# USE OF CHLORINE, CHLORAMINE, OR CHLORINE DIOXIDE TO CONTROL BIOLOGICAL GROWTH IN POWER PLANT RECIRCULATING COOLING SYSTEMS USING TREATED MUNICIPAL WASTEWATER

by

Shih-Hsiang Chien

Bachelor of Engineering, National Center University, 2004

Master of Science in Civil Engineering, University of Pittsburgh, 2009

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SWANSON SCHOOL OF ENGINEERING

This dissertation was presented

by

Shih-Hsiang Chien

It was defended on

November 20, 2012

and approved by

Radisav D. Vidic, Ph.D, Professor, Civil and Environmental Engineering Department

David A. Dzombak, Ph.D, Professor, Civil and Environmental Engineering Department (CMU)

Leonard W. Casson, Ph.D, Associate Professor, Civil and Environmental Engineering Department

Janet E. Stout, Ph.D, Associate Professor, Civil and Environmental Engineering Department

Dissertation Director: Radisav D. Vidic, Ph.D, Professor, Civil and Environmental Engineering Department

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Shih-Hsiang Chien, Ph.D

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Cooling water deficiency due to limited freshwater sources posed an obstacle of expending current thermoelectric power generation in the U.S. and has led the power industry to seek an alternative water resource to meet its cooling water requirement. Of all the potential alternatives, secondary treated municipal wastewater is prominent because of its vast allocation and abundant quantity. However, the impaired water quality and unique environment make the cooling tower management more challenging. Therefore, prudent water quality management with chemicals is required to prevent corrosion, scaling, and biological growth in the cooling systems.

This study focused on the understanding of the kinetic, effectiveness, and dosage requirement of chlorine-based biocides (chlorine, chloramine and chlorine dioxide) in the recirculating cooling systems using treated municipal wastewater as makeup. Laboratory-scale studies and pilot-scale cooling systems were used to evaluate the biological growth under realistic conditions associated with full-scale cooling systems. Results of 30-day field tests indicated that the pilot-scale cooling towers developed in this study are reliable for evaluating different chemical regimes by maintaining steady cooling performance under various operating conditions.

Direct use of secondary treated effluent for cooling water is a feasible option when using monochloramine as major biocide. The low oxidizing ability of monochloramine resulted in a high residence time and high penetrating ability, and thus provided better biocidal effectiveness against planktonic and sessile heterotrophic bacteria and *Legionella* in recirculating cooling systems. A minimum monochloramine residual above 3 mg/L in the recirculating cooling water is needed for proper biological growth control with this impaired water.

Biological growth potential is comparable in secondary treated effluent subjected to different tertiary treatment (i.e., nitrification, sand filtration, activated carbon adsorption) regardless of total organic carbon concentration in the wastewater. The performance of monochloramine was optimized when the secondary treated effluent was subjected to nitrification and sand filtration.

The key findings of this study indicate that biological growth can be controlled in cooling systems using treated municipal effluents as makeup. The biocide regime demonstrated in this study offers a useful guideline to meet biological growth control criteria in recirculating cooling systems.

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## ACRONYMS AND NOMENCLATURE

| Parameter | Name | Description | Unit |
|---|---|---|---|
| Air | $c_S$ | Specific heat of humid air | kJ/kg·°C (Btu/lb·°F) |
| | $G_x$ | Vapor-free air mass velocity | kg/h·m$^2$ (lb/h·ft$^2$) |
| | $H_a$ | Air enthalpy exiting the cooling section | kJ/kg (BTU/lb) |
| | $H_b$ | Air enthalpy entering the cooling section | kJ/kg (BTU/lb) |
| | $H^*$ | Air enthalpy at equilibrium with water | kJ/kg (BTU/lb) |
| | $h_b$ | Humidity | % |
| | $M_a$ | Molecular weight of air | g/mole |
| | $P'$ | Saturated air vapor pressure | Atm |
| | $P$ | Total air vapor pressure | Atm |
| | $Q_y$ | Vapor-free air mass flow rate | kg/h (lb/h) |
| | $T_{yb}$ | Air temperature entering the cooling section | C° (F°) |
| Water | $c_L$ | Specific heat of water | kJ/kg·°C (Btu/lb·°F) |
| | $G_y$ | Water mass velocity | kg/h·m$^2$ (lb/h·ft$^2$) |
| | $M_w$ | Molecular weight of water | g/mole |
| | $N$ | Cycles of concentration | - |
| | $Q_x$ | Water mass flow rate | kg/h (lb/h) |
| | $Q_b$ | Blowdown water flow rate | kg/h (lb/h) |
| | $Q_m$ | Makeup water flow rate | kg/h (lb/h) |
| | $Q_e$ | Evaporation water flow rate | kg/h (lb/h) |
| | $Q_{e,d}$ | Designed evaporation water flow rate | kg/h (lb/h) |
| | $T_h$ | Water temperature in the heating bath | C° (F°) |
| | $T_{xa}$ | Water temperature entering the cooling section (exiting the heating bath) | C° (F°) |
| | $T_{xb}$ | Water temperature exiting the cooling section (entering the heating bath) | C° (F°) |
| Packing | $A_b$ | Cross-sectional area | m$^2$ (ft$^2$) |
| | $a$ | Packing volumetric surface area | m$^2$/m$^3$ (ft$^2$/ft$^3$) |
| | $R$ | Water-to-air mass loading ratio | - |
| | $Z$ | Length of cooling zone | m (ft) |
| | $Z_T$ | Height of packing material | m (ft) |
| Heat exchanger | $A_C$ | Inner surface area of the heat exchanger tube | m$^2$ (ft$^2$) |
| | $K_y$ | Overall water vapor mass transfer coefficient | kg/h·m$^2$ (lb/h·ft$^2$) |
| | $q_T$ | Heat removal/transfer rate | kJ/h (BTU/h) |
| | $U$ | Local overall heat-transfer coefficient | kJ/h·m$^2$·°C (BTU/h·ft$^2$·°F) |

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*To Them I dedicate*

*My Love, Wen-chi*

*My Parents, Li-Ching and A-Ching*

*My sisters, Wei-Chen and Shu-Yu*

# 1.0 INTRODUCTION

Water, the essential element for all living organisms, is also essential for modern civilization. In the U.S., total freshwater usage has increased by 2.3 % since 1995, and the total freshwater withdrawal reached 349 billion gallons per day (Kenny et al., 2009). Among the major freshwater users, thermoelectric power generation has recently become the top user (143 Bgal/day, 39%). A reliable and abundant water source is required to ensure thermoelectric power generation. However, the increasing population and global warming effects, e.g. increase in sea level, decrease in annual precipitation, etc., further exacerbate the fierce competition for available freshwater (Hinrichsen et al., 1996). Several cases in arid areas, such as Arizona and Texas, have shown that lack of available cooling water sources can result in suspension in operation of existing power plants and delay in construction of new power plants (Feeley and Ramezan 2003; Dishneau 2007).

Increased demand for electricity in those areas will force difficult decisions about allocating priorities and finding reliable water sources for electricity production. Therefore, alternative sources of water for cooling tower operation are likely to be in great demand in the near future. Among all the alternatives, municipal wastewater is considered the most promising water source because of its accessibility and steady water quality (Vidic and Dzombak, 2009).

The main challenges when using treated municipal wastewater as cooling tower makeup are corrosion, scaling, and biofouling (biological growth) due to the impaired water quality. The high concentrations of ammonia, organic matter, alkalinity, hardness, total suspended solids, and biological oxygen demand, result in a greater potential for the occurrence of corrosion, scaling, and biological growth problems (Wijesinghe et al., 1996; Selby et al., 1996; Puckorius, 2003). Therefore, prudent cooling water quality management is required when using the treated municipal wastewater for power plant cooling systems.

Biological growth caused by a wide variety of microorganisms, such as bacteria, fungi, and algae, is one of the most common and most significant problems in the operation of cooling systems (Adams et al., 1980; Melo and Bott, 1997; Frayne, 1999, Flemming, 2002). Typical operating conditions maintained in a cooling system, such as temperature range, pH, continuous airflow and sunlight, make it ideal for biological growth. In addition, favorable growth conditions available in the cooling system due to high levels of organic matter and nutrients in the makeup water make biological control an even more challenging task.

One of the main sources of microbiological contamination is usually the makeup water for cooling processes. In addition to the microorganisms in the makeup water, airborne microorganisms can aid the bacterial growth in recirculating water as they move through the cooling tower. Biofilm growth in cooling systems causes heat transfer resistance, and microbiologically induced corrosion under the biofilm can cause failure of both the heat exchanger and the cooling system (Characklis, 1990; Ludensky, 2005). Most microorganisms can form biofilms (Costerton et al. 1987) and are able to accumulate on heat exchanger surface within 4~8 hours (Rossmoore, 1995). Large portion of a biofilm is simply water (Zhang et al., 1998) but the exact composition and structure is determined by the available nutrients and

surrounding environment (Stoodley et al., 1999). Exopolysaccharides (EPS) is known to protect the biofilm from being penetrated by foreign materials, such as oxidizing chemicals, metals, etc., and makes the disinfection even more difficult (Sutherland, 2001).

Another notable microbial induced problem in recirculating cooling systems is the presence of *Legionella* species due to poor biological control in the recirculating water (Fraser et al., 1977; Edelstein, 1993). The Cooling Tower Institute proposed that cooling tower operators shall monitor for Legionella regularly and ensure that planktonic bacteria count in the bulk water is maintained below $10^4$ CFU/mL and sessile bacteria count on surfaces is maintained below $10^5$ CFU/$cm^2$ to reduce health risk caused by airborne bacterial emission through evaporation (CTI, 2008).

A methodology in controlling these problems in cooling systems is to mitigate the biological growth instead of sterilizing the entire system (Rossmoore, 1995). In other words, it is more practical to prevent the biological growth than to completely clean the system once it is contaminated. Mitigation of biological growth can be achieved through chemical or physical methods. Selection of a proper biocide is based on cooling system design and makeup water quality. However, none of the previous work provides sufficient details to demonstrate the actual effectiveness and demand of specific biocides when using the treated municipal wastewater for cooling purpose. It is important to develop a guideline for selecting the chemical regime for specific cooling system using this impaired water as makeup.

Most disinfection studies focus on the chemical kinetics and the disinfection efficiency in unconcentrated municipal wastewater (Morris, 1967; Margerum et al., 1978; Morris and Issac, 1983). However, findings of these studies may not be applicable for recirculating cooling water, i.e. 4-10 cycles of concentration, using treated municipal wastewater as makeup. In addition, wastewater disinfection usually focuses on inactivating planktonic bacteria, while biological growth control in recirculating cooling systems must focus on inactivating both planktonic and sessile bacteria.

Hydrodynamic forces were known to affect the formation of biofilm in many ways (Costerton et al., 1995; Stoodley et al., 1999; Liu and Tay, 2002; Donlan, 2002). Liu et al. (2006) showed that a turbulent flow in a piping system can promote Legionella colonization. Therefore, a bench-scale recirculating system incorporating variable flow rate is required to evaluate the biological growth in recirculating cooling systems. The laboratory analyses may be helpful to understand the mechanisms involved with chemical and microbiological corrosion and fouling processes and their control. However, most industrial cooling systems still require full-scale evaluation of water quality management strategies due to the complexity and variability of recirculating water systems (Bentham and Broadbent, 1995; Carducci et al., 2010).

## 1.1 RESEARCH OBJECTIVES

This study aims to encourage the use of treated municipal wastewater where freshwater is not readily available for power plant cooling systems. To evaluate the feasibility of using this impaired water source for cooling, specific goals of this study were to evaluate the biological growth potential of treated municipal wastewater, to optimize the biological growth control when

using treated municipal wastewater in cooling towers, and to elucidate the corresponding impacts of chlorine-based biocides based on their cost-effectiveness as well as environmental and public health impacts. In order to fulfill these major goals, experimental investigations were conducted to achieve the following specific objectives: 1) develop a methodology for evaluating the biological growth under realistic conditions by employing a pilot-scale recirculating cooling tower; 2) determine the effectiveness of pre-formed monochloramine in recirculating cooling systems using secondary treated municipal wastewater; 3) determine the impact of tertiary treatments on the performance of pre-formed monochloramine in recirculating cooling systems 4) conduct comprehensive evaluation of the applicability of three chlorine-based biocide, i.e. sodium hypochlorite, monochloramine, and chlorine dioxide, under a broad range of conditions relevant to cooling system operation in both lab-scale and pilot-scale systems.

## 1.2 SCOPE AND WORKS OF THE DISSERTATION

This dissertation incorporates four journal manuscripts and is presented in seven chapters. The core of the dissertation consists of Chapters 2, 3, 4, and 5, which include major findings of this study.

The present chapter (Chapter 1) introduces the background and motivation of the study. Chapter 2 demonstrates the design of a pilot-scale cooling tower based on fundamental thermodynamic and heat transfer relationships in a recirculating cooling system with induced draft cooling. This pilot-scale method presents a reliable and useful tool for evaluating corrosion, scaling, and biological growth subjected to the use of impaired water (e.g. treated municipal wastewater) as cooling tower makeup water. This chapter was published in Review of Scientific Instruments (Chien et al., 2012a).

Chapter 3 evaluated the biocidal effectiveness of monochloramine in recirculating cooling systems using secondary treated municipal wastewater. The feasibility of using monochloramine to control biological growth, i.e. planktonic and sessile heterotrophic bacteria and Legionella, was investigated through a comparison between in-situ and pre-formed chloramine in laboratory and field experiments. The influence of operating parameters, i.e. ammonia concentration, water temperature, etc., on the biocidal effectiveness was further studied in a well-controlled bench-scale system. Systematic evaluation of monochloramine through batch-, bench-, and pilot-scale tests were conducted to determine the optimal chemical residual and dosage for proper biological growth control. This chapter was published in Water Research (Chien et al., 2012b).

Chapter 4 focuses on the impact of different tertiary treatments on the biocidal performance of pre-formed monochloramine in recirculating cooling system. Influence of water quality on biological growth potential without biocide addition was identified through batch- and bench-scale tests. Optimal chemical dosage and residual were determined by carefully analyzing laboratory- and filed-scale results. The benefits and impacts of each tertiary treatment were shown based on the performance of monochloramine in pilot-scale studies. This chapter has been submitted for publication (Chien et al., 2012c).

Chapter 5 provides comprehensive evaluation to compare the performance of chlorine-based biocides (chlorine, chloramine and chlorine dioxide) in controlling biological growth in recirculating cooling system using tertiary-treated municipal wastewater. Optimal residual and dosage for biological growth control were first determined in laboratory tests. Successful chemical regimes identified in bench-scale studies were validated by conducting field tests. Field tests results were combined with cost analysis to provide critical information for advancing the use of municipal wastewater as cooling water in thermoelectric power plants. This chapter has been submitted for publication (Chien et al., 2012d).

Chapter 6 summarizes the original contributions, major findings, and conclusions of this work. Specific future work that can be carried out from this dissertation is also provided in this chapter.

# 2.0 PILOT-SCALE COOLING TOWER TO EVALUATE CORROSION, SCALING, AND BIOFOULING CONTROL STRATEGIES FOR COOLING SYSTEM MAKEUP WATER

Pilot-scale cooling towers were used to evaluate corrosion, scaling and biofouling control strategies when using particular cooling system makeup water and particular operating conditions. To study the potential for using a number of different impaired waters as makeup water, a pilot-scale system capable of generating 27,000 kJ/h heat load and maintaining recirculating water flow with a Reynolds number of $1.92 \times 10^4$ was designed to study these critical processes under conditions that are similar to full-scale systems. The pilot-scale cooling tower was equipped with automatic makeup water control system, automatic blowdown control system, semi-automatic biocide feeding system, and corrosion, scaling, and biofouling monitoring system. Observed operational data revealed that the major operating parameters, including temperature change (6.6 ℃), cycles of concentration (N = 4.6), water flow velocity (0.66 m/s), and air mass velocity (3660 kg/h·$m^2$), were controlled quite well for an extended period of time (up to 2 months). Overall, the performance of the pilot-scale cooling towers using treated municipal wastewater was shown to be suitable to study critical processes (corrosion, scaling, and biological growth) and evaluate cooling water management strategies for make-up waters of complex quality.

This chapter was published in Review of Scientific Instrument (Chien et al., 2012a)

## 2.1 INTRODUCTION

The availability of freshwater for use in industrial cooling water systems is becoming increasingly limited (USGAO, 2003). Alternative (lower quality) water sources for industrial cooling are thus of growing interest. However, cooling tower performance is strongly related to the intake water quality, which may lead to undesirable outcomes due to inappropriate cooling water management (Isozumi et al., 2005; Jack, 2002; Bhopal and Barr, 1990). The main challenges when using alternative cooling water sources of degraded water quality are enhanced corrosion, scaling, and biological fouling processes (EPRI, 2003). Evaluation of effective control strategies at bench- and pilot-scale is necessary for such waters.

