FCIP, suggesting the possible influence of varying disinfection on water pH as shown in Figure 8-A.

The influent temperature varied throughout the study, decreasing from 25.13 ± 1.16 C° during FCIP-1 to 23.61 ± 1.84 C° during CP where it remained constant into the FCIP-2 at 23.32 ± 0.57 C°. All three filter filtrate samples are observed to have similar temperature trends as the influent samples, as shown in Figure 8-B. There exist a steep decrease of tap (influent) samples from an all-time maximum of 27.5 C° before FCIP-1 in September to a low temperature of 19.7 C° post-FCIP-1 in January. However, before the second FCIP, the temperature began to steadily increase in February all through the second FCIP. These temperature changes reflect the influence of external seasonal variation, transitioning from summer in September to winter in January, and spring thus justifying that the rapid changes in temperature across the influent water and filtrate of all three filters as a function of seasonal changes.
### Table 2 Physiochemical characteristics of influent water by secondary disinfection

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>7.90 ± 0.06</td>
<td>8.01 ± 0.9</td>
<td>7.95 ± 0.07</td>
</tr>
<tr>
<td>Temp °C</td>
<td>25.13 ± 1.16</td>
<td>23.61 ± 1.84</td>
<td>23.32 ± 0.57</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>5.64 ± 0.35</td>
<td>6.43 ± 1.23</td>
<td>7.46 ± 0.28</td>
</tr>
<tr>
<td>Total Cl₂ (mg/L)</td>
<td>2.44 ± 0.27</td>
<td>3.83 ± 0.59</td>
<td>3.60 ± 0.57</td>
</tr>
<tr>
<td>Free-Cl₂ (mg/L)</td>
<td>4.76 ± 0.59</td>
<td>1.13 ± 1.55</td>
<td>3.34 ± 0.59</td>
</tr>
<tr>
<td>Monoamine (mg/L)</td>
<td>0.11 ± 0.06</td>
<td>3.04 ± 0.80</td>
<td>0.10 ± 0.06</td>
</tr>
<tr>
<td>Free NH₃ (mg/L-N)</td>
<td>0.02 ± 0.02</td>
<td>0.05 ± 0.10</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>Nitrate (mg/L-N)</td>
<td>1.7 ± 0.22</td>
<td>2.30 ± 0.25</td>
<td>1.83 ± 0.45</td>
</tr>
<tr>
<td>Nitrite (mg/L-N)</td>
<td>0.01 ± 0.00</td>
<td>0.02 ± 0.00</td>
<td>0.013 ± 0.01</td>
</tr>
<tr>
<td>Total ATP (RLU)</td>
<td>0.78 ± 0.44</td>
<td>9.72 ± 4.49</td>
<td>1.10 ± 1.37</td>
</tr>
<tr>
<td>Free Cl₂ (mg/L)</td>
<td>4.76 ± 0.59</td>
<td>-</td>
<td>3.34 ± 0.59</td>
</tr>
</tbody>
</table>
Figure 8 Unfiltered and filtered pH and temperature (°C) changes by influent raw tap water, filter by the dates of filter operation in month, and grey bars represent the FCIPs.
4.1.2 Disinfection Residual

Disinfection residuals measured in terms of total chlorine in the influent averaged 3.6 ± 0.7 mg/L-Cl₂ throughout the study signifying high-quality influent water. Chloramine Period (CP) residuals were statistically significantly different (P < 0.05) from FCIP residuals. Influent total chlorine residuals averaged 4.04 ± 1.02 mg/L-Cl₂ prior to the August 2020 FCIP 1, reducing during the FCIP 1 to 2.44 ± 0.27 mg/L-Cl₂. After FCIP 1, total chlorine residuals increased to 3.81 ± 0.54 mg/L-Cl₂ and finally decreasing during the second FCIP to a mean of 3.60 ± 0.57 mg/L-Cl₂.

Influent monochloramine residual averaged 3.04 ± 0.80/L-Cl₂ for the entire CP, decreasing to 0.11 ± 0.06 mg/L-Cl₂ during FCIP, as presented in Table 2. Free- chlorine was only measured during the period of conversion and the results presented in Table 2 only represent data collected during the free chlorine disinfection period. Free-chlorine during the conversion averaged 4.01 ± 0.93 mg/L-Cl₂.

Figure 9 shows the time series of residuals throughout the study period. It was observed that filtrate residual chlorine significantly decreased relative to influent residuals irrespective of the FCIP. This has been associated with the catalytical decomposition of chloramine releasing ammonia by carbon following equations 2 – 12 to 2 – 14 and coupled with the rapid increase in residual demand and decay due to biological activities (Bauer & Snoeyink, 1973; Fairey et al., 2007).

Even though shorter contact time is expected to result in minimal chloramine destruction, it was observed that 5 minutes of flushing resulted in a 90% decrease in monochloramine relative to influent concentrations for all three filters as indicated in Figure 9, thus strengthening the argument that carbon can significantly decrease chlorine concentrations.
Figure 9 Unfiltered and filtered (post flush) residual disinfection concentration profiles of total chlorine and monochloramine by influent tap water, filter, and the dates of filter operation in month. Grey rectangles represent FClP

The impact of filter installation time and FClP is observed in all three filters: in filter one, both chlorine disinfectant residuals remained below 1 mg/L-Cl₂ throughout the study period while
filter 2 and 3 recorded an increase in residual chloramines before approaching a steady concentration which coincided with the onset of nitrification, potentially signifying an increase in residual demand and decay because of the ongoing biological processes.

4.1.3 Biological Characteristics

Following the decomposition of chloramine and the decrease in residual disinfection concentrations within filters, it is expected that filter media will be predisposed to microbial growth. The presence and extent of microbiological processes were monitored using DO and total ATP as indicators. Influent DO ranges between a maximum of 9 mg\L and a minimum of 4 mg\L throughout the study. As shown in Figure 10 -A and in appendix B Table A, before FCIP-1, influent DO average 6.36 ± 1.76 mg\L, decreasing during the FCIP-1 to 5.64 ± 0.35 mg\L. Post-FCIP-1, DO increased to 6.44 ± 1.19 mg\L, a continuous increase is observed, with an average of 7.46 ± 0.28 mg\L during FCIP 2. DO during the two FCIPs were different, suggesting less influence of disinfection residual on DO concentration. However, this observation was associated with the possible influence of seasonal and temperature changes. An MWW p-test indicates no statistically significant difference (P > 0.05) between influent DO and the filtrate (post flush) DO, further indicating the limited influence of carbon on DO concentrations.

In Figure 10, DO approach a stable concentration during FCIP-1 and remains relatively constant immediately post FCIP-1 ranging between 5.0 and 6 mg\L until it starts to rise four months post-FCIP-1. A similar trend post 4 months is observed in all filters, a subsequent increase in DO is observed reaching as high as 8 mg\L. During the CP, the three filter effluents, when run in a flow-through (flushed) manner, all had a similar DO trend.
Table 3 Physiochemical characteristics of water filter effluent

<table>
<thead>
<tr>
<th></th>
<th>Filter 1</th>
<th>Filter 2</th>
<th>Filter 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chloramine</td>
<td>FCIP</td>
<td>Chloramine</td>
</tr>
<tr>
<td>PH</td>
<td>7.63</td>
<td>7.68</td>
<td>7.95</td>
</tr>
<tr>
<td>Temp C°</td>
<td>23.21</td>
<td>23.38</td>
<td>23.37</td>
</tr>
<tr>
<td>DO (mg\text{L})</td>
<td>3.89</td>
<td>5.13</td>
<td>6.43</td>
</tr>
<tr>
<td>Total Cl2 (mg/L)</td>
<td>0.10</td>
<td>0.12</td>
<td>0.93</td>
</tr>
<tr>
<td>Free-Cl2 (mg/L)</td>
<td>0.00</td>
<td>0.04</td>
<td>0.20</td>
</tr>
<tr>
<td>Monoamine (mg\text{L})</td>
<td>0.07</td>
<td>0.09</td>
<td>0.65</td>
</tr>
<tr>
<td>Free NH3 (mg/L-N)</td>
<td>0.30</td>
<td>0.02</td>
<td>0.43</td>
</tr>
<tr>
<td>Nitrate (mg/L-N)</td>
<td>2.77</td>
<td>0.88</td>
<td>1.20</td>
</tr>
<tr>
<td>Nitrite (mg/L-N)</td>
<td>0.93</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>Total ATP (RLU)</td>
<td>419.26</td>
<td>158.45</td>
<td>20.13</td>
</tr>
</tbody>
</table>
This similarity was associated with the short contact and retention time within filters during a flow-through event, enabling filters to mimic similar conditions of influent water. Also, the sudden inflection point in DO concentration was associated with the influence of seasonal and temperature changes.

Figure 10 Unfiltered and filtered dissolved oxygen (mg/L-O_2) and total ATP counts (RLU) profiles by influent raw tap water, filter by the dates of filter operation in month throughout the investigation.

Total ATP as an indicator of microbial presence was monitored throughout the study. Influent water had relatively low microbial concentrations compared to all filter effluents, as shown in Figure 10. Most apparent in Figure 10-A is the significant difference in the influent ATP
counts relative to all three-filter effluent ATP concentrations. In general, all filter effluents had relatively greater total ATP counts as compared to influent concentrations, thus demonstrating that carbon can harbor microorganisms.

During the FCIP, a significant decrease in ATP was observed in the influent and filtrate of both filters 1 and 2, recording their lowest microbial counts throughout the study. From Figure 10-B, the influent total ATP profile indicates a decrease by a log RLU during FCIP-1, averaging $0.95 \pm 1.03$ RLU during the FCIP and finally increasing to an average of $9.72 \pm 4.49$ RLU during CP. This result indicates that within the distribution system, there is a great reduction in ATP count during both free-chlorination periods relative to the chloramine period.

In all three filters, the highest ATP counts throughout the study were recorded during CP disinfection, as indicated in Table 3. The observed immediate regrowth of microorganisms in Figure 10-B after FCIP-1 strengthens the argument that free-chlorine is a better germicide compared to chloramine (Lee et al., 2011). Furthermore, the relationship between increasing total ATP counts and the corresponding decrease in residual disinfection is observed when comparing the results profiles of Figure 9 and Figure 10-B. These observed results demonstrated the possible impact of removing disinfection residual and support the hypothesis that filters can become microbially active.

Further observation in Figure 10-B indicates that, whereas post-FCIP in filter 1, a 2-week continuous decrease was observed followed by a steep rise until the maximum inflection point was reached. A slight delay of 2 and 3 weeks in filters 2 and 3, respectively, was observed before an abrupt rise in ATP levels. This observation of a decrease in filter 1 and the lag in filters 2 and 3 was associated with the continuous after mark effects of the FCIP until a point was reached after
the switch to chloramine where the favorable conditions were restored, and microbes were fully acclimatized to grow.

### 4.2 Filter Use Impact on Filtrate Water Quality

The impact of filter use on filtrate water quality is discussed in this section. Varying filter use conditions can significantly influence filtrate water quality. To investigate and monitor the impact of filter use conditions, various use scenarios were developed simulating household filter usage. These three sampling techniques replicate the impact of drinking from a source that has water stagnating in the filter for a specified period (stagnation), drinking from the same source after only 1.6x the volume was exchanged (first flow), and drinking from a fully flushed source (post-flush). If these filters were, hypothetically, installed at a water fountain, you can imagine the sampling representing the first kid in line, the second kid in line, and the last kid in line to drink at a fountain. In Figure 11, stagnation, first flow, and post flush data are plotted as both a scatter plot (Figure 11-A) and as a boxplot Figure 11-B. The boxplot Figure 11-B only contains the data from the monochloramine period after the first FCIP in August 2020 as this gives a comparable baseline for all three filters. Looking first at Figure-A, with an average influent water pH of 8, it was observed that post flush samples had the least decrease with an average of 7.90 in all three filters. Stagnant and first flow samples averaged a pH of 7.67 and 7.60 respectively across all filters, thus indicating the production of H⁺ ions in stagnation and first flow samples. This result demonstrates the influence of detention time on filtrate water pH. Using the Kruskal Wallis mean non-parametric significance test, it was observed that there was a statistically significant difference between the group with (P < 2.2e -16). A pairwise comparison using Wilcoxon showed that each paired pH group was significantly different (p<0.05) as shown in Figure 11 plot B.
Figure 11 Effects of filter use on filtrate water pH. (A) pH profiles by filter and filter age (month), with color codes relating to filter use and grey rectangle as the FCIP. (B) Boxplot comparing filter use and age impact of filtrate pH for filter water

Temperature profiles as illustrated in Figure 12, show a comparison of stagnant, first flow, and post flush filtrate. Influent water temperature averaged 23.7 ± 0.09 C° across the entire study with a maximum of 27.5 C° during the 4th week of the study on 03 Aug 2020 and a minimum of 19.7 C° during the 28th week of the study on 18 Jan 2021. As the influent water temperatures declined, a similar decrease was observed in the flushed filtrate samples as indicated in Figure 8 and Figure 12. The temperature changes observed correlated with seasonal temperature changes, transitioning from summer to spring. A similar trend was observed for first flow samples, although the rate of decline was relatively slower compared to post flush and the temperatures of the first flow samples stabilized in all three filters at an average of 23 ± 0.74 C° after December. However,
the temperature of stagnant water samples remained stable with an average temperature of 23.4 ± 0.47°C for all three filters irrespective of the time of the year, indicating the absence of external influence on stagnating filter water temperature. A Kruskal Wallis p-test on the temperature data for the three groups indicates a statistically significant difference among the groups while an MWW pairwise comparison of each pair showed no significant difference between first flow and post flush samples as shown in Figure 12 plot B.

Figure 12 Effects of filter used on filtrate water temperature. (A) temperature profiles by filter and filter age (month), with color codes relating to filter use. (B) Boxplot comparing filter use and age impact of filtrate temperature.
A dissolved oxygen profile can give significant information about the presence and the extent of ongoing microbial processes within a system. Influent water DO average 6.46 mg/L-$O_2$ across the entire study with a maximum of 9.65 mg/L-$O_2$ during the 34th week on 03 Mar 2021 and a minimum of 4 mg/L-$O_2$ during the 4th week on 05 Aug 2020. As presented in Figure 13 plot C, stagnant water samples obtained a continuously lower DO concentration compared to post flush and first flow samples through the entire study period indicating a significant increase in microbial presence and activities within the filters. Stagnant samples DO in all filters greatly decline from a maximum of 10.2 mg/L-$O_2$ to an average of $3.65 \pm 1.5$ mg/L-$O_2$, first flow and post flush samples average 4.27 mg/L-$O_2$ and 6.48 mg/L-$O_2$ respectively.