Preliminary evaluation can be performed through bench-scale tests in a laboratory. Such tests can provide rapid evaluation of the corrosion, scaling, and biological fouling tendencies of the makeup water, as well as enable preliminary screening of possible chemical control agents (Hsieh et al., 2010a; Li, et al., 2011a). Laboratory analysis may be helpful to understand the mechanisms involved with chemical and microbiological corrosion and fouling processes and their control. However, most industrial cooling systems still require full-scale evaluation of water quality management strategies due to the complexity and variability of recirculating water systems (Bentham and Broadbent, 1995; Carducci et al., 2010).

Site-specific validation of selected control strategies can be performed using on-site pilot-scale cooling tower testing, with operational conditions similar to those employed in full-scale systems. The operational conditions include water temperature entering and exiting the tower, cycles of concentration, water chemistry, water mass velocity, air mass velocity, and cooling tower packing height and characteristics. Transportable pilot-scale cooling towers have been used to evaluate the feasibility of using particular waters as cooling water makeup, but no details

regarding the design, construction, and operation of pilot-scale cooling towers have been provided (Palo and Pothier, 2003; Swart and Engelbrecht, 2004). There have been studies using pilot-scale cooling towers to evaluate biofouling control strategies but no information about the design of the cooling towers was provided (Duda et al., 2011). A small-scale cooling tower has been designed for thermal performance study but not for corrosion, scaling, and biofouling evaluation (Lemouari et al., 2007).

Numerous studies have focused on thermal analysis, cooling performance, and simulation models for cooling towers (Webb, 1984; Braun et al., 1989; Brenier, 1994; Khan et al., 2002). These studies have shown how the theory of heat exchanger design may be applied to cooling towers and thermal analysis of cooling towers, evaporative condensers and evaporative coolants.

The overall goal of this study was to establish a pilot-scale method for the evaluation of strategies for control of corrosion, scaling, and biofouling when using alternative, low quality water sources as makeup water for recirculating cooling systems. The design of the pilot-scale cooling tower was based on fundamental thermodynamic and heat transfer relationships for a wet recirculating cooling system with induced draft cooling in thermoelectric power plants. Specifically, the study focused on 1) design and construction of a pilot-scale cooling tower, 2) demonstrating the operational performance and utility of the pilot-scale cooling tower to study the effectiveness of cooling water management strategies relevant for successful operation of a full-scale system.

## 2.2 DESIGN METHODOLOGY

In order to apply the results obtained from pilot-scale testing to full-scale systems, the pilot-scale cooling tower should have design features and operational conditions similar to those in a full-scale cooling system. A basic process diagram for a counter-flow evaporative cooling tower is provided in Figure 2.1. Two critical components for a pilot-scale cooling tower are: 1) the evaporative cooling system, and 2) the heating system.

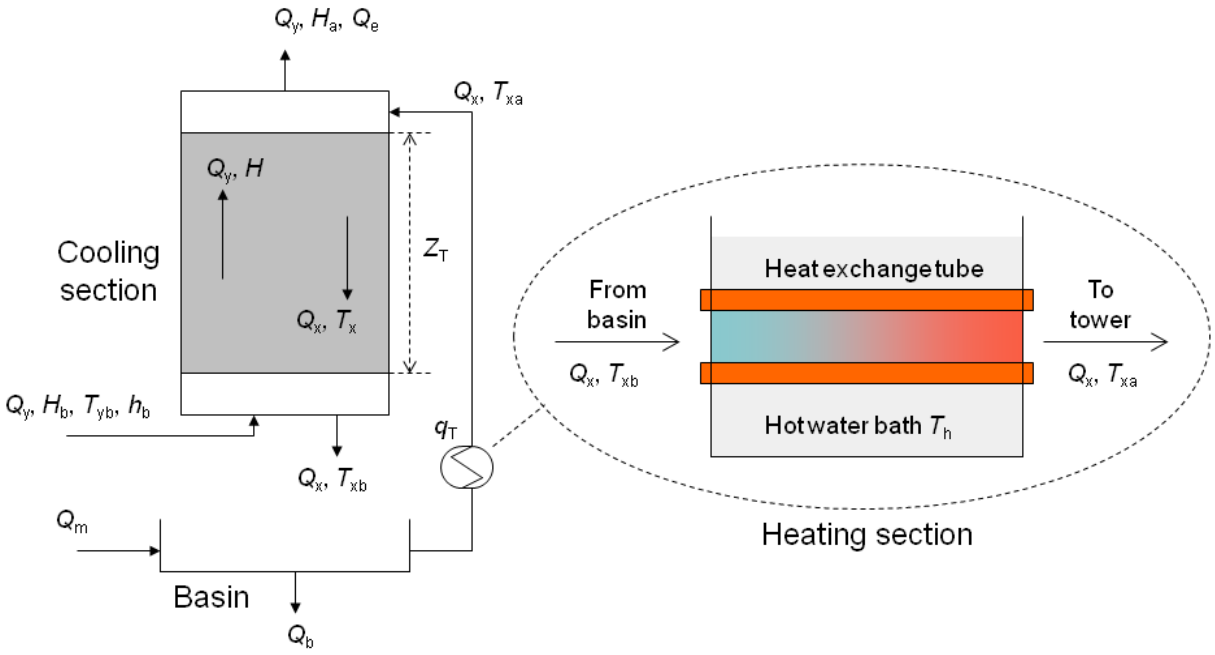



**Figure 2.1.** Flow diagram of a cooling tower with a counter-flow cooling system and a heating section.

### 2.2.1 Evaporative cooling system

In the cooling section of Figure 2.1, air at enthalpy $H_b$ (kJ/kg; Btu/lb), temperature $T_{yb}$ (C°; °F), and humidity $h_b$ (unitless) with vapor-free air mass flow rate $Q_y$ (kg/h; lb/h) enters the bottom of the tower and leaves at the top at enthalpy $H_a$ (kJ/kg; Btu/lb). Water at temperature $T_{xa}$ with mass flow rate $Q_x$ (kg/h; lb/h) enters the top of the tower and leaves at the bottom at temperature

$T_{xb}$ with flow rate $Q_x$, assuming that water evaporation, which is usually only 1 to 2 percent of $Q_x$, can be neglected. At a distance $Z$ (m; ft) from the bottom of the cooling tower, the air enthalpy is $H$ (kJ/kg; Btu/lb) and the water temperature is $T_x$. The cooling tower packing cross-sectional area is $A_b$ ($m^2$; $ft^2$) and the packing height is $Z_T$ (m; ft). The cooling water mass velocity is $G_y$ (kg/h·$m^2$; lb/h·$ft^2$), which is defined as $Q_x/A_b$. The vapor-free air mass velocity is $G_x$ (kg/h·$m^2$; lb/h·$ft^2$), which is defined as $Q_y/A_b$. The cooling tower has makeup water flow rate of $Q_m$ (kg/h; lb/h), blowdown $Q_b$ (kg/h; lb/h), and evaporation $Q_e$ (kg/h; lb/h).

The main objective in cooling tower design is to determine the proper length of water/air contact zone, $Z_T$, for particular packing type and given cooling tower cross-sectional area ($A_b$), cooling water temperatures ($T_{xa}$ and $T_{xb}$), cooling water and air mass flow velocities ($G_x$ and $G_y$) and ambient conditions ($h_b$ and $T_{yb}$).These design constraints are usually governed by the required heat removal rate, $q_T$ (kJ/h; Btu/h) from the heat exchanger design.

The key cooling tower design equation is (Green and Perry, 2007):

$$\frac{K_y a Z_T}{G_x} = c_L \int_{T_{xb}}^{T_{xa}} \frac{dT_x}{H^* - H} \tag{1}$$

where $K_y$ is the overall water vapor mass transfer coefficient (kg/h·$m^2$; lb/h·$ft^2$), $a$ is the packing volumetric surface area ($m^2/m^3$; $ft^2/ft^3$), $H$ is air enthalpy and $H^*$ is air enthalpy at equilibrium with water, and $c_L$ is the specific heat of water (Btu/lb·°F). $K_y a Z_T/G_x$ is the cooling tower characteristic (dimensionless) and is mainly a function of packing type and water-to-air mass loading ratio, $R$ ($R$ is defined as $G_x/G_y$). The relationship between $K_y a Z_T/G_x$ and $R$ for a specific packing is usually provided by the packing manufacturer. The right-hand side of Equation 1 can be approximated numerically using the Chebyshev method(Green and Perry, 2007):

$$\int_{T_{xb}}^{T_{xa}} \frac{dT_x}{H^* - H} \cong \frac{T_{xa} - T_{xb}}{4}\left(\frac{1}{\Delta H_1} + \frac{1}{\Delta H_2} + \frac{1}{\Delta H_3} + \frac{1}{\Delta H_4}\right) \quad (2)$$

where, $\Delta H_1$ is the value of $H^*$-$H$ at $T_{xb}$+0.1$\Delta T_x$, $\Delta H_2$ is the value of $H^*$-$H$ at $T_{xb}$+0.4$\Delta T_x$, $\Delta H_3$ is the value of $H^*$-$H$ at $T_{xa}$-0.4$\Delta T_x$, and $\Delta H_4$ is the value of $H^*$-$H$ at $T_{xa}$-0.1$\Delta T_x$. $\Delta T_x$ is defined as $T_{xa}$-$T_{xb}$. With ambient conditions ($h_b$ and $T_{yb}$), cooling water temperatures ($T_{xa}$ and $T_{xb}$), and cooling water and air mass flow velocity ($G_x$ and $G_y$) given or assigned, Equation (2) can be solved as follows:

Air enthalpy, $H$, is calculated using the following equation (Green and Perry, 2007):

$$H = c_S T_y + \lambda_0 h \quad (3)$$

where $c_S$ is the specific heat of humid air (kJ/kg·℃; Btu/lb·°F), $\lambda_0$ is evaporation heat of water (kJ/kg; Btu/lb), $h$ is humidity, and

$$c_S = 0.43 + 0.81h \quad (4)$$

Equations 3 and 4 can be used to calculate $H$ at $T_{xb}$, that is, $H_b$. Further, the enthalpy balance for the tower in a particular section is

$$G_y \Delta H = G_x c_L \Delta T_x \quad (5)$$

where the $c_L$ is the specific heat of water (kJ/kg·℃; Btu/lb·°F). Equations 5 can be used to calculate $H$ at $T_{xb}$+0.1$\Delta T_x$ , $T_{xb}$+0.4$\Delta T_x$, $T_{xa}$-0.4$\Delta T_x$, and $T_{xa}$-0.1$\Delta T_x$. Equations 3 and 4 can also be used to calculated $H$* at various temperature points ($T_{xb}$, $T_{xb}$+0.1$\Delta T_x$ , $T_{xb}$+0.4$\Delta T_x$, $T_{xa}$-0.4$\Delta T_x$, and $T_{xa}$-0.1$\Delta T_x$) if saturated humidity at the various temperature points are known. In this study, an empirical equation was used to describe the relationship between air temperature ($T_y$) and saturated vapor pressure, ($P'$, atm) (Dexter and Richard, 2009):

$$P' = 6.1121\exp\{(18.678 - T_c/234.5)[T_c/(257.14 + T_c)]\} \times 9.8692 \times 10^{-4} \quad (6)$$

where, $T_c$ is the dry-bulb air temperature in degrees Celsius. It should be noted that the empirical equation was optimized and limited to the temperature range 0 to 100 ℃ (32 to 212 ℉). The saturated humidity, $h^*$ (unitless), is then related to $P'$ through

$$h^* = P'M_w/[M_a(P-P')] \quad (7)$$

where $P$ is the total air vapor pressure (atm), $M_w$ and $M_a$ are the molecular weights (g/mol) of water and air, respectively.

After resolving the right-hand side of Equation 1, $Z_T$ can be determined through the plot of $K_y a Z_T/G_x$ vs. $R$ provided from the packing manufacturer. A summary of cooling tower design process is provided in the first three columns of Table 2.1.

The water mass balance in the system is

$$Q_m = Q_b + Q_e \quad (8)$$

and the cycles of concentration, $N$, is defined as

$$N = Q_m/Q_b \quad (9)$$

Strictly speaking, $Q_e$ is the product of air mass flow velocity and air humidity difference. However, the outlet air humidity, $h_b$, is an unknown parameter in the design of a cooling tower. A general rule of thumb to estimate $Q_{e,d}$ (Designated evaporation rate) is based on inline water mass flow rate through the cooling section (Green and Perry, 2007):

$$Q_{e,d} = \beta Q_x \quad (10)$$

Where, $\beta$ is $0.00085\Delta T_x$ (unitless) and $\Delta T_x$ is $T_{xa}–T_{xb}$.

### 2.2.2 Heating system

Since the primary purpose of pilot-scale cooling tower is to evaluate corrosion, scaling, and biofouling of metals and metal alloys surfaces in the cooling side of the heat exchanger and

related piping, important design parameters for the heating system are the cooling water temperatures, $T_{xb}$ and $T_{xa}$, and water flow velocity. A heater is needed in the pilot-scale system to provide sufficient heat to increase the water temperature from $T_{xb}$ to $T_{xa}$. Figure 2.1 shows a schematic of a heat exchange tube in a heating bath. To simulate the heating process in a real heat exchanger, the cooling water is indirectly heated by passing it through a heat exchange tube immersed in a hot water bath with an immersed heating cartridge.

Heat removal rate in the heating section by the cooling water can be expressed as

$$q_T = Q_x c_L (T_{xa} - T_{xb}) \tag{11}$$

where, $q_T$ is the total rate of heat transfer into the cooling water (kJ/h; Btu/h). At a particular point in the heat exchange tube, the heat transfer rate in differential form can be expressed as

$$dq/dA_C = U\Delta T \tag{12}$$

where $q$ is the rate of heat transfer into the cooling water (kJ/h; Btu/h), $A_C$ is the inner surface area of the heat exchange tube ($m^2$; $ft^2$), and $U$ is the local overall heat-transfer coefficient based on the inner surface area (kJ/h·$m^2$·℃; Btu/h·$ft^2$·°F), $\Delta T$ is $T_h - T_x$ (℃; °F), where $T_h$ is the water temperature (℃; °F) of the hot water bath.

Assuming that (1) the overall heat transfer coefficient $U$ is constant, (2) the heat exchange with the ambient air is negligible, and (3) steady state has been reached, the slope of a graph of $\Delta T$ vs. $q$ is constant (McCabe et al., 2001). Therefore,

$$d\Delta T/dq = (\Delta T_a - \Delta T_b)/q_T \tag{13}$$

where $\Delta T_a$ and $\Delta T_b$ are $T_h$-$T_{xa}$ and $T_h$-$T_{xb}$ (℃; °F), respectively. By solving Equations 11-13 simultaneously, the following expression for $U$ can be obtained:

$$U = Q_x c_L \ln(\Delta T_b/\Delta T_a)/A_C \tag{14}$$

Equation 14 shows the relationship between the overall heat-transfer coefficient and cooling water flow rate, cooling water and hot water bath temperatures, and total inner surface area of the heat exchanger tube.

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Pilot-scale cooling tower design

A schematic of the complete pilot-scale cooling tower design is shown in Figure 2.2. Constructed pilot-scale cooling towers are shown Figure 2.3. In addition to evaporative cooling and heating systems, each tower also included a corrosion, scaling, and biofouling monitoring system, a makeup water control system, a blowdown control system, a biocide feeding system and a power control system. Design and construction details for these six systems are outlined below.

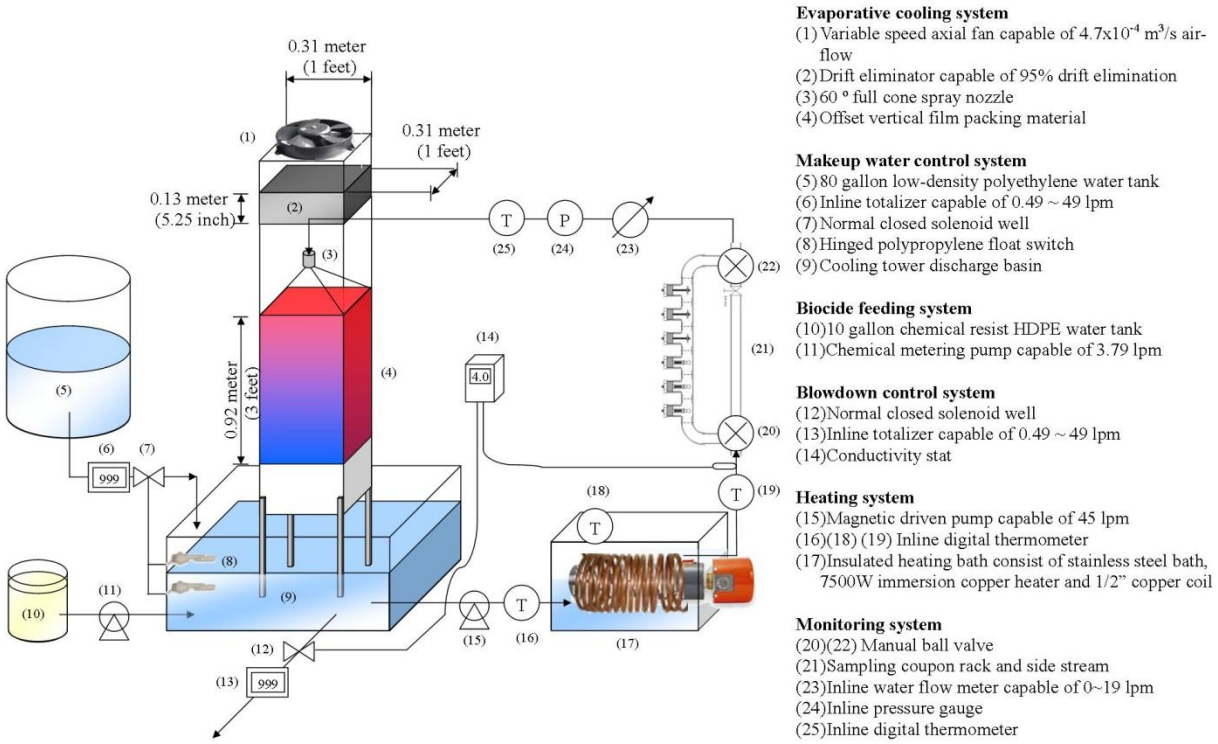



**Figure 2.2.** Schematic of the pilot-scale cooling tower design.

**Figure 2.3.** Pilot-scale cooling towers, which were modified to withstand the outdoor environment.

#### 2.3.1.1 Evaporative cooling system

The values of the design parameters for a pilot-scale cooling tower were determined by following the design procedure outlined in the first two columns of Table 2.1 and by considering the general design parameters employed in full-scale evaporative cooling systems listed in the third column in Table 2.1. Selected design parameters are presented in the fourth column in Table 2.1. The counter-flow evaporative cooling tower was constructed of 0.95 cm (0.375 inch) thick Plexiglas acrylic. The packing material (OF21-MA; Brentwood Industries, Reading, PA) was selected for water mass velocity of 11.4 LPM (3 GPM) and maximal temperature allowance of 60 ℃ (140℉). This PVC vertical counterflow packing was selected for the study due to its low fouling tendency for cooling water with less than 200 mg/L total suspended solids. The packing is comprised of 21 corrugated sheets and has a specific surface area of 147.8 $m^2/m^3$ ($45ft^2/ft^3$). The evaporative cooling system was supported on four 0.6 m (2-ft) long stainless steel legs of size 2.54 cm x 2.54 cm (1-in × 1-in) inside a water collection basin. The cross-section area ($A_b$) of the cooling tower was 0.09 $m^2$ (1 $ft^2$). The evaporative cooling system was equipped with a mist eliminator (CF80Max, 0.16 m (0.525 ft) in height, Brentwood Industries, Reading, PA) to reduce the water loss through drift. The fan (EBM Papst W3G250-CC54-01, Germany) was mounted on top of the tower and the fan speed could be adjusted through a potentiometer in the electrical control system. The variable speed axial fan is capable of generating $4.7x10^{-4}$ $m^3/s$ (1000 CFM) of air flow. The cooling system was mounted on a cart with brake-lock wheels, allowing for easy transportation.

**Table 2.1.** Counter-flow cooling tower design procedures and values of parameters used in this study.

| Steps | Description | General value or calculation equation | Pilot tower design value |
|---|---|---|---|
| 1 | Determine heat removal rate ($q_T$) | Depending on the associated system to be cooled. | 23760 kJ/s (22520 Btu/h) |
| 2 | Determine "*Range*", that is, cooling water temperature difference ($\Delta T_x$) | 5.6-16.7 ℃[a] (10-30℉) | 8.3 ℃ (15℉) |
| 3 | Calculate cooling water flow rate ($Q_x$) | $Q_x = \frac{q_H}{c_L \Delta T_x}$ | 680 kg/h[1] (11.4 LPM) 1500 lb/h (3 GPM) |
| 4 | Select a particular type of packing | --- | --- |
| 5 | Determine cooling water mass velocity ($G_x$) | 81.5-203.7 LPM/m$^2$ (2-5 GPM/ft$^2$), or suggested by packing manufacturer [b] | 7320 kg/h·m$^2$ (122 LPM/m$^2$) 1500 lb/h·ft$^2$ (3 GPM/ft$^2$) |
| 6 | Determine water-air mass loading ratio ($R$=$G_x/G_y$) | Usually 1.5-2 for fill type packing, or suggested by packing manufacturer [c] | 2 |
| 7 | Calculate air mass velocity ($G_y$) | $G_y = G_x/R$ | 3660 kg/h·m$^2$ (0.86 m$^3$/s·m$^2$) 750 lb/h·ft$^2$ (170 CFM/ft$^2$) |
| 8 | Calculate cooling tower base area ($A_b$) | $A_b = Q_x/G_x$ | 0.09 m$^2$ (1 ft$^2$) |
| 9 | Determine design ambient temperature ($T_{yb}$) | Depending on locality | 28.3 ℃ (83℉) [d] |
| 10 | Determine design ambient relative humidity ($h_r$) | Depending on locality | 0.83 [e] |
| 11 | Determine cooling water inlet temperature ($T_{xa}$) | Depending on heat exchanger optimal operational condition: power plant condenser $T_{xa}$ of 110℉ is general | 43.3℃ (110℉) |
| 12 | Calculate cooling water outlet temperature ($T_{xb}$) | $T_{xb} = T_{xa} - \Delta T_x$ | 35℃ (95℉) |
| 13 | Use Chebyshev method to calculate cooling tower characteristic: $\frac{K_y a Z_T}{G_x} = c_L \int_{T_{xb}}^{T_{xa}} \frac{dT_x}{H^* - H}$ | $\int_{T_{xb}}^{T_{xa}} \frac{dT_x}{H^* - H} \cong \frac{T_{xa} - T_{xb}}{4}\left(\frac{1}{\Delta H_1} + \frac{1}{\Delta H_2} + \frac{1}{\Delta H_3} + \frac{1}{\Delta H_4}\right)$ | 0.83 |
| 14 | Determine $Z_T$ through the plot of cooling tower characteristic ($K_y a Z_T/G_x$) vs. water-air mass loading ratio ($R$, which is defined as $G_x/G_y$) provided from the packing manufacturer, such as the one shown in Figure 2.2. | --- | 0.91m (3 ft) |

[a] Strigle, 1987; [b] Green and Perry,2007; [c] UNEP, 2006; [d] NCDC, 2008a; [e] NCDC, 2008b

#### 2.3.1.2 Heating system

As indicated in Figure 2.2, the water was transported to the heating system using a centrifugal pump. The water was heated through a copper coil immersed in a hot water bath which was heated by an immersion electric heater controlled through a thermostat. Water is heated using an external heater immersed in a heating bath (3656K117, McMaster-Carr, OH) capable of generating 27000 kJ/h (25,600 Btu/h). The hot water bath was made of stainless steel and was filled with DI water. Polyacrylic cover was installed on the bath to reduce evaporative losses. In order to decrease the heat loss from the direct heat conduction and to protect the heating element, the stainless steel hot water bath was installed inside an insulated plastic storage box. The insulation between the stainless steel bath and the walls of the plastic box was Owens Corning PINK R-19 Fiber Glass (Owens Corning, USA).

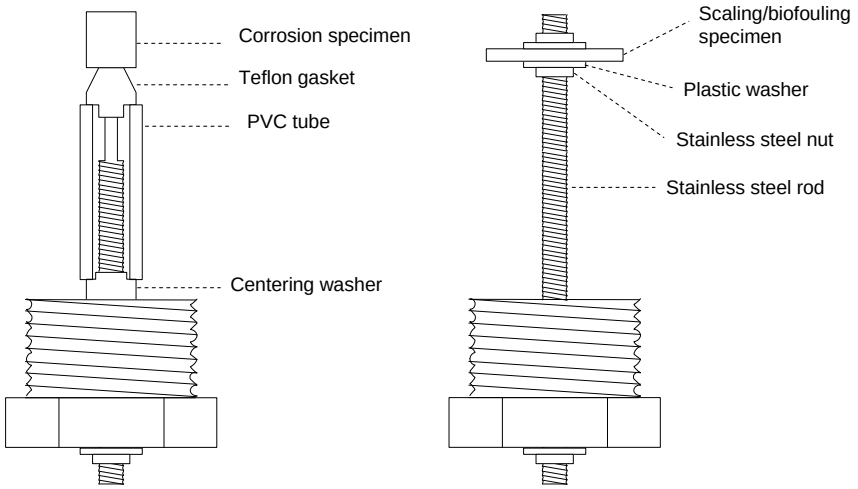
A copper tube with inner diameter of 1.09 cm (0.43 in), outer diameter of 1.27 cm (0.5 in), and length of 13 m (42.6 ft) was rolled into a coil and immersed in the heating bath. The overall heat-transfer coefficient of the copper tube was determined to be 504.7 kJ/h·$m^2$·℃ (80 Btu/h·$ft^2$·°F) when water flow rate was 11.4 LPM (3 GPM), which gives flow velocity of 2.0 m/s (6.6 ft/s) in the tube. The low overall heat-transfer coefficient was due tp the fact that there was no mixing in the hot water bath. Based on Equation 14, it was determined that the hot water bath temperature has to be maintained at 71.1 ℃ (160°F) to ensure proper heating of the recirculating water in the pilot-scale cooling tower system. The copper coil was replaceable and both ends of the copper coil had a 1.27 to 1.91 cm (0.5-in to 0.75-in) copper fitting reducer connected to a CPVC union that can withstand temperature up to 104.4℃ (220°F) without any deformation.

#### 2.3.1.3 Corrosion, scaling, and biofouling monitoring system

Corrosion, scaling, and biofouling on metal components of the piping and heat exchanger of a cooling system were studied by immersing metal and metal alloy specimens in the recirculating water after the heating system and before the evaporative cooling system. The metal and metal alloy specimens for corrosion monitoring were cylinder-shaped with a diameter of 0.95 cm (0.375-in) and a length of 1.27 cm (0.5-in) (Metal Samples Company, Munford, AL). Metal coupons for scaling and biofouling monitoring were circular stainless steel discs with exposed surface area of 5.61 $cm^2$. The metal specimen holders were designed for easy insertion into the pilot-scale cooling tower piping via a modified tee-section. Figure 2.4(a) shows the schematics of the metal specimens mounted on the corrosion and scaling/biofouling specimen rack.

After passing through the heating system, heated water entered the specimen rack, which was divided into two 19.1 cm (0.75-in) PVC pipe sections: one with several tee fittings for the insertion of corrosion/scaling/biofouling specimens, and another section which served as a by-pass during the specimen removal period. Thus, there was no interruption of the operation of the cooling tower during the specimen sampling. Both sections merged prior to the tower distribution nozzle and each flow section can be isolated using ball valves. Detailed design of the coupon rack is depicted in Figure 2.4(b), which shows the schematics of the monitoring rack with the insertion of the specimen holders containing specimens.

(a)




(b)

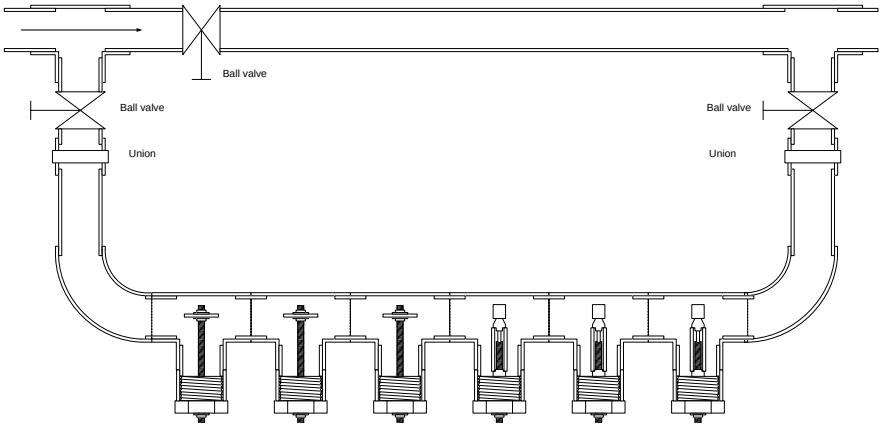



**Figure 2.4.** (a) Corrosion monitoring metal alloy specimen and the specimen holder (left) and scaling/biofouling metal alloy specimen and the specimen holder (right). (b) Detailed design of the corrosion/scaling/biofouling monitoring system.

#### 2.3.1.4 Makeup water control system

Since precise and reliable flow measurements were required to ensure appropriate makeup water supply for the pilot-scale cooling tower, several monitoring and control devices were integrated in the system to achieve automated control. Figure 2.5 shows the design of the makeup water control system. The system included a water meter, a normally closed solenoid valve, and two float switches. When the water level reached float switch A, a signal was sent to cut the power to the solenoid valve, thus discontinuing makeup water flow into the water collecting basin. When the water level triggered float switch B, the valve was energized thus allowing the injection of makeup water. During the water injection, the water totalizer recorded the total amount of makeup water being injected. A water meter (4155K41, McMaster-Carr) with the lowest recordable flow of 0.49 LPM (0.13 GPM) was used to ensure accurate recording of the total amount of makeup water addition. This dual-point control approach together with the sensitive water meter recording provided precise control of the amount of recirculating water in the cooling system and measurement of the amount of required makeup water for the cooling operation.

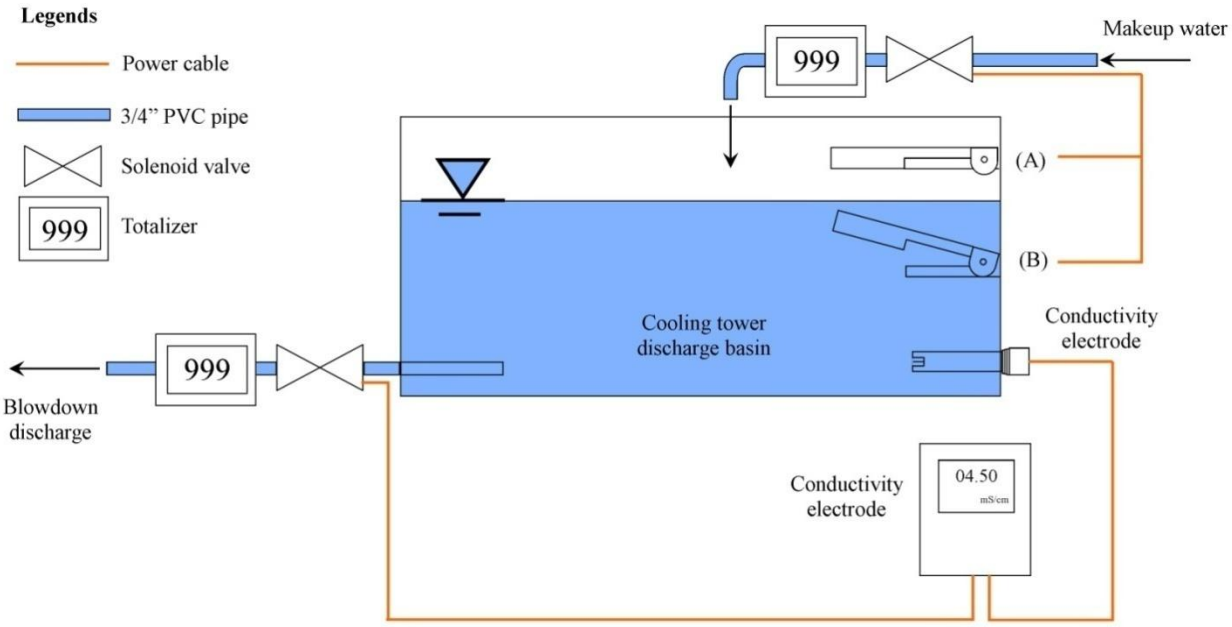



**Figure 2.5.** Schematic of dual-point makeup water control system based on water surface level and automatic blowdown discharge control system based on conductivity measurement.

#### 2.3.1.5 Blowdown control system

The blowdown control system was designed and constructed to provide automatic blowdown discharge based on specified conductivity of the system water. A schematic design of the blowdown control system is shown in Figure 2.5. Specific conductivity was used as the parameter to monitor cycles of concentration in the cooling water. The system included an in-line specific conductivity meter, a specific conductivity probe, and a normally closed solenoid valve. The specific conductivity probe was located in the cooling tower discharge basin. The specific conductivity meter had an internal set point which produced a signal to open the solenoid valve for blowdown discharge. The cycles of concentration in the cooling system were controlled based on the conductivity of the makeup water by adjusting the discharge set point to a desired conductivity value. Similar to the makeup water control system, a water totalizer (4155K41, McMaster-Carr) with the measurement limit of 0.49 LPM (0.13 GPM) was used to ensure accurate recording of the total amount of blowdown.