These results support the notion that as filters age, stagnant water can result in significantly higher consumption of DO (MWW <0.05). Even though first flow samples had a lower DO level compared to post-flush samples, no specific trend was established. Relatively higher DO concentrations in the post flush samples are associated with the reduced contact time and a short microbial acclimatization time within filters for the microbial presence to be established thus limiting the utilization of DO. While there was a significantly lower concentration of DO in the stagnating samples, the concentrations do not indicate anaerobic conditions which typically begin at DO concentrations below 1 mg/L (US EPA, n.d.; Julia and Ronald, 2007) nor do they cross the lower DO threshold of 2.5 mg/L where nitrification is impacted (Zhang et al., 2009a; AWWA M56, 2013).

Furthermore, post-flush DO levels reached an inflection point in November, where stagnation and post-flush sample temperature was nearly equal. The sudden rapid rise in post flush DO concentration with corresponding decreasing temperature changes as a reference point as shown in Figure 12-A and Figure 13-B, indicating the influence of temperature on DO utilization.
Spearman ranking correlation test shown in Table 4 indicates a significant negative correlation coefficient between temperature and DO concentrations for post flush samples ($\rho = -0.63$), whereas stagnant samples resulted in a week positive correlation ($\rho = 0.32$). According to the United States Geological Survey (2019) and Michaud (1991), cold water can hold more DO than warm water, suggesting higher loss of DO in warm water consistent with the current observed results as post flush samples had relatively lower temperature compared to stagnant water samples.

![Figure 13 Effects of filter use on filtrate water DO concentration](image_url)

Figure 13 Effects of filter use on filtrate water DO concentration. (A) DO profiles by filter and filter age (month), with color codes relating to filter use. (B) Boxplot comparing filter use and age impact of filtrate DO.

The MWW statistical pairwise significance test indicates no significant difference between influent and flow-through, flushed filter effluent DO concentration as mentioned in section 4.1.3.
However, as shown in Figure 13-B, in general, a significant statistical difference among groups in DO concentration in all three filters is observed (p< 2.2e-16). A pairwise comparison using MWW indicates a significant difference between all paired groups (p< 0.05) aside from first flow and stagnant samples in filters 1 and 3, with no significant difference (p = 0.05).

Following discussions in section 4.1.2, according to equations (2 − 12) to (2 − 14), carbon significantly decomposed chlorine to form Cl⁻ and H⁺, and chloramine releasing NH₃, H⁺, and N₂.

\[
C^* + HOCL \rightarrow CO^* + H^+ + Cl^- \quad 2 - 12
\]
\[
2NH₂CL + H₂O + C^* \rightarrow NH₃ + H^+ + Cl^- + CO^* \quad 2 - 13
\]
\[
2NH₂CL + CO^* \rightarrow N₂ + C^* + 2H^+ + 2Cl^- + H₂O \quad 2 - 14
\]

In all filters, there was a significant reduction in both total chlorine and monochloramine residuals relative to influent concentrations. A Spearman correlation test between total chlorine and monochloramine indicates a strong positive correlation (ρ = 0.83*** for post flush samples and for stagnant samples (ρ = 0.3*), with a strong negative correlation between monochloramine and free-ammonia (ρ = -0.48*** strengthening the argument that carbon can decompose monochloramine to release free-ammonia.

Stagnant and first flow samples parallel each other with a recorded lowest residual concentration averaging 0.09 ± 0.05 mg/L Cl₂ total chlorine and 0.07 ± 0.06mg/L Cl₂ monochloramine as presented in Figure 14 and Figure 15-A. In all three filters, stagnation and first flow samples had a constant total chlorine residual concentration, with no statistical difference (p>0.05) between the two. This observation was associated with a longer contact time between water and carbon resulting in a greater reaction time and decomposition of chlorine residuals.
Furthermore, longer stagnation can increase microbial activities that can contribute to higher chlorine demand and disinfectant residual loss. Based on residual chlorine, the results presented establish that stagnant filtered water can result in decreasing water quality, like stagnation within distribution systems and home pipes. At the recorded residual disinfectant concentrations and stagnating filter water temperatures, a conducive environment can be created for the growth of microbes and potential opportunistic pathogens.

Figure 14 Effects of filter use on residual total chlorine concentration. (A) Total chlorine profiles by filter and filter age (month), with color codes relating to filter use. (B) Boxplot comparing filter use and age impact of filtrate total chlorine.
Figure 15 Effects of filter age on monochloramine concentration. (A) Monochloramine profiles by filter and filter age (month), with color codes relating to filter use and grey rectangle representing FCIP. (B) Boxplot comparing filter use and age impact of filtrate monochloramine.

For post flush samples, Figure 15 and Figure 15, it is observed that there are much higher chlorine residuals relative to stagnation and first flow samples. Post flush samples had average
total chlorine residuals of $0.65 \pm 0.48$ mg/L Cl$_2$ while monochloramine averaged $0.44 \pm 0.34$ mg/L Cl$_2$. It was further observed that whereas filters 2 and 3 both experience similar trends in post flush residual concentrations, filter 1 had a significantly different post flush residual profile as shown in Figure 14 and Figure 15. A relatively constant post flush total and monochloramine residual are observed in filter 1, correlating with a rapid increase in chlorine residual in filters 2 and 3 before an observed decline towards a concentration like a filter 1 in post flush samples. This observation is explained by the hypothesis that increasing filter age coupled with the presence of an already seeded and growing biofilm can significantly impact filtrate chlorine residuals. Results from this observation strongly strengthen the view that periodic flushing of filters can significantly improve filtrate water quality based on residual chlorine disinfection.

The impact of filter use conditions and microbial cell counts in terms of ATP were examined in the filter effluent as presented in Figure 16. Filter age coupled with varying filter use appears to increase the possibility that planktonic cells can be found in the filtrate. In all three filters, the response to filter use conditions and microbial growth are quite similar. Stagnation samples recorded the highest microbial counts with first flow samples reporting the lowest counts throughout the study.

The higher counts observed in stagnant samples were associated with the increased detention time in poorly disinfected water within the carbon filters. This gives microbial cells enough time to fully utilize the available substrate for growth. One would expect the post flush samples to have the least cell counts giving the amount of filter exchange and the water to carbon contact time. It is a hypothesis that the increase in post flush microbial counts could be attributed to the sloughing of the biofilm into filter effluent due to the high flow rate at which the filters were flushed compared to the flow rate at which first flow samples were collected.
Figure 16 Filter use impact on filtrate microbial counts. (A) Total ATP profiles by filter and filter age (month), with color codes relating to filter use. (B) Boxplot comparing filter use and age impact of filtrate total ATP.