#### 2.3.1.6 Biocide feeding system

The biocide feeding system consisted of a biocide storage tank (7456500, C&H Distributors) and a chemical metering pump with speed-adjustable knobs (PHP-501-G, Omega). The biocide solution was injected directly into the cooling tower discharge basin through a flexible vinyl (PVC) tube. The metering pump was adjusted based on the desired disinfectant residual in the recirculating water and was verified using the daily disinfectant measurements. The amount of biocide stock solution consumed for each pilot-scale unit was measured manually.

#### 2.3.1.7 Power control system, cooling tower support, performance monitoring

As shown in Figure 2.3, the main cooling tower column was secured by a unistrut structure. Three beams and one pillar were combined to prevent the column from tilting and to provide support for the electrical J-box.

The electrical J-box (15.2x15.2x 30.4 $cm^3$ /6x12x12 $inch^3$) included three power switches, five terminal blocks, one breaker, potentiometer for fan control, and integrated power system. Major power supply was 3 phase 230V power, transmitted through #4 wire rated for 50A current.

Three switches controlled the power for solenoid valves, float switches, conductivity meter, pump, and fan. The heater had a separate power control and its temperature was controlled by a thermostat. A potentiometer was installed to control the airflow rate provided by the fan on top of the cooling column.

The entire pilot-scale cooling tower was instrumented with temperature sensors, pressure gauges, and flow sensors at critical points in the system. The locations of these sensors and gauges are shown on Figure 2.2. The total water capacity (volume) of the pilot-scale cooling tower was about 83.27 liters (22 gallons).

### 2.3.2 Pilot-scale cooling tower performance

The usefulness of employing pilot-scale cooling tower testing to evaluate scaling, corrosion, and biofouling potential when using a particular type of water was demonstrated over a 2-month period. Treated municipal wastewater was selected for testing since it is a readily available alternative cooling water resource (Li et al., 2011b), which is likely to require precise control of scaling, corrosion, and biofouling.

The treated wastewater was collected from the Franklin Township Municipal Sanitary Authority (FTMSA, Murrysville, PA). The facility employs a series of treatment processes consisting of primary clarification, secondary treatment by trickling filter, secondary clarification, nitrification, sand filtration, and UV disinfection in series. The effluent used in three identical pilot towers (CTA, CTB, and CTC) in this study was collected after sand filtration but before UV disinfection. The testing period was performed from May 21st to July 18th, 2010.

The main objectives of pilot testing were to test the pilot-scale cooling tower performance as well as to evaluate corrosion, scaling, and biofouling control strategies when using a particular type of water for cooling (corrosion, scaling, and biofouling evaluation results are reported by Li et al. (2011a) and Hsieh et al. (2010a). It was desired to maintain the cooling water temperature ($T_{xa}$ and $T_{xb}$) in the range of 32.2- 43.3 ℃ (90-110°F). After initial system shakedown, the heating power was adjusted to approximately 20-25 % below the designed value (23760 kJ/h or 22520 Btu/h) so that $T_{xa}$ and $T_{xb}$ and other values of cooling tower operational parameters were within the designed range. The need for this adjustment was due to the lower actual cooling tower characteristic ($K_y a Z_T/G_x$) of the pilot towers than the design value, as discussed below.

In the pilot testing, the three towers were operated almost identically (except that water chemistry was modified to reflect different corrosion, scaling, and biofouling strategies). Most parameters were monitored on a daily basis for the 2-month testing period. Air flow mass velocity was monitored approximately once every 4 days. The average values and standard deviation of the parameters that characterize ambient conditions (temperature and ambient humidity), and system performance (water flowrate and cycles of concentration, evaporative cooling, heating) are reported in Table 2.2.

**Table 2.2.** Pilot-scale cooling tower performance (SI units)

| Parameters | Unit | Method | CTA | CTB | CTC | Average |
|---|---|---|---|---|---|---|
| ***Ambient conditions*** | | | | | | |
| $T_{yb}$ | ℃ (°F) | Measured | --- | --- | --- | 20.6 ± 2.9 (69 ± 5) |
| $h_r$ | --- | Measured | --- | --- | --- | 0.61 ± 0.11 |
| ***Evaporative system performance*** | | | | | | |
| $G_x$ | kg/h·m$^2$ (lb/h·ft$^2$) | Measured | 6842 ± 98 (1400 ± 20) | 6940 ± 98 (1420 ± 20) | 7037 ± 195 (1440 ± 40) | 6940 ± 147 (1420 ± 30) |
| $\Delta T_x$ | ℃ (°F) | Measured | 6.3 ± 0.7 (11.3 ± 1.3) | 7.2 ± 0.7 (13.0 ± 1.3) | 6.3 ± 1.7 (11.3 ± 3.0) | 6.6 ± 1.2 (11.8 ± 2.2) |
| $G_y$ | kg/h·m$^2$ (lb/h·ft$^2$) | Measured | 5034 ± 733 (1030 ± 150) | 4642 ± 489 (950 ± 100) | 3274 ± 977 (670 ± 200) | 4301 ± 1075 (880 ± 220) |
| $R$ | --- | $R=G_x/G_y$ | 1.4 ± 0.2 | 1.5 ± 0.2 | 2.3 ± 0.6 | 1.7 ± 0.6 |
| $T_{xa}$ | ℃ (°F) | Measured | 40.2 ± 1.2 (104.3 ± 2.2) | 40.0 ± 1.5 (104.0 ± 2.7) | 40.4 ± 2.4 (104.8 ± 4.4) | 40.2 ± 1.8 (104.3 ± 3.3) |
| $T_{xb}$ | ℃ (°F) | Measured | 33.9 ± 1.2 (93.0 ± 2.2) | 32.8 ± 1.3 (91.0 ± 2.4) | 34.2 ± 1.3 (93.5 ± 2.4) | 33.6 ± 1.4 (92.5 ± 2.5) |
| $\frac{K_y a Z_T}{G_x}$ | | Eqs 1, 2 | 0.33 ±0.08 | 0.41 ± 0.09 | 0.34 ± 0.13 | 0.36 ± 0.11 |
| ***Water flow rate and cycles of concentration*** | | | | | | |
| $Q_m$ | kg/h (lb/h) | Measured | 6.8 ± 0.6 (15.1 ± 1.4) | 7.9 ± 0.9 (17.5 ± 2.0) | 7.2 ± 1.5 (15.9 ± 3.4) | 7.3 ± 1.2 (16.2 ± 2.6) |
| $Q_b$ | kg/h (lb/h) | Measured | 1.7 ± 0.3 (3.8 ± 0.6) | 1.5 ± 0.4 (3.4 ± 0.8) | 1.6 ± 0.4 (3.6 ± 0.9) | 1.6 ± 0.4 (3.6 ± 0.8) |
| $N$ | --- | Eq 9 | 4.1 ± 0.6 | 5.2 ± 0.9 | 4.5 ± 1.1 | 4.6 ± 1.0 |
| $Q_e$ | kg/h (lb/h) | Eq 8 | 5.2 ± 0.5 (11.4 ± 1.1) | 6.5 ± 0.9 (14.3 ± 1.9) | 5.9 ± 1.5 (12.9 ± 3.3) | 5.8 ± 1.2 (12.8 ± 2.6) |
| $Q_{e,d}$ | kg/h (lb/h) | Eq 10 | 6.1 ± 0.7 (13.5 ± 1.6) | 7.1 ± 0.7 (15.7 ± 1.5) | 6.3 ± 1.7 (13.8 ± 3.7) | 6.5 ± 1.2 (14.3 ± 2.6) |
| ***Heating system performance*** | | | | | | |
| $q_T$ | kJ/h (Btu/h) | Eq 11 | 15071 ± 1706 (15900 ± 1800) | 17441 ± 1706 (18400 ± 1800) | 15355 ± 4076 (16200 ± 4300) | 15924 ± 2938 (16800 ± 3100) |
| $T_h$ | ℃ (°F) | Measured | 58.8 ± 1.7 (137.9 ± 3.0) | 61.8 ± 2.3 (143.3 ± 4.1) | 58.4 ± 3.8 (137.2 ± 6.9) | 59.7 ± 3.1 (139.5 ± 5.6) |
| $U$ | kJ/h·m$^2$·°C (Btu/h·ft$^2$·°F) | Eq 14 | 536 ± 63 (85 ± 10) | 530 ± 38 (84 ± 6) | 568 ± 139 (90 ± 22) | 543 ± 88 (86 ± 14) |

#### 2.3.2.1 Ambient conditions

The ambient temperature ($T_{yb}$) and relative humidity ($h_r$) recorded daily at around 10 AM were lower than the pilot tower design values, which were calculated based on the average values in July in Pittsburgh, PA. Intuitively, the lower $T_{yb}$ and $h_r$ than the design values should cause the water temperature to be lower. The $T_{yb}$ observed throughout the experiment was 27.8 ± 3.2℃ (82.0 ± 5.8 ℉), which was slightly lower than the designated criterion. As a result, the average hot water temperature was 40.2 ± 1.8 ℃ (104.3± 3.3℉). In addition, although the humidity may vary dramatically through a 24-hour period, and an average relative humidity of 61 ± 11% was observed throughout the testing period. Since the design humidity was 82%, there was a straight increase in water temperature drop across the tower due to enhanced cooling capacity.

#### 2.3.2.2 Evaporative cooling system performance

Table 2.2 shows that water mass velocity ($G_x$), air mass velocity ($G_y$), loading ratio ($R$), and cooling water temperature ($T_{xa}$ and $T_{xb}$) were within the range of the design values (the design values are listed in Table 2.1). Cooling tower characteristics calculated using Equations 1 and 2 were found to be significantly lower than the design value. This might be due to the overestimation of the performance of the packing in the pilot-scale cooling tower. For example, the cooling water might not be homogeneously distributed across the packing. However, other parameters can be adjusted to compensate for lower packing performance on water temperature. In this study, heat input from the heating system was adjusted to approximately 20-25% below the design value to balance the reduction in cooling efficiency. Thus, the value of $\Delta T_x$ was also 20-25 % lower than the design value but still within the range of general industrial cooling system design values (5.6-16.7 ℃ or 10-30°F). The $T_{xa}$ and $T_{xb}$ were still in the range of interest (32.2- 43.3 ℃ or 90-110°F) for corrosion, scaling, and biofouling studies.

#### 2.3.2.3 Water flow rate and cycles of concentration

Measured makeup water flow rate ($Q_m$) and blowdown flow rate ($Q_b$) and calculated evaporation flow rate ($Q_e$) and cycles of concentration ($N$) are shown in Table 2.2. Generally $N$ was maintained in the range of 4-5 for corrosion, scaling, and biofouling studies. Average value of $Q_e$ derived from the empirical equation for actual cooling towers (Equation 10) was close (less than 10 % difference) to the average actual $Q_e$ derived from Equation 8. This observation indicates that the pilot-scale cooling towers are representative of actual towers in terms of water evaporation behavior.

### 2.3.2.4 Heating system performance

Hot water temperature ($T_h$) measurements and calculated heat input ($q_T$) and overall heat transfer coefficient ($U$) are also shown in Table 2.2. As discussed, the heat input was purposely adjusted 20-25 % below the design value to compensate for the reduction in cooling tower performance to maintain water temperature in the range of interest. Values of $U$ for the three towers were close to the results found in tests listed in Table 2.2.

Figure 2.6 summarizes the deviation of actual pilot tower parameters from the design values. Despite the fact that the ambient conditions ($T_{yb}$ and $h_r$) were below than the design values, most operational parameters were maintained fairly well within the design range. The only exception was the cooling tower characteristic ($K_y a Z_T/G_x$) that was found to be lower than the design value. Therefore, the heat input ($q_T$) had to be adjusted lower. This adjustment resulted in lower cooling water temperature difference ($\Delta T_x$) and hot water bath temperature ($T_h$).

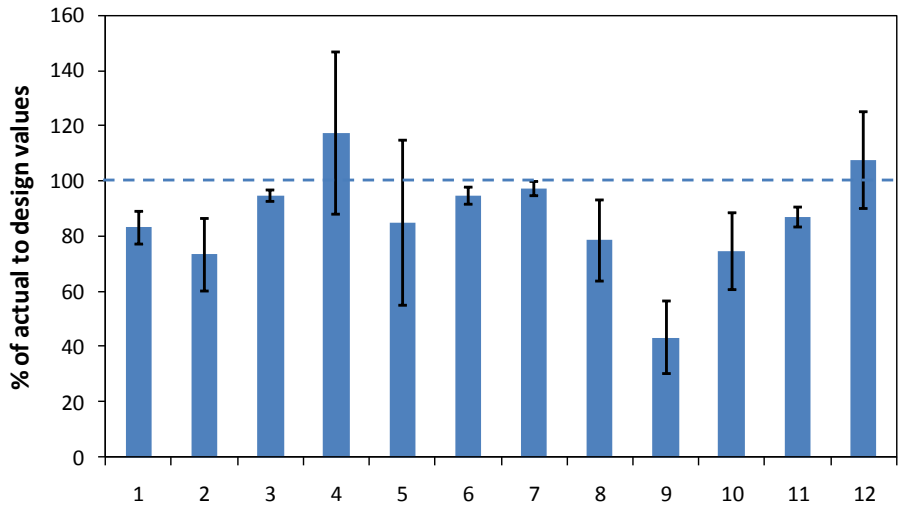



**Figure 2.6.** Percentage of actual monitored results (average and standard deviation) with respect to design values for pilot-scale cooling tower parameters: 1) $T_{yb}$, 2) $h_r$, 3) $G_x$, 4) $G_y$, 5) $R$, 6) $T_{xa}$, 7) $T_{xb}$, 8) $\Delta T_x$, 9) $K_y a Z_T/G_x$, 10) $q_T$, 11) $T_h$, 12) $U$.

As expected, the pilot scale cooling systems reaches steady state performance after the adjustment of operating parameters based on precise measurement and assessment of system performance. Therefore, the pilot-scale system can be used to study corrosion, scaling, and biofouling problems and the effectiveness of chemical treatment approaches. Detailed evaluation of the use of field monitoring methods presented in Figure 2.4 are discussed elsewhere (Li et al., 2011a; 2011b; Hsieh et al., 2010a; 2010b; Vidic et al., 2009).

## 2.4 SUMMARY AND CONCLUSIONS

A pilot-scale cooling tower was designed for the purpose of testing different scaling, corrosion, and biofouling control strategies for potential use in full-scale recirculating cooling systems. The pilot-scale cooling tower includes a counter-flow evaporative cooling system, heating system, corrosion/scaling/biofouling monitoring system, makeup control system, blowdown control system, and power control system. The pilot-scale cooling tower was successfully tested in the study of corrosion, scaling, and biofouling control strategies for use of treated municipal wastewater as cooling system makeup water. The pilot-scale cooling system was demonstrated to be useful for evaluation of changing water conditions and a range of control strategies with a makeup water of complex quality.

# 3.0 CONTROL OF BIOLOGICAL GROWTH IN RECIRCULATING COOLING SYSTEMS USING TREATED SECONDARY EFFLUENT AS MAKEUP WATER WITH MONOCHLORAMINE

Secondary treated municipal wastewater, an abundant and widely distributed impaired water source, is a promising alternative water source for thermoelectric power plant cooling. However, excessive biological growth is a major challenge associated with wastewater reuse in cooling systems as it can interfere with normal system operation as well as enhance corrosion and scaling problems. Furthermore, possible emission of biological aerosols (e.g., *Legionella pneumophila*) with the cooling tower drift can lead to public health concerns within the zone of aerosol deposition. In this study, the effectiveness of pre-formed and in-situ formed monochloramine was evaluated for its ability to control biological growth in recirculating cooling systems using secondary treated municipal wastewater as the only makeup water source. Bench-scale studies were compared with pilot-scale studies for their ability to predict system behavior under realistic process conditions. Effectiveness of the continuous addition of pre-formed monochloramine and monochloramine formed in-situ through the reaction of free chlorine with ammonia in the incoming water was evaluated in terms of biocide residual and its ability to control both planktonic and sessile microbial populations. Results revealed that monochloramine can effectively control biofouling in cooling systems employing secondary treated municipal wastewater and has advantages relative to use of free chlorine, but that bench scale studies

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seriously underestimate biocide dose and residual requirements for proper control of biological growth in full-scale systems. Pre-formed monochloramine offered longer residence time and more reliable performance than in-situ formed monochloramine due to highly variable ammonia concentration in the recirculating water caused by ammonia stripping in the cooling tower. Pilot-scale tests revealed that much lower dosing rate was required to maintain similar total chlorine residual when pre-formed monochloramine was used as compared to in-situ formed monochloramine. Adjustment of biocide dose to maintain monochloramine residual above 3 mg/L is needed to achieve successful biological growth control in recirculating cooling systems using secondary treated municipal effluent as the only source of makeup water.