Given the observed results, it remains unclear if filter use was the sole influencing factor resulting in the observed trend as it is apparent that filter installation timing with respect to FCIP significantly influenced filter microbial seeding time in both filters 2 and 3. Furthermore, it is observed in Figure 16 that, in all three filters, microbial counts initially increased rapidly up to an
inflection point where a gradual decline in total ATP counts is later observed. Further discussion on the impact of filter installation time and limited FCIP on microbial growth is later discussed in sections 4.4 and 4.5.

To clearly understand the impact of filter use on filtrate microbial counts as represented in Figure 16-B, statistical significance test based on mean values indicates all groups were statistically significantly different (Kruskal-Wallis, $p<2.2e-16$ in filter 1 and 3, and $p<6.1e-15$ in filter 2). MWW p-test based on pairwise mean comparison shows that stagnation samples were statistically significantly different to post flush and first flow samples of all three filters, supporting the argument that stagnation can result in greater microbial counts.

4.3 AC Filters and Nitrification Occurrence Potential

The release of ammonia due to the decomposition of chloramine in carbon filter systems can significantly influence the nitrification occurrence potential of these systems. Nitrification follows a two-step process according to equation 2-15 and 2-16 as stated previously in section 2.5 where, AOB oxidize available ammonia to nitrite, which is subsequently oxidized by NOB to nitrate, in all two steps the release of $H^+$ signifies a reduction in pH. Throughout the nitrification process, the changes of ammonia, nitrite, and nitrate can serve as great indicators of nitrification in various water systems. To assess the nitrification potential of all three carbon filters, a concentration profile of these indicators was measured and monitored over the study period as presented in Figure 17.

To ascertain the relationship between free-ammonia, nitrite, and nitrate, the Spearman correlation test was conducted. As a baseline, data collected during the CP of filter 3 (stagnant samples) were used in the correlation test as these most represented all filters. The test indicated a strong negative correlation between free-ammonia and both nitrite and nitrate ($\rho=-0.42^{**}$ and $\rho=$
-0.38**), while a very strong positive correlation existed between nitrite and nitrate (ρ=0.96***), as expected. Detailed correlation test results are presented in Table 4 for stagnant samples and in appendix C for post-flush samples.

As the filter ages, following different use scenarios, it is apparent that there is a significant change in various concentrations of these indicators in the filter effluent. As shown in the Spearman correlation test in Table 4, there is a strong significant positive correlation (ρ >0.5) between filter age and nitrite, nitrate, and total ATP, while free ammonia is negatively correlated with filter age. There is very little free-ammonia in the influent as free-ammonia ranged between levels below the instrument detection limit and 0.49 mg/L-N (mean 0.05) (see Table 2). It is worth noting that all free-ammonia measurements below the instrument detection limit were represented as 0 mg/L. In Figure 17, in all three filters, free-ammonia concentrations peaked twice in the weeks immediately after both FCIPs for both stagnant and post flush samples when chloramination was reintroduced. However, stagnant samples in all filters rapidly decreased and remained at constantly low concentrations throughout the CP. This demonstrates that the sudden introduction of chloramine and its subsequent decomposition resulted in an influx of free-ammonia concentrations in all filters from their lowest concentration during the FCIP.

However, immediately after FCIP, filter 3, which only experienced phase 3, it is observed that free-ammonia concentrations in both post-flush and stagnant samples rapidly reduced. The observed results and the significant changes in ammonia concentration relative to the influent strengthen the argument of ongoing nitrification within the filters. In filter 1 and 3, even though the periodic spike in free ammonia is seen, it is hypothesized that this was associated it to desorption, although further investigation is required to clearly understand the observation.
Table 4 Spearman correlation rank test coefficients (ρ): filter 3 stagnant samples

<table>
<thead>
<tr>
<th></th>
<th>Age (days)</th>
<th>pH</th>
<th>Temp</th>
<th>DO</th>
<th>Total Cl₂</th>
<th>Mono</th>
<th>Free-NH₃</th>
<th>NO₂</th>
<th>NO₃</th>
<th>ATP</th>
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<td></td>
<td>-0.16</td>
<td>-0.42**</td>
<td>-0.35*</td>
<td>0.56***</td>
<td>0.40**</td>
<td>-0.33*</td>
<td>0.95***</td>
<td>0.96***</td>
<td>0.59***</td>
<td></td>
</tr>
<tr>
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<td>0.08</td>
<td>-0.027</td>
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<td>-0.23</td>
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<tr>
<td>Temp</td>
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<td>-0.35*</td>
<td>0.22</td>
<td>-0.34*</td>
<td>-0.37*</td>
<td>-0.43**</td>
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<tr>
<td>DO</td>
<td>-0.45**</td>
<td>-0.19</td>
<td>0.45**</td>
<td>-0.42**</td>
<td>-0.42**</td>
<td>-0.68***</td>
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<tr>
<td>Total Cl₂</td>
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<td>0.52***</td>
<td>0.56***</td>
<td>0.61***</td>
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<tr>
<td>Mono</td>
<td>0.082</td>
<td>0.32*</td>
<td>0.34*</td>
<td>0.12</td>
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<tr>
<td>Free-NH₃</td>
<td>-0.42**</td>
<td>-0.38**</td>
<td>-0.32*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NO₂</td>
<td>0.96***</td>
<td>0.64***</td>
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<td></td>
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</tr>
<tr>
<td>NO₃</td>
<td></td>
<td>0.66***</td>
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<td></td>
<td></td>
</tr>
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Notes: * indicates Significance α=0.05
To clearly understand the impact of filter, use on free-ammonia concentrations, an MWW pairwise significant comparison indicates no significant difference between first flow and post flush samples in all three filters (p > 0.05). A higher significant difference was observed between post flush and stagnant samples as compared to the first flow and stagnant samples as shown in Figure 18. These results demonstrate that stagnant water can significantly decrease free-ammonia concentration thus increasing the potential for nitrification occurrence.
Following a strong spearman correlation between nitrite and nitrate, in all three filters, similar concentration profile trends were exhibited. A correlated increase in stagnant and first flow
nitrite and nitrate concentrations was observed in all three filters. This increase matched the rapid decline in free ammonia concentration as discussed earlier, reemphasizing the fact of ongoing nitrification in each filter. Very low post-flush nitrite concentrations matched that of the influent concentrations, demonstrating that in a flushed, throughput configuration there is no change in nitrite concentrations caused by the filter block. On the other hand, post-flush nitrate concentrations decrease as compared to influent nitrate concentrations irrespective of the filter use condition. It is unclear if carbon adsorbed nitrate or a possible conversion of nitrate to nitrogen gas was occurring. This observation goes beyond the scope of the present study; however, previous research has demonstrated in a multi salt solution, AC can absorb more nitrate than other anions such as chloride (Mubita et al., 2019; Mahmudov & Huang, 2011). A further in-depth adsorption investigation is required to understand the adsorptive capacity of this specific carbon.

A pairwise statistical significance test using the MWW test indicates a greater significance difference in stagnant and post-flush nitrite and nitrate samples in all three filters relative to other pairs. In filters 2 and 3, no statistically significant difference was established between stagnant, and first flow samples as shown in Figure 19. Giving that the proposed action level nitrification occurrence in distribution water systems is 0.025 mg/L-N, from Figure 19-A, both stagnant and first flow mean concentrations are considerably higher compared to the action level. Thus, stagnation and first flow can increase nitrification in carbon filters and further stagnation can increase nitrite concentrations higher than the USEPA set MCL for nitrite (Wilczak et al., 1996).