## 3.1 INTRODUCTION

Freshwater withdrawal for thermoelectric power plant cooling exceeds withdrawals for agricultural irrigation in the U.S. (Kenny et al., 2009). Limited availability of water in some regions has led to denial of construction permits for some proposed thermoelectric power plants (Feeley and Ramezan, 2003; Dishneau, 2007). Increasing competition for fresh water resources and restrictions on fresh water withdrawals are expanding interest in finding alternative sources of water for thermoelectric power plant cooling.

Secondary treated municipal wastewater (MWW is used to denote this specific impaired water in the rest of the text) is abundant and widely available as an alternative source of cooling water for thermoelectric power production (Li et al., 2011a). Use of MWW as cooling water has been studied and implemented for some time. However, previous studies suggested blending freshwater with small proportion of secondary effluent or significant pre-treatment of secondary

effluent prior to the addition to recirculating cooling systems (Osborn, 1969; Rebhun and Engel, 1988; Wijesinghe et al., 1996). Only recently has treated secondary effluent been considered a promising alternative as the sole makeup water source for recirculating cooling systems (Hsieh et al. 2010; Li et al, 2011a, 2011b).

Biological growth caused by a variety of microorganisms, such as bacteria, fungi, and algae, is one of the most common and most significant problems in the operation of cooling systems (Frayne, 1999). Suspended (planktonic) biological growth is significant because of the potential for aerosol emissions that may pose environmental and public health risk. This is particularly true in the case of *Legionella pneumophila* which has the potential to cause pneumonia-like symptoms in immunocompromised individuals (Dondero et al., 1980; Morton et al., 1986; Yu, 2008). Sessile (attached) biological growth, also known as biofilm growth, is commonly observed on pipe surfaces and packing material in cooling systems where it reduces heat transfer efficiency and/or contributes to microbially-induced corrosion (Ludensky, 2005). Inadequate sessile biological growth control results in continuous release of microbial colonies back into the recirculating water and impedes overall biological growth control in recirculating cooling systems.

Biological seed in cooling towers comes from the microorganisms in the makeup water and airborne microorganisms in the air moving through the cooling tower. Typical operating conditions maintained in a recirculating cooling system, including elevated temperature, near neutral pH, continuous aeration and sunlight, provide ideal conditions for biological growth. The favorable growth conditions in a cooling system combined with the use of treated municipal wastewater as makeup water, which contains abundant organic matter and nutrients, make biological growth control even more challenging in such systems. The challenge is exacerbated by the additional concentration of nutrients and organic matter in the cooling tower due to continuous evaporation of the recirculating water.

Heterotrophic bacterial population is commonly used as an indicator of biological growth in cooling systems. The Cooling Tower Institute (CTI) has proposed biological growth control criteria of $10^4$ CFU/mL and $10^5$ CFU/cm$^2$ for planktonic and sessile bacteria, respectively (CTI, 2008). The criteria were developed based on the control of *Legionella* species in heating, ventilation and air conditioning (HVAC) systems to ensure public health. A stricter criterion of $10^4$ CFU/cm$^2$ for sessile microorganisms was used in the present study as a measure for adequate control of biological growth control when using secondary treated municipal effluent.

Chlorination is often used to control biological growth in cooling systems using tap or surface water (Frayne, 1999). Sodium hypochlorite is dosed in sufficient quantity to achieve a free chlorine residual. For cooling systems utilizing MWW as makeup water, a hypochlorite dose of at least 10 mg/L would be required to satisfy each 1.0 mg/L of ammonia and organic matter in order to reach breakpoint chlorination (White, 1999). Considering that typical ammonia and total organic carbon concentrations in secondary effluent can be above 20 mg/L (Vidic et al., 2009) and that the constituents in the makeup water become concentrated through evaporation in the

cooling tower as many as 4-5 times, it is clear that the breakpoint chlorination would not be an economically feasible control strategy for such cooling systems. Because MWW contains dissolved organic nitrogen, it is expected that other forms of combined chlorine, especially organic chloramines, would be created in the concentrated MWW when chlorine-based biocides are used. Lee and Westerhoff (2009) have shown that hypochlorite reacts with dissolved organic nitrogen to form organic chloramines within 10 minutes. Another concern with the use of hypochlorite is the byproducts formed in the reactions between hypochlorite and organic matter, which can have adverse impact on ecosystems and human health (Schwarzenbach et al., 2006; Nieuwenhuijsen et al., 2000).

Monochloramine is regarded as a weaker disinfectant than free chlorine (hypochlorite) and higher dosing levels may be required when it is used as primary biocide (Wolfe et. al., 1984; Morris, 1967). Turetgen (2004) observed that a 1 mg/L dose of monochloramine was significantly more effective than a 1.5 mg/L dose of free chlorine against cooling tower biofilm growth with 30 minutes contact time when using potable water as makeup water in both full scale and model cooling systems. Rao et al. (1998) demonstrated that initial doses of 1, 2, and 3 mg/L of monochloramine and free chlorine showed similar biocidal activity in controlling biofilm growth formed on piping surfaces in a once-through cooling system. However, there have been no studies on the use of pre-formed monochloramine for biological growth control in recirculating cooling systems using only secondary treated municipal wastewater as makeup water.

Monochloramine has been tested as an alternative to hypochlorite for biological growth control in wastewater treatment (Aieta et al., 1980; Havelaat and Nieuwstad, 1985). Previous studies evaluated the biocidal efficiency of monochloramine for planktonic microorganisms in

MWW using simple batch tests. However, these results are not relevant for recirculating cooling towers systems using MWW for the following reasons: cooling tower systems typically include significant sessile growth; these systems are operated at elevated temperatures and with continuous aeration; and organic matter and nutrients present in treated municipal wastewater are concentrated 4-6 times by evaporation in these systems.

The objectives of this study were: (1) to evaluate the efficiency of monochloramine for the control of biological growth in recirculating cooling tower systems using MWW under realistic process conditions; (2) to examine the effectiveness of monochloramine generated through two different pathways to control biological growth in recirculating cooling systems using MWW as makeup water at 4-5 cycles of concentrations; and (3) to evaluate the potential for treated municipal wastewater to promote the growth of *Legionella pneumophila* in full-scale recirculating cooling tower systems. First, the appropriate dosing strategy and residual biocide concentration range required to control planktonic biological growth in cooling water were determined using batch studies. Impacts of ammonia concentration in the wastewater and cycles of concentration on the biocidal efficacy of in-situ formed monochloramine were also explored in batch tests. A recirculating bench-scale system was then employed to study both planktonic and sessile biological growth under the influence of hydrodynamic forces and to test the effectiveness of monochloramine to control both biological growth modalities. Based on the results from batch and bench-scale recirculating tests, pilot-scale field tests were designed and conducted at a municipal wastewater treatment facility for two consecutive 21-day periods to observe biological growth control under conditions representative of full scale cooling systems. The pilot-scale studies were conducted to validate findings from laboratory-scale studies and to

compare pre-formed monochloramine against in-situ formed chloramine in terms of stability and effectiveness in controlling biological growth under realistic process conditions.

## 3.2 MATERIALS AND METHODS

### 3.2.1 Municipal wastewater

Secondary treated municipal wastewater collected at Franklin Township Municipal Sanitary Authority (FTMSA) near Murrysville, PA was used in all experiments. Samples of this water were refrigerated at 5 °C in 5-gallon carboys and were used within two weeks of collection. The characteristics of the water are presented in Table 3.1. Secondary-treated wastewater effluent was designated as municipal wastewater at one cycle of concentration (CoC 1 FTMW). Two major differences between wastewater disinfection and biological growth control in cooling tower systems are water temperature and chemical contact time. Previous studies have shown increased biocide demand and faster disinfection kinetics in drinking water distribution systems at elevated temperatures (Wolfe et al., 1984; Ndiongue et al., 2005). However, no studies have been conducted on the impact of temperature on biocide demand and disinfection efficiency in highly concentrated treated municipal wastewater.

To reflect typical conditions in recirculating cooling systems, the FTMSA wastewater was concentrated to four cycles of concentration (CoC4) by maintaining the wastewater at 40 ℃ until the volume of the sample was reduced to one-fourth its initial volume. Throughout the evaporation process, almost all of the ammonia was volatilized. This loss was compensated by adding the expected amount of ammonium ion as ammonium chloride ($NH_4Cl$) to the concentrated water samples.

**Table 3.1.** Key water quality parameters of Franklin Township Municipal Sanitary Authority (Murrysville, PA) secondary treated effluent (Sampled on September 3, 2008)

| **Parameters** | **Unit** | **Concentration** |
|---|---|---|
| Al | mg/L | 0.2 |
| Ca | mg/L | 41.5 |
| Cu | mg/L | 0.03 |
| Fe | mg/L | 0.5 |
| K | mg/L | 16.3 |
| Mg | mg/L | 10.7 |
| Mn | mg/L | 0.3 |
| Na | mg/L | 94.2 |
| $SiO_2$ | mg/L | 8.5 |
| Zn | mg/L | 0.07 |
| pH | | 7.1 |
| $NH_3$-N | mg/L | 21.0 |
| Bicarbonate Alkalinity | mg/L as $CaCO_3$ | 177 |
| BOD | mg/L | 31.9 |
| Cl | mg/L | 106 |
| $NO_3$-N | mg/L | 3.6 |
| $SO_4$ | mg/L | 86.0 |
| Total P | mg/L | 4.5 |
| Total Alkalinity | mg/L as $CaCO_3$ | 177 |
| TOC | mg/L | 27.0 |
| TSS | mg/L | 24.5 |
| TDS | mg/L | 593 |
| Conductivity | µs/cm | 810 |

### 3.2.2 Batch experiments

Biocide demand and decay rate in secondary treated municipal wastewater was determined in batch experiments using 250-mL Erlenmeyer flasks wrapped with aluminum foil to minimize the impact of photodecomposition and photosynthesis. Each test included four flasks filled with 200 mL of treated wastewater dosed with either sodium hypochlorite or pre-formed monochloramine and one flask with deionized water as a blank for biocide decay analysis. Water temperature was controlled at 23 ℃ or 40 ℃ to simulate ambient temperature and actual water temperature in the cooling system. The duration of each test was 3 hours. Biocide residual concentration and pH were measured at the beginning of the test and after 10, 40, 80, and 140 minutes. Water samples were collected from the flasks at 30 and 120 minutes for planktonic heterotrophic plate counts that were analyzed using the spread plate method (Method 9215 C. Spread Plate Method, APHA, 1998). Plate count agar (Fisher Scientific, USA) was used as the culture medium and the plates were incubated for at least 48h at 35℃. Samples were also collected from a control flask filled with treated wastewater without any chemical additions to serve as a control indicating biological growth without disinfection.

Four different biocide dosages (0.5, 1, 2, 4 mg/L as $Cl_2$) were added into flasks 1 to 4. Free chlorine stock solution was prepared by diluting a 5% commercial sodium hypochlorite (NaOCl) solution (Ricca Chemical). Monochloramine (MCA) stock solution at 500 mg/L was prepared by mixing stock solutions of 5% NaOCl and 1000 mg/L ammonia at pH 10 in a $Cl_2$ :$NH_3$ weight ratio of 4 to 1.

Free and total chlorine residuals were measured using a chlorine pocket photometer (HF Science Inc. Fort Myers, FL) following the DPD colorimetric method (Method 4500-Cl G, APHA, 1998). This photometer was calibrated using a CARY 300 Bio UV-visible

spectrophotometer (Varian Inc., Palo Alto, CA). Ammonia was measured using the Phenate Method (Method 4500-$NH_3$ F, APHA, 1998) and a HACH nitrogen test kit (Model NI-8, color disc; Method 4500-$NH_3$ B&C, APHA, 1998). Monochloramine (MCA) residuals were measured using a Hach DR/890 portable datalogging colorimeter (Hach, Loveland, CO) following the Indophenol method 10171 (Hach, Loveland, CO).

### 3.2.3 Bench-scale recirculating system

The effectiveness of biocide in controlling biological growth was further tested in a bench-scale recirculating system designed to simulate temperature, flow velocity and water quality similar to those in a full-scale recirculating cooling system. The total duration of each bench scale experiment was 24 hours with intermittent biocide dosing to maintain the desired residual. The bench-scale system included a centrifugal pump, a water bath on a hotplate to control water temperature, and a sampling rack made of 0.75-inch PVC pipe to hold coupons for sessile biological growth monitoring (Figure 3.1). Temperature was controlled at approximately 40℃, and flow rate through the system was maintained at 11.4 L/min (3 gpm) to achieve flow velocity of 0.66 m/s (2.18 ft/s) and Reynolds number of $1.9 \times 10^4$.

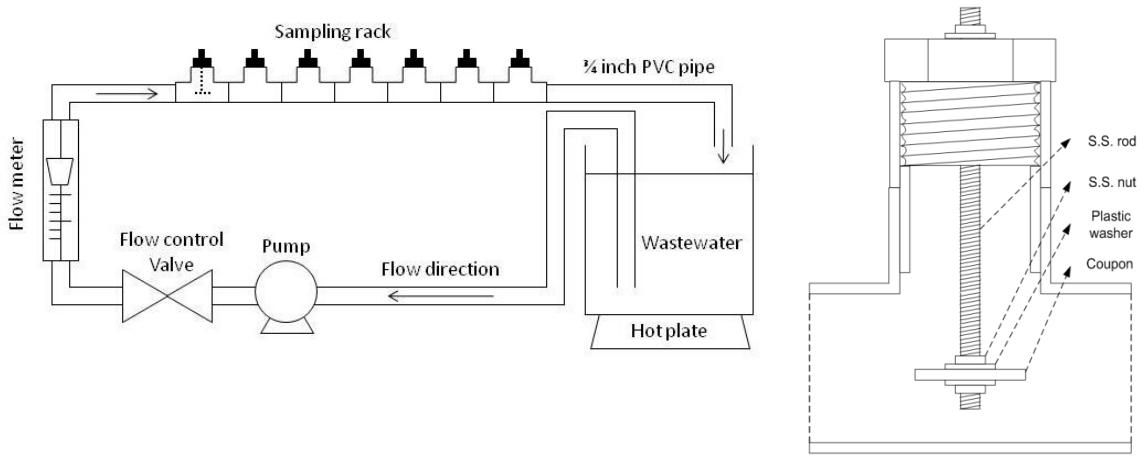


**Figure 3.1.** Schematic diagram of bench scale recirculating system (left) and circular coupon with coupon holder for biofilm sampling (right)

Circular stainless steel coupons (5.61 $cm^2$ in area) that were first sterilized by autoclaving were suspended in the recirculating flow (Figure 3.1) to monitor biofilm growth in the system. Collection of sessile biological growth from the coupons was performed according to the ASTM E 1427 Method (ASTM, 2000). After withdrawing the coupons aseptically from the coupon rack, visible water residual was carefully removed from the coupon surface (Bradshaw et. al., 1996) and the coupon was then immersed in a 50 mL phosphate buffered saline solution. The solution was sonicated for 5 minutes to dislodge accumulated biological growth from the coupon and then vortexed for 30 seconds to make it homogeneous (Prosser et. al., 1987). The most probable number of sessile heterotrophic bacteria was measured by plating serial dilutions of this solution, and the result was converted to CFU per $cm^2$ of the coupon area to obtain the sessile heterotrophic bacterial count. In addition, planktonic heterotrophic bacteria, total chlorine and monochloramine residuals in the system were also monitored throughout the experiments.

### 3.2.4 Pilot-scale cooling system

To examine the effectiveness of biological growth control under conditions similar to those in full-scale cooling systems, three pilot-scale cooling towers were constructed and deployed at FTMSA (Chien et al., 2012). These pilot-scale cooling towers were also used to evaluate corrosion and scaling control strategies when using treated municipal wastewater as cooling system makeup (Hsieh et al., 2010; Li et al., 2011b). Schematic representation of the cooling tower system is shown in Figure 2.2. The pilot-scale cooling towers were operated in the field for two consecutive 21-day tests.

The first test was conducted from July 11, 2008 to August 4, 2008. Sodium hypochlorite solution was applied continuously in this test to form monochloramine in-situ utilizing the ammonia already available in the secondary treated municipal wastewater. An additional test with NaOCl was performed to investigate whether a higher biocide dose would improve biofouling control in the cooling tower.

For the second run conducted from August 11, 2008 to September 4, 2008, pre-formed monochloramine was applied to the two towers. The monochloramine was pre-formed in the field by mixing sodium hypochlorite and ammonium chloride at a $Cl_2$:$NH_3$ weight ratio of 4:1 at pH 9.0 (EPA, 1999; Palin, 1950; Kirmeyer et al., 1993).

Secondary treated municipal wastewater was stored in a 75-gallon tank and was added to the cooling system as makeup water when 25% of the recirculating cooling water was lost through evaporation and blowdown. At the beginning of a pilot-scale test, wastewater was gradually concentrated through evaporation at 40℃. The CoC in a pilot-scale test was controlled by maintaining the desired conductivity of recirculating cooling water, which was determined by multiplying the conductivity of makeup water by the desired CoC. Whenever the conductivity of

recirculating cooling water exceeded the desired conductivity, the blowdown was automatically initiated, which subsequently initiated the makeup water feed into the system. The difference between CoC calculated using water balance and that calculated using conductivity was less than 8% (Vidic et al., 2009).

Both planktonic and sessile heterotrophic bacteria were monitored during the pilot scale tests. Sessile bacteria were monitored by immersing circular stainless steel coupons into recirculating cooling water. Coupons were inserted after achieving CoC4-5 in the system. The coupons were pre-treated with ethanol solution for sterilization (Obuekwe et al., 1981). The coupons were withdrawn from the coupon rack after 4, 7, 14 and 21 days of exposure. Removal and analysis of biofilm from the coupons was done in the same manner as for the bench-scale experiments.

Additional microbiological analysis was conducted to investigate the occurrence of *Legionella pneumophila* in the pilot-scale cooling systems. A total of eight water samples were analyzed for *Legionella pneumophila* throughout the experiment. At the end of the field test, a small section (4 $cm^2$) of drift eliminator from each pilot unit having visible sessile biological growth was also analyzed for the presence of *Legionella*. Water samples were sent to a specialized laboratory (Special Pathogen Laboratory, Pittsburgh, PA) for *Legionella pneumophila* analysis.

## 3.3 RESULTS AND DISCUSSION

### 3.3.1 Biocide demand and disinfection efficiency in secondary treated municipal wastewater at 40 ºC.

Biocide residual measurements in a batch reactor were used to determine the biocide demand, which refers to the biocide dose required to achieve a given biocide residual at a prescribed contact time, pH, and temperature following standard method (Method 4500-Cl G, APHA, 1998).

Total chlorine demand of unconcentrated Franklin Township Municipal Wastewater (CoC1) was first analyzed at 23 ºC (data not shown). It was determined that an initial dose of 2 mg/L NaOCl was required to maintain a total chlorine residual above 0.5 mg/L as $Cl_2$ at room temperature for a 2 hour contact time. Similar results were reported by Aieta et al. (1980) and Havelaar and Nieuwstad (1985), another confirmation that the wastewater used in this study was representative of secondary treated municipal wastewaters used in other studies.

Table 3.2 shows the initial biocide dose, biocide residual, demand, and biocidal efficiency for both in-situ formed and pre-formed chloramines, respectively, in CoC1 FTMSA MWW at 40ºC. Initial biocide dose represents the amount of biocide added to the reactor. Biocide demand was determined by subtracting the biocide residual and self-decomposition from initial biocide dose after contact time of two hours. It should be noted that the sum of biocide demand and biocide residual does not necessarily equal the initial biocide dose because of self-decomposition and analysis interference. An important observation from this study was the 100% increase in the initial biocide dose required to maintain total chlorine residual at 0.5 mg/L in CoC1 FTMSA MWW at 40 $^{o}$C for in-situ formed or pre-formed chloramines when compared to the results obtained at 23 ºC (data not shown). Part of total chlorine demand increase was due

to faster hydrolysis of monochloramine at higher temperature (Vikesland et al, 2001). Gould et al. (1984) showed that in-situ formed chloramines can have a half-life of 3.9 days at room temperature, thus contributing to the high total chlorine residual but low monochloramine measurement. Previous studies have shown that about half of the pre-formed monochloramine can be transformed to organic chloramines within hours (Morris and Isaac, 1983). However, the loss of pre-formed monochloramine within a 2-hour period was quite limited (between 20-34%) for the experimental conditions used in this study and the residual monochloramine concentration was proportional to the initial dosage used in these batch tests (Table 3.2). Result for a parallel blank test under identical experimental conditions indicated a 10% loss of residual monochloramine due to self-decomposition in the absence of organic matter.

**Table 3.2.** Total chlorine demand and disinfection efficiency after 2-hour contact time with secondary treated municipal wastewater at 40 ℃

| Biocide dose, mg/L as $Cl_2$ | In-situ formed monochloramine | | | Pre-formed monochloramine | | |
|---|---|---|---|---|---|---|
| | TC[a] residual, mg/L as $Cl_2$ | TC demand, mg/L as $Cl_2$ | Disinfection efficiency | TC residual, mg/L as $Cl_2$ | TC demand, mg/L as $Cl_2$ | Disinfection efficiency |
| 0.5 | 0.00 (0.00)[b] | 0.43[c] | 78.87% | 0.04 (0.00) | 0.08 | 97.37% |
| 1 | 0.00 (0.00) | 0.93 | 99.55% | 0.07 (0.01) | 0.58 | 99.76% |
| 2 | 0.00 (0.00) | 1.93 | 99.98% | 0.29 (0.19) | 1.49 | 99.95% |
| 4 | 0.61 (0.09) | 3.32 | 99.98% | 0.78 (0.61) | 2.97 | 99.97% |

a: Total chlorine; b: (#): # indicates the monochloramine residual; c: Biocide demand = Initial biocide dose - (biocide residual in sample - analysis interference) - (biocide dose in blank - biocide residual in blank);

Planktonic heterotrophic bacteria counts in each sample were normalized to initial values (t = 0 min) to calculate the disinfection efficiency (%) of chlorine-based biocides (Table 3.2). The average initial planktonic heterotrophic bacteria count in 16 different samples of secondary treated wastewater collected from FTMSA throughout 2008 was $10^{6.33} \pm 10^{6.60}$ CFU/mL.

Therefore, inactivation efficiency above 99.5% was needed to reach the planktonic biological growth control criteria in cooling towers of $10^4$ CFU/mL (Ludensky, 2005). At 40℃, both NaOCl and MCA were able to reach the required planktonic bacteria levels within a contact time of 2 hours at the initial dosage of 1 mg/L. The result is in agreement with a previous study (Wolfe et al., 1984), which suggested that the higher temperature will enhance bactericidal and viricidal efficiency of chloramine. This suggests that pre-formed MCA is at least equal to free chlorine in its ability to control biological growth in MWW at elevated temperatures present in cooling tower systems. It is notable that even the low initial disinfectant dose could successfully reduce planktonic bacterial population after 2 hours of contact time.

It is important to note that the inorganic ammonia concentration in the experiments with in-situ formed chloramine tests decreased from 21 mg/L to 15 mg/L, while it decreased from 22 ± 0.6 mg/L to 16 ± 1.1 mg/L in the experiments with pre-formed monochloramine. Although every attempt was made to reduce water evaporation rate, elevated water temperature (40℃) and mild agitation contributed to 25-28% volatilization of inorganic ammonia during the 3-hour test. It was observed that only a small amount of inorganic ammonia (less than 1 mg/L) was utilized when adding NaOCl to generate monochloramine in-situ at 40℃. Therefore, the stability of monochloramine formation in concentrated secondary effluent was further studied.

### 3.3.2 Impact of ammonia concentration and cycles of concentrations on biocide efficacy

Batch experiments with different ammonia concentrations were conducted to investigate the impact of inorganic ammonia on the efficacy of the biocides formed through two different pathways. As can be seen in Figure 3.2, maintaining the total chlorine residual between 0.5-1 mg/L as $Cl_2$ in CoC1 FTMSA MWW containing 1 mg/L $NH_3$-N reduced planktonic

heterotrophic bacteria by about three orders of magnitude after 60 minutes of contact time. However, maintaining 0.5-1 mg/L of total chlorine in CoC4 FTMSA MWW containing just 1 mg/L $NH_3$-N could not reduce planktonic HPC at all. Such behavior was most likely due to the extremely high free chlorine demand in CoC4 FTMSA MWW with little $NH_3$-N present so that the entire NaOCl dose was consumed by side reactions instead of forming combined chlorine. Once the initial ammonia concentration in CoC4 FTMSA MWW was adjusted to 100 mg/L, planktonic HPC decreased by about two orders of magnitude within one hour. The abundance of ammonia in this test ensured adequate in-situ chloramine formation. The chloramine thus formed was much less reactive with organic and inorganic constituents in CoC4 FTMSA MWW and a lot more effective in HPC inactivation.

Similarly, when pre-formed MCA at 0.5-1 mg/L as $Cl_2$ was added to FTMSA MWW at CoC4 containing just 1 mg/L $NH_3$-N, planktonic HPC decreased by about three orders of magnitude in one hour. These findings are consistent with those reported by Wolfe et al. (1985), who demonstrated that adding pre-formed MCA to achieve biological growth control in drinking water was significantly better than forming MCA in-situ in the presence of organic nitrogen compounds.

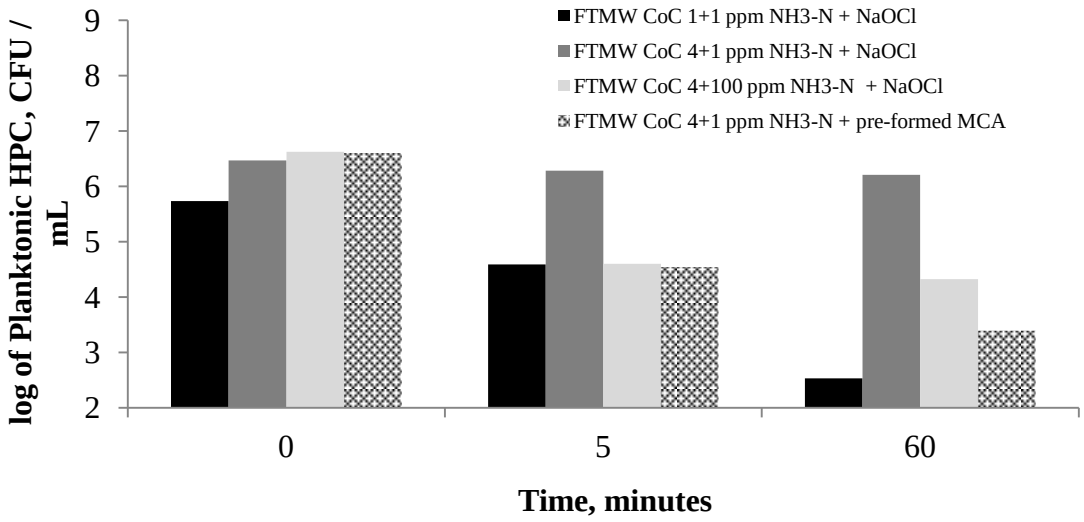


**Figure 3.2.** Effect of ammonia concentration and cycles of concentration on biocidal efficacy of total chlorine formed with NaOCl addition and pre-formed MCA at 0.5-1 mg/L in batch tests.

### 3.3.3 Control of biological growth in bench-scale recirculating system

The effectiveness of monochloramine formed in-situ at doses identified in the batch experiments as being effective in controlling biological growth were further evaluated in a bench-scale recirculating system that was operated at pH 8.2. As shown in Figure 3.3, the initial HPC concentration in CoC4 FTMSA MWW with 100 mg/L $NH_3$-N present in the bench-scale recirculating system was 1.2 x $10^5$ CFU/mL. After adding 1 mg/L of NaOCl, the total chlorine measured after a few minutes was 0.79 mg/L as $Cl_2$ and was predominantly in the form of MCA. The HPC immediately decreased below the target criterion of $10^4$ CFU/mL. Maintaining the total chlorine between 0.5 - 1 mg/L as $Cl_2$ and MCA between 0.31 - 0.77 mg/L as $Cl_2$ for 10 hours from the beginning of the test kept planktonic HPC below the detection limit of 300 CFU/mL for Standard Method 9215C. Spread Plate Method. The last chlorine addition occurred after 10 hours of continuous system operation. The planktonic HPC increased to 4.5 x $10^3$ CFU/mL after 14 hours from the last NaOCl addition when the residual MCA was not detectable. A sessile

sample taken after 24 hours of system operation contained 3.9 x $10^3$ CFU/$cm^2$ of total heterotrophic bacteria. Based on these results, it can be concluded that maintaining total chlorine between 0.5-1 mg/L as $Cl_2$ can control biological growth in CoC4 MWW with 100 mg/L $NH_3$-N present. Similar results were observed when the total chlorine in CoC4 FTMSA MWW was maintained between 1-2 mg/L as $Cl_2$ (data not shown).

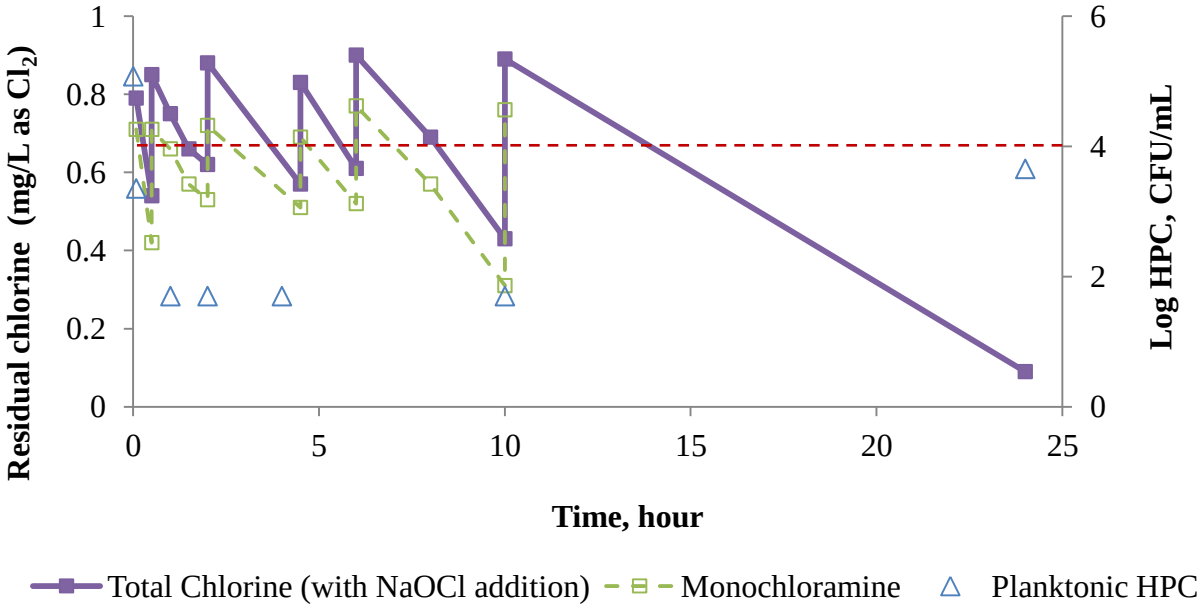


**Figure 3.3.** Disinfection efficiency of total chlorine formed with NaOCl addition at 0.5-1 mg/L as $Cl_2$ in CoC 4 FTMW containing 100 mg/L $NH_3$-N in a bench-scale recirculating system. The pH was controlled at 8.2 throughout the experiment.

Results obtained with the bench-scale system must be viewed with consideration that the system did not include continuous replenishment of organic compounds, nutrients and microorganisms with MWW makeup water and excluded environmental influences, such as sunlight, temperature variations, continuous aeration, and may underestimate biocide demand. Thus, additional experiments were conducted in pilot-scale cooling towers to simulate realistic process conditions and to test the findings from laboratory studies relative to the ability of in-situ-formed and pre-formed monochloramine to control biological growth.

### 3.3.4 Control of biological growth in pilot-scale experiments

Three tests with pilot-scale cooling tower systems were conducted to evaluate the effectiveness of chloramine in controlling biological growth when secondary treated municipal wastewater was used as the only cooling system makeup. All pilot-scale cooling towers had similar operating conditions as described previously (Vidic et al., 2009; Chien et al., 2012). In the first test, MCA was formed in-situ through the reactions between NaOCl that was added to the system and ammonia that was already present in the MWW (Table 3.1). Sodium hypochlorite was added to the bottom sump from a stock solution (500 mg/L as $Cl_2$) using a peristaltic pump operated on a timer at a preset feeding schedule. In the second run, pre-formed MCA was used to control biofouling in both towers. Pre-formed MCA stock solution at 1,000 mg/L as $Cl_2$ was added following the same procedure as in the case of NaOCl.