While a significant difference in the onset and rate of nitrification in each filter was further observed, it was unclear if the filter use condition, filter installation time, or the impact of the limited FCIP influenced the observed results.
Figure 19 Effects of filter use on nitrite and nitrate concentrations. Boxplot comparing filter use and age impact of filtrate (A) Nitrite (B) Nitrate
4.4 Stagnation Length Effects on Nitrification

A stagnation study was conducted to reflect the infrequent use of filters at homes and in public places such as schools, parks, and churches. To evaluate the impact of stagnation on the occurrence and extent of nitrification, factors indicative of nitrification as mentioned in section 4.3 including free-ammonia, nitrite, and nitrate were carefully examined at various stagnation lengths (overnight and weekend). Stagnation studies were carried out at 1080 minutes and 3980 minutes representing overnight and weekend stagnation, respectively. Figure 21, shows results of the profiles of nitrogen species concentrations compared to varying stagnation length throughout the investigation.

From Figure 21, it is apparent that stagnation can significantly influence nitrification occurrence as there is an observed concurrent decrease in free-ammonia and increase in nitrite and nitrate concentrations, signifying the utilization of free-ammonia in the nitrification process. Post-FCIP-1, in filters 2 and 3, immediate utilization of free ammonia is observed until an established constant concentration is reached matching with the point at which nitrite and nitrate concentration begins to increase. In filters 1 and 2, a statistically significant difference in means is observed (p=1e-0.5 and p=0.03) between overnight and weekend free-ammonia samples. One explanation for the observation is the fact that filter 1 was pre-seeded with microbes, had an existing, and developed microbial community before filters 2 and 3, and could result in the significant utilization of available substrate increasing nitrification potential and the observed changes.

A careful analysis of the effects of varying stagnation length on nitrification indicates no significant difference in all filters concerning nitrite and nitrate profiles. Both overnight and weekend nitrite and nitrate concentration followed a similar linear profile rising at a similar rate above the EPA nitrite MCLs (1 mg/L) signifying that, even though stagnation can increase
nitrification thus raising the nitrite and nitrate concentration, varying stagnation length between over a single or two nights (overnight and weekend) had no impact on these concentrations.

A mass balance on nitrogen using stagnant samples demonstrated an average deficit of 0.1063 mol/L-N and 0.066 mol/L-N for overnight and weekend respectively in filter 2 and 3 while in filter one there was an excess of 0.21 mol/L-N and 0.18 mol/L-N as shown in Figure 20 details are found in appendix C. This was associated with the possible adsorption of some nitrogen species in filters 2 and 3 as these were new, while filter 1 experienced desorption possibly due to its age. Although further investigation is required to substantiate this hypothesis.

![Figure 20 Mass balance of filter 1 accounting for nitrogen speciation and distribution using overnight stagnant samples](image)

Mann-Whitney's statistical analysis test further strengthens this observation as no statistically significant difference (p>0.05) between overnight and weekend samples was observed in all filters as indicated in Figure 22. Implying that a consumer is vulnerable to similar risk exposure of nitrite and nitrate irrespective of the two stagnation lengths tested.
Figure 21 Stagnation effect on nitrification occurrence; changing concentration of (A) free ammonia, (B) nitrite, and (C) nitrate by filter and the dates of since operation (months). The FCIP is represented by the dark grey bars and periods of transition in the lighter grey bars.
4.5 Impact of Limited FCIP on Nitrification Occurrence

To examine the impact of FCIP on nitrification occurrence and microbial growth, stagnant and post-flush samples in all three filters were monitored at various phases of the study. The occurrence of nitrification is defined in this study by the increase in nitrite concentration above the proposed action level of 0.025 mg/L-N as stated by Fleming et al., (2008). During FCIP 1 and 2, nitrite concentrations were reduced below 0.025 mg/L-N and 0.05 mg/L-N. Figure 23 illustrates
the concentration profiles of nitrogen species while Figure 27 shows the microbial count profiles of stagnant and post flush samples as a function of dates of filter operation in months.

Before the FCIP 1, even though, filter 1 was pre-seeded with ongoing nitrification and a corresponding increase in nitrite, nitrate, and total ATP counts, it was observed that the FCIP significantly reduced all factors indicative of nitrification, signifying its effectiveness at mitigating nitrification. In general, during the FCIP, irrespective of the sample type collected, free-ammonia concentrations were reduced due to the absence of chloramine (decreasing from 0.05 mg/L-N to 0.02 mg/L-N in influent and an average of 0.45 mg/L-N at CP to 0.025 mg/L-N during the FCIP) in all three filters combined). This represents the influence of an FCIP at limiting the availability of substrate for microbial utilization. Table 3 and Table 5 show the detailed breakdown of measured post flush and stagnant samples parameters respectively.

Table 5 Water physiochemical characteristics of stagnant filter effluent during chloramine and FCIP period

<table>
<thead>
<tr>
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<th>Filter 1</th>
<th>Filter 2</th>
<th>Filter 3</th>
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<tbody>
<tr>
<td>Residual</td>
<td>Chloramine</td>
<td>FCIP</td>
<td>Chloramine</td>
</tr>
<tr>
<td>PH</td>
<td>7.65</td>
<td>7.71</td>
<td>7.67</td>
</tr>
<tr>
<td>Temp C°</td>
<td>22.95</td>
<td>23.09</td>
<td>22.99</td>
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<tr>
<td>DO (mg/L)</td>
<td>3.35</td>
<td>5.32</td>
<td>3.35</td>
</tr>
<tr>
<td>Total Cl₂ (mg/L)</td>
<td>0.10</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Free-Cl₂ (mg/L)</td>
<td>0.01</td>
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<td>0.01</td>
</tr>
<tr>
<td>Monoamine (mg/L)</td>
<td>0.06</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>Free NH₃ (mg/L-N)</td>
<td>0.16</td>
<td>0.02</td>
<td>0.24</td>
</tr>
<tr>
<td>Nitrate (mg/L-N)</td>
<td>3.54</td>
<td>0.98</td>
<td>2.97</td>
</tr>
<tr>
<td>Nitrite (mg/L-N)</td>
<td>1.31</td>
<td>0.11</td>
<td>1.03</td>
</tr>
<tr>
<td>Total ATP (RUL)</td>
<td>814.24</td>
<td>305.82</td>
<td>196.46</td>
</tr>
</tbody>
</table>

It was further observed that during the FCIP, nitrite, and nitrate concentrations were significantly decreased. Nitrite concentrations in filter 1 before the FCIP 1 had reached an average of 0.74 mg/L-N while nitrate was at 2.1 mg/L-N as indicated in Figure 23. Nitrite concentrations
decreased during the FCIP 1 to 0.024 mg/L-N, below the 0.025 mg/L action level. Similarly, effluent nitrate concentrations decreased to 0.72 mg/L-N. This observation was associated with the combined effects of free-chlorine in inactivating microbes and the absence of free-ammonia (substrate) through the decomposition of chloramine, it remains unclear, however, which one has a dominant effect.

Figure 23 Effects of FCIP on the changes in (A) free ammonia, (B) nitrite, and (C) nitrate concentration profile by filter and dates of filter operation in month.

However, a resurgence of nitrification post FCIPs resulted in the immediate decline in free ammonia, correlating with a rapid increase in NO₂ and NO₃ concentrations far above the USEPA
MCL in all filters, thus indicating the short-lived effectiveness of FCIP in deactivating nitrification within a POU filter. Post-FCIP, a statistically significant difference is observed in all three filter use conditions as shown in Figure 24 and Figure 25. Interestingly, the onset of nitrification varied post-FCIP-1, immediate and rapid onset of nitrification is observed in filter 1 with a 2-week delay in filters 2 and 3. In contrast, within a week post-FCIP-2, immediate initiation of nitrification is observed in all three filters, with filter 3 nitrite concentration rising to similar levels before FCIP-2.

Figure 24 Impact of limited FCIP on free-ammonia concentration. Box plot comparing free-ammonia nitrate profiles by filter use and varying residual disinfectants
Figure 25 Impact of limited FCIP on nitrite and nitrate concentration. Box plot comparing (A) nitrite and (B) nitrate profiles by filter use, and varying residual disinfectants.

Throughout the post-FCIP investigation periods, it was observed that stagnant samples recorded the highest nitrification occurrence with nitrite concentration greater than the EPA MCL, while post-flush samples resulted in the lowest concentrations and remained below the MCL. This strengthens the argument that irrespective of the FCIP, periodic flushing can significantly reduce
nitrification impact thus improving water quality. More testing is required to understand the lasting impacts of periodic flushing. Furthermore, the resurgence of nitrification post the FCIP indicates that periodic FCIP is only but a short-term mitigation measure and nitrification reoccurrence is possible after FCIP.

In general, even though stagnant samples had a greater nitrate concentration compared to post flush, stagnant nitrate concentrations immediately increased above post flush samples post-FCIP-1 for filter 1. In contrast, in Figure 26, filters 2 and 3 produced effluent nitrate concentrations highest in post flush samples for approximately 40 days and 20 days, respectively. After this initial period of higher post-flush nitrate concentrations, nitrate remained constant in the post flush samples but nitrite and increased in the stagnation and first flow samples. It remains unclear why nitrate concentrations varied between the filters and require further investigation.

![Chart of nitrate concentration](chart.png)

Figure 26 Impact of FCIP on nitrate concentration: comparison of stagnant and post flush sample before, during, and immediately after the FCIP 1
However, if the entire post-FCIP-1 set of results are considered, the MWW p-test indicates a statistical significance difference in stagnant and post flush with stagnation greater than post flush as indicated in Figure 25.

A careful observation of the impact of FCIP-1 on microbial counts revealed a change of about 0.7 log RLU in total ATP counts in filter 1 between periods before and during the FCIP-1. In Figure 27, for filter 1, the total ATP counts of stagnant samples averaged 200 ± 131 RLU for the initial CP, increasing to 988 ± 1089 RLU during the FCIP-1, and averaging 859 ± 1245 RLU upon returning to chloramine after FCIP-1. Suggesting that, for a pre-seeded filter, even though nitrifiers were controlled thus reducing nitrification, it is possible that other microbial communities present (heterotrophs) were resistant to free chlorine inactivation resulting in an increased ATP count. Furthermore, autotroph metabolism and lysis can produce soluble microbial products which can be utilized by heterotrophs for their growth thus explaining the increase in ATP even though a decline in nitrification was observed (Rittmann and McCarty, 2001). However, due to the limitation of the current enumeration process, we are unable to ascertain if these counts were associated with inactive autotrophs or heterotrophs.

Lee et al., (2011), observed a relatively less free-chlorine penetration in a nitrifying biofilm after periods of monochloramine exposure resulting in minimal microbial inactivation. While other researchers have associated the increase in microbial counts in free-chlorinated and AC filtrate with the particle-associated bacterial from carbon breakthrough of which free-chlorine is ineffective at inactivating (LeChevallier et al., 1984; Skadsen, 1993).

In filter 2 total ATP counts remained at very low concentrations during the FCIP-1 period averaging 3.2 ± 1.79 RLU and increasing to 203 ± 337 RLU post the FCIP-1 suggesting that free chlorine was effective at controlling microbial growth in a new filter, however, upon switching to
chloramine, a gradual increase in ATP counts suggest that chloramine was less effective at controlling microbial growth rendering the carbon biologically active.

Figure 27 Impact of limited FCIP on total ATP counts: comparing time series of stagnant and post plush samples

After the FCIP-1, at approximately 75 days in the filter life, an inflection point in all three filter ATP counts is observed as represented in Figure 27, suggesting a possible changing microbial community, as the microbial count in all filters began to decline. This observation is consistent with other studies (Alfredo et al., 2020; Wu et al., 2017) although much investigation is required to clearly understand the sudden decline in ATP counts and the possible communities present. Another possible explanation for the observed decline is cell lysis during the microbial growth cycle, however, further study of the microbial growth kinetics is required to fully understand the observed results.
4.6 Effect of Filter Installation Time and Nitrification Reoccurrence

The FCIP significantly reduced nitrite concentrations below the USPA MCL threshold. and the nitrification action level of 0.025 mg/L. During the CP we can see an immediate decline in free ammonia and, concurrently, a rapid increase in nitrite and nitrate concentrations as shown in Figure 28. The impact of varying filter installation time and the onset of nitrification was demonstrated by the immediate resurgence of nitrification post-FCIP-1 as marked by the increase in nitrite above the 0.025 mg/L thresholds, and a lag period in filters 2 and 3, delaying the onset of nitrification consistent with findings for distribution systems within the literature (Alfredo, 2021; H. Wang et al., 2014). However, once nitrification was initiated, a continuous and unending rapid linear increase in nitrite and nitrate concentration was observed until the next FCIP as indicated in Figure 28. This delay was potentially due to, albeit short-lived, benefits to installing a filter during or immediately after the FCIP. One further explanation for the observed delay of nitrification post-FCIP-1 in filters 2 and 3 is the fact that nitrifiers are reputed to be slow growers and highly sensitive to chlorinated compounds, therefore the asynchronous switch between disinfectants can greatly influence nitrifier growth and colonization of a fresh filter process, thus delaying the onset of nitrification (Rittmann and McCarty, 2001).

On the contrary, post-FCIP-2, all three filters resumed nitrification within a week above the 0.05 mg/L-N threshold as proposed by Wilczak et al. (1996) as an indication of ongoing severe nitrification. Post-FCIP-2, an immediate resurgence of nitrification is further supported by the observed correlated increase in nitrite and nitrate concentration and a decrease in free ammonia in filter 3 only after 2 days post-FCIP-2 while filter 1 and 2 resumed nitrification after a week post-FCIP 2.
Figure 28 Impact of limited FCIP on nitrification occurrence; concentration profiles of (A) Free ammonia, (B) nitrite, and (C) nitrate by filter age in days. Showing only weekend stagnation data for all the filters.
Chapter 5: Conclusion and Recommendation

5.1 Summary of Findings

The overall objective of this experimental investigation was aimed at understanding the impact of a temporary FCIP on activated carbon block filtrate water quality in a chloraminated water system. The scope of work was based on two main research objectives, with corresponding two underlining hypotheses, which guided the research findings and conclusions. This chapter presents the conclusions of the investigation based on observations and results obtained.