### 3.3.5 Pilot-scale tests with in-situ chloramine formation

The NaOCl feeding strategy employed in the first test of this study resulted in an average total chlorine residual of 0.90±0.67 mg/L as $Cl_2$, when the average pH was 8.5 (Figure 3.4). The results shown on Figure 5 indicate that the planktonic HPC were below the target criterion of $10^4$ CFU/mL when total chlorine and MCA were above 1.0 mg/L as $Cl_2$ (e.g., Days 1, 3, 9, 21). When total chlorine decreased below 0.5 mg/L as $Cl_2$, planktonic HPC increased to $10^6$ CFU/mL level (e.g., Days 6, 7, and 12). The average planktonic HPC values throughout the test were 4.1 x $10^5$ ± 6.5 x $10^5$ CFU/mL, which exceeded the target criterion of $10^4$ CFU/mL. Sessile bacterial growth exceeded the biofouling control criteria within 5 days from the beginning of the experiment and the average sessile HPC in this test was 9.9 ± 9.7 x $10^4$ CFU/cm$^2$.

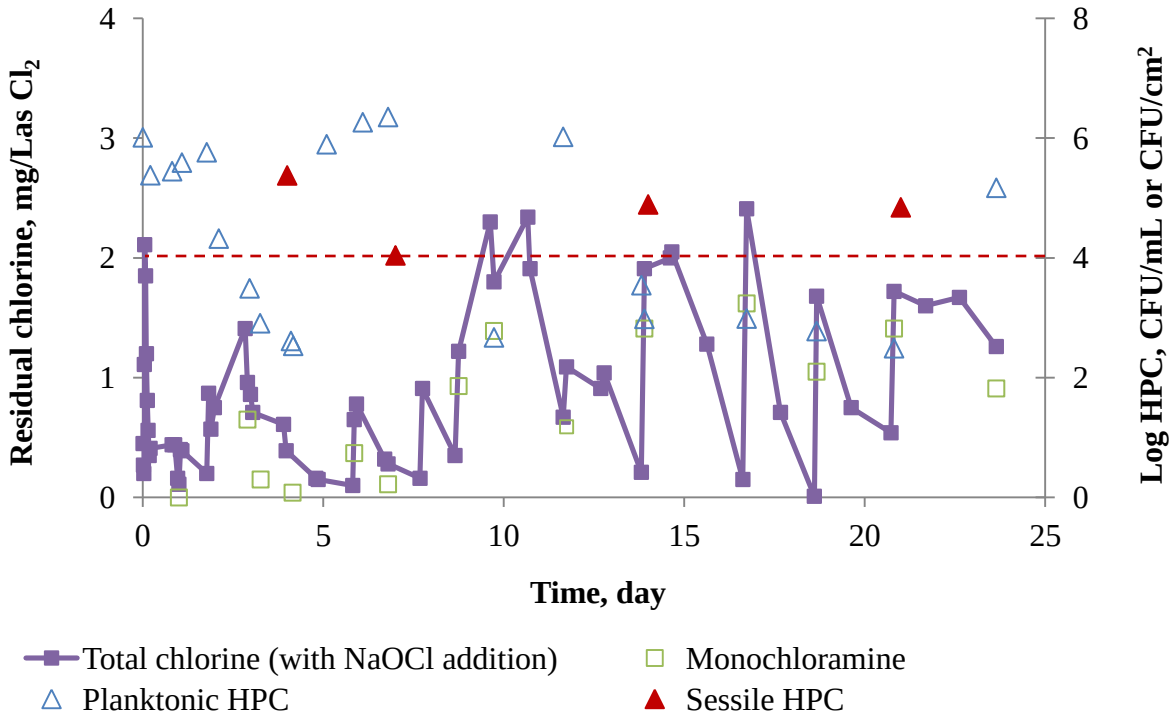


**Figure 3.4.** Total chlorine, MCA, planktonic and sessile HPC in the first pilot-scale test with NaOCl addition.

The data in Figure 3.4 indicate that once total chlorine concentration decreased below 0.5 mg/L, the planktonic bacteria proliferated in the system to the point that the total chlorine residual had to be maintained above 1 mg/L for at least 24 hours to control biological growth. Therefore, the second experiment was designed to maintain total combined chlorine residual of 3-4 mg/L (Figure 3.5). In the repeated test, monochloramine residual was maintained at 1.01 ± 0.55 mg/L as $Cl_2$ and total chlorine residual was maintained at 4.41 ± 1.46 mg/L. Although the monochloramine residual was maintained above 0.5 mg/L, both planktonic and sessile bacterial populations still exceeded the biofouling control criteria after 24 days of continuous tower operation.

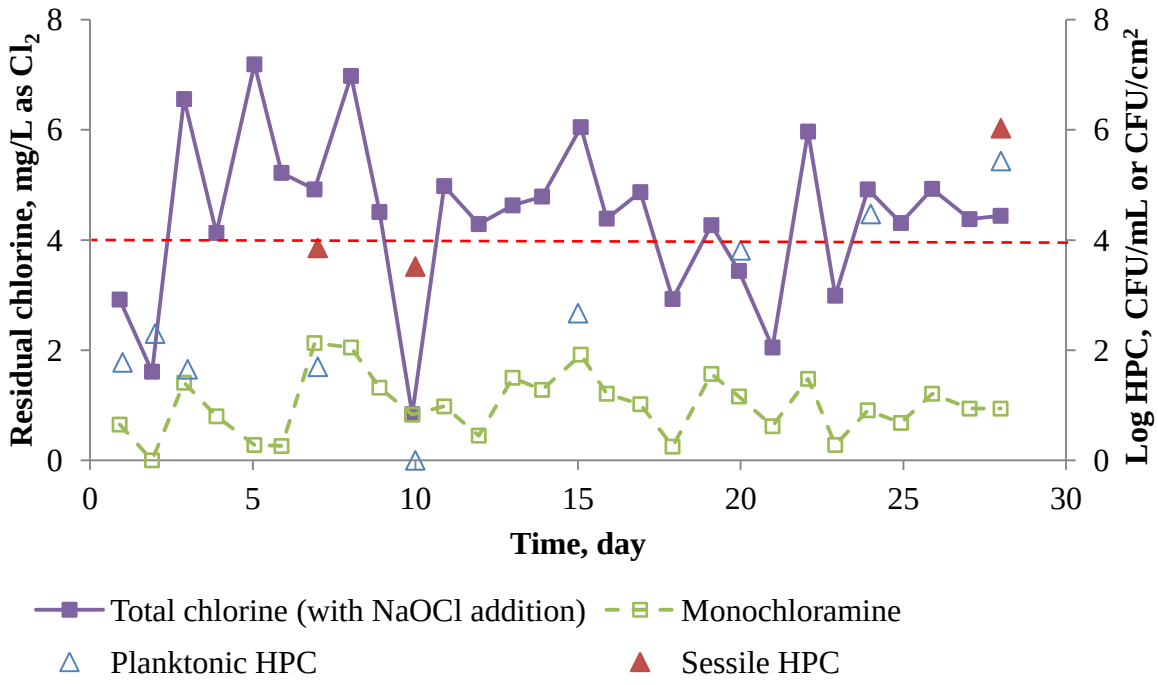


**Figure 3.5.** Total chlorine, MCA, planktonic and sessile HPC in the second pilot-scale test with NaOCl addition.

Comparing these results to those from the bench scale recirculating system, it is clear that the total chlorine residual required to control biological growth in the pilot-scale system was significantly higher than in the bench-scale studies. This was due to the fact that the pilot scale system incorporated continuous replenishment of planktonic bacteria with makeup water addition and was exposed to outdoor environment. However, even when the total chlorine residual was maintained at 3-4 mg/L, in-situ formed monochloramine was not able to control the growth of sessile bacteria in the pilot-scale cooling system. It was also difficult to maintain stable monochloramine residual in the pilot-scale tests due to variations in ammonia concentration present in the recirculating cooling water caused by stripping (Hsieh et al., 2012). Therefore, the second experiment was conducted using pre-formed MCA to control biological growth.

### 3.3.6 Pilot-scale tests with pre-formed MCA

In this test, MCA stock solution was pre-formed in the field and added to the bottom sump of the pilot-scale cooling tower using the chemical metering pump. The average total chlorine residual in the recirculating water during the 21 days of continuous tower operation was 3.64±2.17 mg/L as $Cl_2$. On average, 76% of total chlorine residual was in the form of MCA. The difference between total chlorine residual and MCA was assumed to be a mix of inorganic and organic chloramines. Although the pH was close to 8.5 throughout the experiment, the hydrolysis of pre-formed MCA may still lead to the formation of dichloramine and organic chloramines (Morris and Isaac, 1983).

The average planktonic HPC in the FTMSA MWW make-up water throughout this test was 9.4 $\pm 1.2 \times 10^6$ CFU/mL, which was almost three orders of magnitude greater than the target criterion of $10^4$ CFU/mL. Planktonic HPC in the cooling tower varied from $1.4 \times 10^1$ CFU/mL to $9.2 \times 10^6$ CFU /mL with an average of $4.26 \times 10^4$ CFU/mL (Figure 3.6). The experiment started with total chlorine residual above 4 mg/L on Day 1 and planktonic microbial population in the recirculating water was controlled below the target criterion of $10^4$ CFU/mL. Between Day 9 and 11, the total chlorine decreased below 2 mg/L as $Cl_2$ and consequently planktonic bacteria increased sharply. After that, the total chlorine residual had to be increased to as much as 7 mg/L to control the biological growth within the target levels. However, in this pilot-scale experiment the planktonic bacteria count generally remained at levels below $10^4$ CFU/mL when the MCA was maintained above 3 mg/L as $Cl_2$.

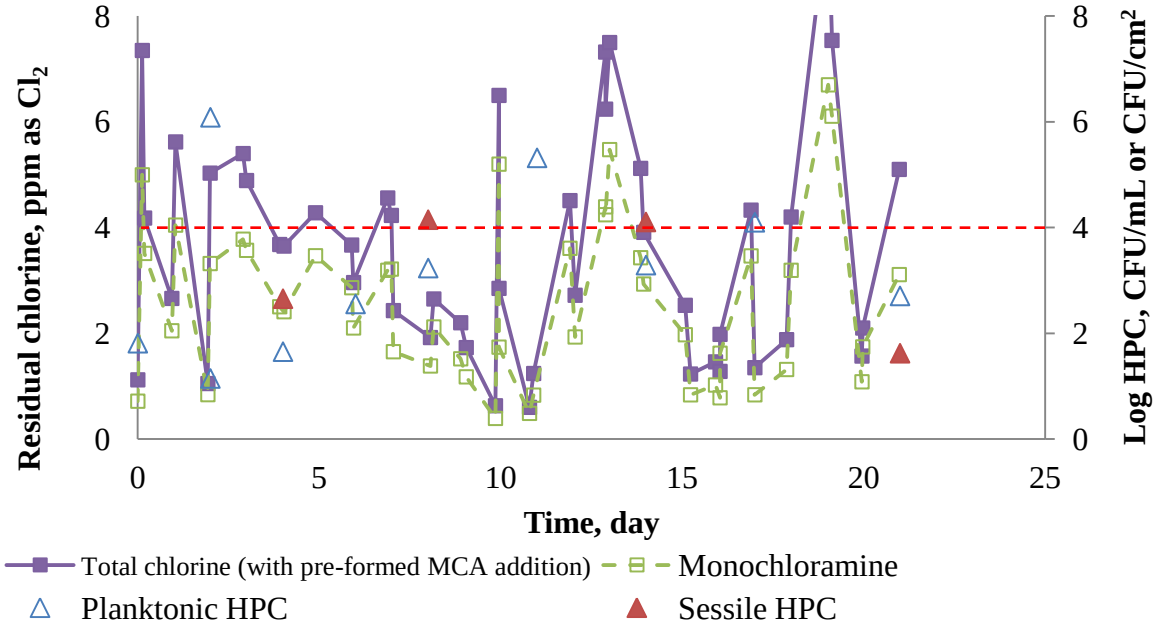


**Figure 3.6.** Total chlorine, planktonic HPC, and sessile HPC in the pilot-scale test with pre-formed MCA addition.

The average sessile HPC during the entire run was 6.8±7.6 x $10^3$ CFU/$cm^2$. Although sessile HPC samples collected at Days 8 and 14 revealed slightly greater bacterial density than the target criteria of $10^4$ CFU/$cm^2$, the sessile microbial population was controlled well by this biocide strategy for 21 days of continuous cooling tower operation. An additional test was conducted to examine the efficacy of monochloramine in treating the pilot-scale cooling systems using FTMSA MWW for a period 28 days and the results confirmed that the adopted disinfection strategy with pre-formed monochloramine successfully controlled biological growth in concentrated secondary treated municipal wastewater (data not shown).

The results of this pilot-scale test suggest that maintaining MCA residual around 3 mg/L as $Cl_2$ can control both planktonic and sessile bacteria in recirculating cooling systems using municipal wastewater as the only makeup water source and operated at 4-5 cycles of concentration. Additional experiments indicated that a slightly higher dosage (i.e., between 3 – 4 mg/L MCA residual) offered even better control of biological growth in the pilot-scale cooling system (data not shown).

### **3.3.7** Legionella control in pilot-scale cooling systems using pre-formed monochloramine

Analysis of both planktonic and sessile samples collected in this study with FTMSA MWW as makeup water revealed complete absence of *Legionella* species in cooling towers operated for 21 days at 4-5 cycles of concentration. Previous studies with a similar pilot-scale cooling tower system revealed that *Legionella* can easily proliferate when dechlorinated drinking water was used as makeup water (Duda et al., 2011). This was not observed in 21-day pilot-scale tests with MWW, or in another two-month long experiment that was operated under almost identical conditions (data not shown). Although the biological control strategy evaluated in this study suppressed the growth of heterotrophic bacteria below $10^4$ CFU/cm$^2$, it is likely that *Legionella* species were simply out-competed by the original microbial population in the treated secondary effluent as it is not likely that monochloramine was selectively controlling *Legionella* proliferation.

### 3.3.8 Comparison of pre-formed and in-situ formed chloramine

The results from the three sets of pilot-scale tests revealed that the control of biological growth with pre-formed monochloramine was more successful than with chloramines formed in-situ following NaOCl addition. The doses of different biocides used in these experiments are summarized in Table 3.3. Pilot-scale tests indicated that the use of NaOCl required much higher dosing rate to achieve similar total chlorine residual when compared to the use of pre-formed MCA. The proportion of monochloramine formed was much lower in the tower that received NaOCl even though the NaOCl addition rate was much higher than in the case of pre-formed MCA. This observation can be explained by the fact that hypochlorite ($OCl^-$) has strong tendency to react with organic nitrogen components in treated secondary effluent to form organic chloramines (Margerum et al., 1978). The performance of in-situ formed monochloramine was also hampered by low and variable ammonia concentration in the recirculating water during the first test. The makeup water had an average ammonia concentration of 24.1 ± 10.2 mg $NH_3$-N/L and the cooling tower operated at CoC4 should have almost 100 mg $NH_3$-N/L. However, ammonia mass balance on the pilot-scale cooling towers revealed that as much as 91 % of ammonia was lost due to stripping since the ammonia concentration in the recirculating water had an average steady-state concentration of only 3.4 mg/L $NH_3$-N at pH 8.5.

**Table 3.3.** Comparison of biocide dosing rate and biocidal effectiveness in pilot-scale tests.

| Test | Biocide | Biocide dosing rate (mg/L-hr) | Residual (mg/L) | Length of experiment | Results |
|---|---|---|---|---|---|
| **CoC 4 FTMW** | NaOCl (In-situ formed MCA) | 2.04 | 0.5-1 TC | 21 day | Unable to control both planktonic and sessile growth due to low active chloramine and unstable $NH_3$ level |
| **CoC 4 FTMW** | NaOCl (In-situ formed MCA) | 7.14 | 3-4 TC | 28 day | Unable to control both planktonic and sessile growth after 24 days |
| **CoC 4 FTMW** | Pre-formed MCA | 4.75 | 3-4 MCA | 21 day | Both planktonic and sessile growth was well controlled for 21 days |

## 3.4 SUMMARY AND CONCLUSIONS

The primary objective of this study was to investigate the effectiveness of monochloramine as a biocide to control biofouling in recirculating cooling tower systems employing treated municipal wastewater as makeup water. Bench- and pilot-scale experiments were conducted to study the effectiveness of in-situ-formed and pre-formed monochloramine for three different types of biological growth control (i.e., planktonic and sessile HPC and *Legionella*).

Ammonia variation in the treated municipal wastewater was found to impact significantly the effectiveness of in-situ monochloramine formation as a biofouling control strategy. Both bench- and pilot- scale recirculating tests demonstrated that it was difficult to achieve requisite biocidal efficacy by the addition of sodium hypochlorite when the ammonia concentration in the cooling water was low.