Objective 1 of the research was focused on evaluating how season, use, and stagnation impact filtrate water quality. It was hypothesized that long periods of stagnation will promote nitrification within filters thus impacting filtrate water quality. To test this hypothesis, the impact of activated carbon on the physio-chemical properties of the filtrate was monitored. Experiments performed to satisfy objective 1 revealed that, for a flowthrough scenario (periodic flushing), carbon filters can rapidly reduce disinfection residuals to as low as 0.1 mg/L Cl₂ (90% reduction) relative to influent water, while pH, and temperature of filtrate matched influent water with no significant difference. Biological characteristics of filtrate indicate that while the carbon filters fostered microbial growth, thus increasing the total ATP counts of the filtrate by about a log RLU relative to influent water, DO of filtrate matched influent water with no statistically significant difference (P > 0.05).

An experimental study on the chemical impact of various filter operating conditions revealed that various filter use scenarios had varying impacts on filtrate water quality. The results indicated that long detention of water in filters resulted in a significant decrease of disinfection
residuals, increased the conversion of free-available ammonia to nitrite and nitrate through nitrification, and overall resulted in deteriorated water quality. The steep rise in nitrate and nitrite concentrations of the stagnant sample relative to other sample types supports and confirms the existence of a positive relationship between stagnating water and the occurrence of nitrification. These results supported the hypothesis and the conclusion that longer detention times of water within the POU filters will increase the occurrence of nitrification and negatively impacted water quality. It was, however, demonstrated that periodic flushing of the carbon filters greatly reduced these chemical concentrations and improved the filtrate quality.

A deeper dive into the impact of varying stagnation length on filtrate quality revealed no significant difference in nitrite and nitrate chemical concentration profiles of an overnight and weekend stagnation. However, longer periods of stagnation resulted in greater microbial counts.

Objective 2 of this experimental study was satisfied by monitoring and evaluating the impact of a limited FCIP and filter installation timing on the onset nitrification within the filters. The second hypothesis relates the role of microbial seeding and filter installation timing, and the recurrence of nitrification during and after an FCIP. The relationship between the FCIP, the timing of when a filter was installed, and the onset of nitrification was demonstrated in Figure 28. The experimental results strongly indicated that even though an FCIP proved to be highly effective at mitigating nitrification in both influent and effluent water systems by significantly reducing the concentrations of nitrite, nitrate, and microbial cell counts below regulatory limits this impact was only temporary. Nitrification reoccurred in all three filters, within 4 weeks post-FCIP 1. It was concluded that the difference in the reoccurrence of nitrification in all three filters was due to the filter's installation time with reference to the FCIP. This conclusion was based on the observations that; the pre-seeded filter (filter 1) immediately resumed nitrification post-FCIP 1 while filters 2
and 3 which were installed during and post the FCIP respectively delayed the initiation of nitrification by 4 weeks, thus strongly supporting the research hypothesis. However, post-FCIP 2, all three filters re-nitrification only after a week post-FCIP-2 with one filter (filter 3) returning to pre-FCIP 2 nitrite concentrations within 2 days.post-FCIP-2.

It is important to note how rare nitrite concentrations of this level are within drinking water systems as the MCL for nitrite is 1 mg/L -N typically measured at the point of entry to the distribution system. Repeatedly the results of this research were contextualized using two thresholds set in the literature to indicate the onset of nitrification within a distribution system: 0.025 mg/L-N and 0.05 mg/L-N. Nitrite concentrations reached maximum concentrations of 3.49 mg/L-N during this study---far exceeding the aforementioned thresholds and MCL. Considering that nitrite and nitrate are not regulated at the point of consumption, there would be no MCL violations related to this study, even though nitrite concentrations exceeded the MCL for a considerable period of the research. The FCIP did little to mitigate nitrite concentrations for an installed POU filter in this research. Therefore, the levels of nitrite measured as part of this study are concerning in a public health context and more research is required to know the impact of prolonged ingestion of concentrations as measured by this research.

Furthermore, this experimental investigation has supported the opinion that the use of an AC POU filter is a risk trade-off between decreased aesthetic effects (taste, odor, and residual chlorine), as against increasing exposure to health effects such as increasing nitrification (nitrite and nitrate concentrations) and microbial counts. A clear understanding of the appropriate filter operation (periodic flushing) is therefore required to reduce the risk of this impact and risk exposures. These research findings call for a review of various manufacturers' recommended filter
use conditions as a higher exposure risk was attained before the manufactures proposed recommended use conditions.

5.2 Limitations

Throughout the investigation, the major limitation encountered within the scope of work was our inability to decipher the microbial communities present and efficiently enumerate microbial counts in terms of live and dead cells. An efficient microbiological study will aid in clearly understanding the micro changes and possibly explain some of the current shortfalls of this investigation. Also, this experimental study only focused on nitrification using effluent nitrite, nitrate, and free-ammonia concentrations as chemical markers to represent the chemical quality of treated water.

The impact of flow rate on the changing quality of filtrate was not considered in this investigation as flow rate was held as a constant parameter; therefore, the influence of flow rate on water quality was not addressed by this research.

5.3 Future Research

Future investigations are required to address and understand the microbial community dynamics present in the filters. This study demonstrated that after 75 days of operation, regardless of when the filter was installed, there was a marked change in ATP counts. Future research examining what caused the change should consider using quantifying methods such as flow cytometry, quantitative polymerase chain reaction (qPCR) enumeration, and metagenomics for genetic sequencing to understand how the planktonic and established biofilm communities changed. A clear understanding and enumeration of these microbial communities will not only significantly inform the extent of nitrifiers and dominant microorganisms distributed throughout the filters, but could also help identify the occurrence of opportunistic pathogens within the filters.
Furthermore, the possible adsorption and desorption capacity of carbon for free-ammonia, nitrite, and nitrate, should be investigated in future research as this can influence water quality. It is hypothesized that the adsorption and desorption of these chemicals can increase and decrease filtrate chemical quality respectively and a clear understanding of this phenomenon will be required to operate the filters with no or limited chemical exposure risks. Finally, more research investigating the impact of flow rate on filtrate quality is needed to understand the correlation between changing flow rate and filtrate water quality.
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**Appendix B: Physiochemical Water Quality Analysis**

Table A Water quality analysis of filter effluent by FCIP period

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pre-FCIP1</th>
<th>FCIP 1</th>
<th>Post-FCIP 1</th>
<th>FCIP 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>7.98 ± 0.06</td>
<td>7.90 ± 0.06</td>
<td>8.02 ± 0.09</td>
<td>7.95 ± 0.07</td>
</tr>
<tr>
<td>Temp C°</td>
<td>25.71 ± 1.71</td>
<td>25.13 ± 1.16</td>
<td>23.41 ± 1.73</td>
<td>23.32 ± 0.57</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>6.36 ± 1.76</td>
<td>5.64 ± 0.35</td>
<td>6.44 ± 1.19</td>
<td>7.46 ± 0.28</td>
</tr>
<tr>
<td>Total Cl2 (mg/L)</td>
<td>4.04 ± 1.02</td>
<td>2.44 ± 0.27</td>
<td>3.81 ± 0.54</td>
<td>3.6 ± 0.57</td>
</tr>
<tr>
<td>Free-Cl2 (mg/L)</td>
<td>NAN</td>
<td>4.76 ± 0.59</td>
<td>1.13 ± 1.55</td>
<td>3.34 ± 0.59</td>
</tr>
<tr>
<td>Monoamine (mg/L)</td>
<td>3.94 ± 0.37</td>
<td>0.11 ± 0.06</td>
<td>2.99 ± 0.79</td>
<td>0.1 ± 0.02</td>
</tr>
<tr>
<td>Free NH3 (mg/L-N)</td>
<td>0.09</td>
<td>0.02 ± 0.22</td>
<td>0.05 ± 0.10</td>
<td>0.02 ± 0.45</td>
</tr>
<tr>
<td>Nitrate (mg/L-N)</td>
<td>2.33 ± 0.33</td>
<td>1.7 ± 0.22</td>
<td>2.3 ± 0.25</td>
<td>1.83 ± 0.45</td>
</tr>
<tr>
<td>Nitrite (mg/L-N)</td>
<td>0.01 ± 0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>Total ATP (RUL)</td>
<td>9</td>
<td>0.78 ± 0.44</td>
<td>9.73 ± 4.52</td>
<td>1.1 ± 1.37</td>
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Table B Filter 3 Spearman correlation test: post flush samples

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<tr>
<th></th>
<th>Age (days)</th>
<th>-0.02</th>
<th>-0.90***</th>
<th>0.52***</th>
<th>-0.42***</th>
<th>-0.39***</th>
<th>0.034</th>
<th>0.85***</th>
<th>-0.15</th>
<th>0.75***</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>0.035</td>
<td>0.028</td>
<td>0.21*</td>
<td>0.32**</td>
<td>-0.25*</td>
<td>-0.077</td>
<td>0.17</td>
<td>-0.28*</td>
<td></td>
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</tr>
<tr>
<td>Temp</td>
<td>-0.63***</td>
<td>0.44***</td>
<td>0.42***</td>
<td>0.012</td>
<td>-0.74***</td>
<td>0.23</td>
<td>-0.65***</td>
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<tr>
<td>DO</td>
<td>-0.43***</td>
<td>-0.32**</td>
<td>-0.018</td>
<td>0.39***</td>
<td>-0.36**</td>
<td>0.33**</td>
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<td>TCl₂</td>
<td>0.83***</td>
<td>-0.45***</td>
<td>-0.44***</td>
<td>0.69***</td>
<td>-0.23*</td>
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<tr>
<td>Mono</td>
<td>-0.48***</td>
<td>-0.43***</td>
<td>0.66***</td>
<td>-0.28*</td>
<td></td>
<td></td>
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<tr>
<td>Free-NH₃</td>
<td>0.10</td>
<td>-0.49***</td>
<td>0.037</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NO₃</td>
<td>-0.066</td>
<td>0.66***</td>
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TATP
Appendix C: Mass Balance for All Filters

<table>
<thead>
<tr>
<th>Filter 1</th>
<th>Weekend stagnation</th>
</tr>
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<tbody>
<tr>
<td><strong>Influent</strong></td>
<td>mg/L</td>
</tr>
<tr>
<td>NO2</td>
<td>0.0350</td>
</tr>
<tr>
<td>NO3</td>
<td>1.0000</td>
</tr>
<tr>
<td>NH3</td>
<td>0.5000</td>
</tr>
<tr>
<td>NH2CL</td>
<td>1.0302</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>2.5652</td>
</tr>
</tbody>
</table>

Figure A Mass balance of filter 1 weekend stagnation samples, showing the pathway of various nitrogen speciation

<table>
<thead>
<tr>
<th>Filter 2</th>
<th>Overnight stagnation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Influent</strong></td>
<td>mg/L</td>
</tr>
<tr>
<td>NO2</td>
<td>0.0220</td>
</tr>
<tr>
<td>NO3</td>
<td>1.2000</td>
</tr>
<tr>
<td>NH3</td>
<td>0.5100</td>
</tr>
<tr>
<td>NH2CL</td>
<td>3.0169</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>4.7489</td>
</tr>
</tbody>
</table>

Figure B Mass balance of filter 2 overnight stagnation samples, showing the pathway of various nitrogen speciation
Figure C Mass balance of filter 2 weekend stagnation samples, showing the pathway of various nitrogen speciation

<table>
<thead>
<tr>
<th>Filter 2</th>
<th>Weekend stagnation</th>
<th>Filter 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Influent</strong></td>
<td>mg/L</td>
<td>mol/L</td>
</tr>
<tr>
<td>NO2</td>
<td>0.0230</td>
<td>0.001643</td>
</tr>
<tr>
<td>NO3</td>
<td>1.3000</td>
<td>0.092857</td>
</tr>
<tr>
<td>NH3</td>
<td>0.4400</td>
<td>0.031429</td>
</tr>
<tr>
<td>NH2CL</td>
<td>3.5926</td>
<td>0.256614</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>5.3556</td>
<td>0.382542</td>
</tr>
</tbody>
</table>

**Species Change**

- NO2: 1.0520 0.075143
- NO3: 1.9000 0.135714
- NH3: -0.4100 -0.02929
- NH2CL: -3.5556 -0.25397
- **Total**: -1.0136 -0.0724

---

Figure D Mass balance of filter 3 overnight stagnation samples, showing the pathway of various nitrogen speciation

<table>
<thead>
<tr>
<th>Filter 3</th>
<th>Overnight stagnation</th>
<th>Filter 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Influent</strong></td>
<td>mg/L</td>
<td>mol/L</td>
</tr>
<tr>
<td>NO2</td>
<td>0.0220</td>
<td>0.0016</td>
</tr>
<tr>
<td>NO3</td>
<td>1.4000</td>
<td>0.1</td>
</tr>
<tr>
<td>NH3</td>
<td>0.2800</td>
<td>0.02</td>
</tr>
<tr>
<td>NH2CL</td>
<td>3.0169</td>
<td>0.2155</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>4.7189</td>
<td>0.3371</td>
</tr>
</tbody>
</table>

**Species Change**

- NO2: -0.1000 -0.0071
- NO3: -0.2500 -0.0179
- NH3: -2.8698 -0.205
- NH2CL: 0.037 | 0.002143
- Total: -2.3718 -0.1694

---

Figure E Mass balance of filter 3 weekend stagnation samples, showing the pathway of various nitrogen speciation

<table>
<thead>
<tr>
<th>Filter 3</th>
<th>Weekend stagnation</th>
<th>Filter 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Influent</strong></td>
<td>mg/L</td>
<td>mol/L</td>
</tr>
<tr>
<td>NO2</td>
<td>0.0230</td>
<td>0.001643</td>
</tr>
<tr>
<td>NO3</td>
<td>1.1000</td>
<td>0.078571</td>
</tr>
<tr>
<td>NH3</td>
<td>0.5200</td>
<td>0.037143</td>
</tr>
<tr>
<td>NH2CL</td>
<td>2.6296</td>
<td>0.187831</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>4.2726</td>
<td>0.305188</td>
</tr>
</tbody>
</table>

**Species Change**

- NO2: 0.7570 0.054071
- NO3: 1.4000 0.1
- NH3: -0.4600 -0.03286
- NH2CL: -2.5556 -0.18254
- **Total**: -0.8586 -0.06133