Chloramination with pre-formed monochloramine was found to be more effective than in-situ formed chloramines in controlling biological growth in cooling systems employing secondary treated wastewater as makeup water. Studies with the bench scale recirculating system indicated that a total chlorine residual of 0.5 – 1 mg/L as $Cl_2$ could control biological growth in that system. However, pilot-scale testing indicated that maintaining a total chlorine residual at 3-4 mg/L and relying on in-situ formed monochloramine was still insufficient to control both planktonic and sessile biological growth.

Maintaining a total chlorine residual at 3–4 mg/L (monochloramine residual above 3 mg/L) as $Cl_2$ by the addition of pre-formed monochloramine was observed to control planktonic and sessile biological growth to desired levels. The higher dosing requirement observed in pilot-scale studies was due to greater variability in the operating conditions relative to the bench-scale

testing. The use of pre-formed monochloramine as biocide for recirculating cooling systems employing secondary treated municipal wastewater was also demonstrated to completely suppress the growth of Legionella species in the pilot-scale cooling systems.

# 4.0 IMPACT OF TERTIARY TREATMENT PROCESSES ON THE EFFECTIVENESS OF CHLORAMINATION FOR BIOFOULING CONTROL IN RECIRCULATING COOLING SYSTEMS USING TREATED MUNICIPAL WASTEWATER

Adequate biocide addition is the key to preventing potential biological growth-related problems in recirculating cooling systems of thermoelectric power plants. The use of monochloramine as primary biocide has been shown previously to be as effective as the use of free chlorine in cooling systems using secondary treated municipal wastewater (MWW) as the sole makeup source. However, severe scaling caused by secondary effluent necessitates incorporation of additional treatment of secondary effluent prior to use as makeup water for recirculating cooling systems. In this study, the effectiveness of MCA as a cooling system biocide was evaluated for three types of tertiary treated MWW: 1) acidification (MWW_pH), 2) nitrification and sand filtration (MWW_NF), and 3) nitrification, sand filtration, and granular activated carbon adsorption (MWW_NFG). The impact of these tertiary treatment processes on chloramination was studied in batch reactors, bench-scale recirculating systems, and pilot-scale cooling systems; reducing the TOC content in MWW had no measurable impact on biological growth potential. Pilot-scale test was the most useful for determining the effectiveness and appropriate doses of monochloramine. A monochloramine residual of 2-3 mg/L was required to achieve biological growth control objective with respect ro planktonic and sessile heterotrophic bacteria in cooling

systems using tertiary-treated wastewaters. *Legionella* analyses suggest that chloramination was effective in controlling proliferation of these species regardless of water quality variation the tertiary-treated wastewaters. Overall, pre-formed monochloramine was effective as a primary biocide with all the tertiary-treated MWW evaluated. Nitrification followed by sand filtration was the optimal tertiary treatment of the three investigated MWW because biological control objectives could be achieved with lower doses. The use of GAC adsorption (MWW_NFG) revealed no additional benefit compared to MWW_NF.

## 4.1 INTRODUCTION

The concept of using secondary-treated municipal wastewater (MWW) as a replacement for freshwater in thermoelectric power plant cooling systems has been implemented for decades (Osborn, 1969; Humphris, 1977; Rebhun and Engel, 1988). Recently, MWW has been re-evaluated as a promising cooling water alternative in the U.S. based on its proximity to power plants, quantity, and consistent quality (Vidic et al, 2009).

MWW usually has elevated concentrations of chemicals that will induce corrosion, scaling, and biological growth. Additional water treatment and/or chemical dosing must be applied to mitigate these problems prior to MWW use as power plant cooling tower makeup. Our previous studies have evaluated the feasibility of direct reuse of MWW as the only cooling system makeup. It was demonstrated that both corrosion and biological growth can be well controlled when using MWW as a sole cooling tower makeup (Vidic et al., 2009; Hsieh et al., 2010; Chien et al., 2012b). However, severe scaling occurs with the use of MWW in cooling systems (Li et al., 2011). Liu et al. (2012) found that additional treatment of secondary effluent

prior to use as cooling tower makeup will ensure lower scaling potential and better overall recirculating water quality. Studies focusing on the challenges of corrosion and scaling control when using tertiary treated wastewaters can be found elsewhere (Choudhury et al., 2012; Liu et al., 2012). This study was conducted to evaluate biological growth control strategies for tertiary treated municipal wastewaters.

Biological growth in cooling systems comprises fungi, algae, bacteria, and other forms of organisms, and it can pose significant challenges for the operation of cooling systems (Frayne, 1999, Bott, 2011, Rajagopal et al., 2012). Specifically, the presence of microorganisms in recirculating cooling systems can lead to system failure as a result of microbial-induced corrosion and organic fouling, which may endanger public health through emission of pathogens from the cooling towers (Dondero et al., 1980; Bentham, 1993; Ludensky, 2005). Generally, both heterotrophic and sessile bacterial populations are monitored for control of biological growth control in cooling systems. Biological growth control criteria of $10^4$ CFU/mL and $10^5$ CFU/cm$^2$ have been proposed by the Cooling Tower Institute (CTI) for planktonic and sessile bacterial populations, respectively (CTI, 2008). A strict criterion for *Legionella pneumophila* of $10^2$ CFU/mL is commonly adopted as a measure for proper biological growth control in full scale cooling systems (AWT, 2003).

Control of biological growth in cooling systems is generally achieved by frequent addition of biocide chemicals (Cloete et al., 1998; Jenner et al., 1998). Criteria for systems using only MWW as cooling tower makeup were first proposed by Rebhun and Engel (1988), who suggested that chlorination is essential to achieve adequate biological growth control. Our previous study demonstrated that a 3mg/L monochloramine (MCA) residual is sufficient to control biological growth when using MWW in power plant cooling systems (Chien et al., 2012b). The weak oxidizing ability of MCA results in a longer period of activity and better penetration into biofilms (Lee et al., 2011).

Ammonia is a major parameter influencing the effectiveness of monochloramine. The Cl to $NH_3$ ratio is known to affect two major pathways for the decomposition of in-situ formed monochloramine in a drinking water system - hydrolysis followed by the reaction with free chlorine and acid catalysis (Diehl et al., 2000). However, the ammonia concentration in cooling systems using MWW as makeup varies dramatically due to the continuous stripping (Hsieh et al., 2012). It is not clear whether the variation in ammonia concentration can affect the stability of pre-formed monochloramine in treated wastewaters.

Organic carbon in drinking water is usually reduced using activated carbon adsorption in order to reduce disinfection byproducts precursors in distribution systems (Kainulainen et al., 1995; Stackelberg et al., 2007). Studies have also demonstrated that organic matter directly affects biocide demand and biocide stability in potable and reclaimed water and thus aggravates the biological growth (Butterfield et al., 2002; Westerhoff et al., 2004; Musikavong et al, 2006). However, the potential benefits of reducing total organic carbon concentration in feed water for a recirculating cooling system have not been investigated.

To determine the impact of tertiary wastewater treatment on chloramination for biological growth control, the effectiveness and usage rate of monochloramine in wastewaters that have been subjected to selected tertiary treatment processes was evaluated in this study. Three different tertiary treatments were investigated together with associated chemical regimen required for adequate biological growth control. Tertiary treatment options tested included: 1) pH adjustment (MWW_pH), 2) nitrification followed by sand filtration (MWW_NF), and 3) nitrification, sand filtration, and granular activated carbon (GAC) adsorption (MWW_NFG). Adjustment of pH in a recirculating system is commonly used to reduce calcium carbonate scaling potential (Asano and Levine, 1998; Frayne, 1999). Nitrification converts a large portion of ammonia into nitrate/nitrite, reduces pH, and reduces some alkalinity. Sand filtration removes suspended solids, including microorganisms, from wastewater and reduces its turbidity. Granular activated carbon adsorption removes organic compounds from wastewater and significantly reduces its total organic carbon (TOC).

Specific objectives of this study were to: (1) evaluate biological growth potential in cooling systems of makeup water subjected to different tertiary effluents under well-controlled laboratory conditions; (2) evaluate the impact of tertiary treatment on biocidal efficacy of pre-formed monochloramine to control both planktonic and sessile biological growth in batch and recirculating laboratory systems; and (3) to examine the effectiveness of pre-formed monochloramine to control biological growth in pilot-scale cooling systems using actual tertiary effluents as makeup under realistic process conditions.

## 4.2 MATERIALS AND METHODS

### 4.2.1 Tertiary Treated Municipal Wastewater Characteristics

Secondary- and tertiary-treated wastewater samples were collected at Franklin Township Municipal Sanitary Authority (FTMSA) in Murrysville, Pennsylvania. FTMSA is a tertiary treatment facility that includes grit removal, primary clarification, aerobic biological treatment using trickling filters, secondary clarification, nitrification, shallow bed sand filtration and UV disinfection. The main wastewater source for the 4.9 MGD facility is municipal sewage and a small amount of urban runoff. Wastewater samples were collected prior to disinfection and general water characteristics of MWW, MWW_NF, and MWW_NFG are shown in Table 4.1 as average values obtained during the summers of 2010 and 2011. MWW_NFG was prepared using a pilot scale GAC filtration column (8" column filled with F400 GAC, Calgon Carbon Pittsburgh, PA) to treat MWW_NF and reduce its TOC concentration from 9 mg/L to about 3 mg/L.

**Table 4.1.** Water characteristics of treated municipal wastewater used in this study

| Parameters | Unit | MWW | MWW_NF | MWW_NFG | Detection limit |
|---|---|---|---|---|---|
| Ca | mg/L | 41.5 | 39.7 | 39.8 | 5 |
| Cu | mg/L | 0.03 | 0.17 | 0.06 | 0.25 |
| Fe | mg/L | 0.5 | 0.31 | 0.09 | 0.1 |
| Mg | mg/L | 10.7 | 9.8 | 8.4 | 5 |
| pH | | 7.1 | 6.7 | 7.9 | |
| $NH_3$-N | mg/L | 21.0 | 1.42 | 0.39 | 0.01 |
| BOD | mg/L | 31.9 | 5.8 | N/A | |
| COD | mg/L | 101.8 | 34.0 | 15.5 | 1 |
| Cl | mg/L | 199 | 174 | 162 | 10 |
| $NO_3$-N | mg/L | 9.6 | 12.1 | 11.8 | 0.1 |
| $SO_4$ | mg/L | 67.0 | 57.8 | 59.4 | 1 |
| Total Alkalinity | mg/L as $CaCO_3$ | 177 | 34.0 | 44.2 | 5 |
| TOC | mg/L | 27.0 | 8.7 | 3.2 | 1 |
| TSS | mg/L | 24.5 | 20.8 | 15.0 | 5 |
| TDS | mg/L | 593 | 474 | 439 | 10 |
| Conductivity | µs/cm | 810 | 870 | 830 | 10 |

**MWW**: Secondary treated municipal wastewater; **MWW_NF**: Secondary treated municipal wastewater plus nitrification and sand filtration; **MWW_NFG**; Secondary treated municipal wastewater plus nitrification, sand filtration, and GAC filtration.

### 4.2.2 Wastewater Sample Preparation

Wastewater samples collected from FTMSA were transported within hours to the laboratory in 5-gallon carboys, stored at 5 ℃, and processed within three days of collection. To reflect typical conditions in recirculating cooling systems, wastewater samples were concentrated to four cycles of concentration (CoC4) by evaporation at 40 ℃ until the volume of the water sample was reduced to one-fourth its initial volume. A fine bubble diffuser was used to provide gentle aeration throughout the evaporation process to simulate the air stripping process in recirculating cooling systems. Table 4.2 summarizes major water parameters in CoC4 MWW, MWW_NF, and MWW_NFG without any chemical addition. As a result of diffusion into air and evaporation, almost all of the ammonia was stripped from concentrated wastewater samples. A portion of these concentrated samples was used in the batch and bench-scale tests within 24 hours while the rest was stored at 5 ℃ and used as replenishing solution for bench-scale recirculating studies.

**Table 4.2.** Key water characteristics of four times concentrated (CoC 4) treated municipal wastewaters used in batch and bench-scale tests

| Parameters | Unit | MWW | MWW_NF | MWW_NFG | Detect limit |
|---|---|---|---|---|---|
| pH | | 8.47 | 8.48 | 8.37 | |
| $NH_3$-N | mg/L | 0.09 | 0.07 | 0.06 | 0.01 |
| COD | mg/L | 369 | 207 | 67 | 1 |
| TOC | mg/L | 85.7 | 24.7 | 6.9 | 1 |
| $NO_3$-N | mg/L | 25.7 | 25.3 | 16.1 | 0.1 |

**MWW**: Secondary treated municipal wastewater; **MWW_NF**: Secondary treated municipal wastewater plus nitrification and sand filtration; **MWW_NFG**; Secondary treated municipal wastewater plus nitrification, sand filtration, and GAC filtration.

Chloramination of recirculating cooling water was achieved by adding pre-formed monochloramine (MCA). Monochloramine used in laboratory tests was pre-formed by mixing sodium hypochlorite (NaOCl) and ammonium chloride ($NH_4Cl$) at a $Cl_2$:$NH_3$ weight ratio of 4:1 (Palin, 1950; Kirmeyer et al., 1993). The pH of the ammonium chloride solution was adjusted to

9 with sodium hydroxide prior to NaOCl addition. In field tests, MCA stock solution at 500 mg/L was prepared by mixing stock solutions of 5% NaOCl and 1000 mg/L ammonia at pH 10 following the procedure identical to that used in the laboratory. Total chlorine residual was measured using an HF chlorine pocket photometer (HF Science Inc. Fort Myers, FL) following standard methods (4500-Cl G, DPD colorimetric method, APHA, 2012). Monochloramine (MCA) residuals were measured using a Hach DR/890 portable datalogging colorimeter (Hach, Loveland, CO) following the Indophenol method 10171 (Hach, Loveland, CO). Ammonia was measured using the Phenate Method (Method 4500-$NH_3$ F, APHA, 2012) and with HACH nitrogen test kit (Model NI-8, color disc; Method 4500-$NH_3$ B&C, APHA, 2012). Nitrate concentration was measured using Hach Method 8171 (Hach, Loveland, CO). Total organic carbon was measured using a total organic carbon analyzer (O.I. Analytical, TX).

### 4.2.3 Experimental design

Evaluation of biofouling control in this study followed the systematic process developed in previous related work (Chien et al., 2012b). The examination process included static batch reactor studies, bench-scale recirculating system studies, and pilot-scale recirculating cooling system studies.

Biological growth potential in different wastewaters was determined based on heterotrophic bacteria plate counts. Wastewater samples were autoclaved and seeded with pre-enumerated microorganism mixture derived from wastewater treatment plants. The enumerated solution contained 20 mg/L of TOC and $10^8$ CFU/mL of heterotrophic bacterial population. A 2.5 μL of 100 times diluted enumerated solution was added to the sterilized samples to provide initial heterotrophic plate counts (HPC) of $10^2$ CFU/mL The batch cell seeded with enumerated

microorganisms was then maintained at 40℃ and exposed to light with mild agitation for 2 hours. Monochloramine was then added to each reactor and monitored for biocide residual concentrations and pH for another 2 hours. Biological growth and biocide residual were monitored following the same procedures described before. Each residual data point represents duplicate results, while each biological growth data represents quadruplicate results.

Tertiary effluents were stored in 75-gallon HDPE tanks to serve as cooling system makeup source and were treated with pre-formed monochloramine at 1 mg/L to represent fresh tertiary effluents discharged from municipal wastewater treatment plants. The average planktonic HPCs in the makeup water tank in all three tests was $10^{3.95} \pm 10^{4.24}$ CFU/mL. Both MWW_NF and MWW_NFG were generated on-site and stored in the makeup water tanks. For the test using MWW_pH as the cooling tower makeup, a pH controller (pH/ORP controller 3675, Jenco Instrument Inc., CA) was installed to add 0.5mM sulfuric acid to the recirculating system and maintain the pH at about 7.7.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Biological growth potential in batch and bench-scale recirculating tests

Unconcentrated MWW_NF and MWW_NFG samples were autoclaved to completely eliminate biological activity. A $10^2$ CFU/mL initial HPC seed rapidly increased to above $10^5$ CFU/mL within 2 hours at 40 ℃ in both samples (Figure 4.1). It was observed that the average HPC in the MWW_NFG was 37% lower than that in the MWW_NF without any biocide addition. However, this result only showed less than 5% decrease in bacterial growth rate in the MWW_NFG during

the exponential growth phases; in MWW_NFG, the TOC level was decreased by almost threefold (i.e., from 8.7 to 3 mg/L) compared to MWW_NF. Studies have shown that planktonic heterotrophic bacterial growth rates can be reduced by 30% depending on the TOC concentration in marine waters (Borsheim, 2000; Kirchman et al., 2000). However, the relatively high initial TOC level in treated municipal wastewater, even after GAC adsorption, and high water temperature in cooling system can lead to a faster metabolism of heterotrophic bacteria and may have minimized the impact of TOC reduction on biological growth rate in this study.

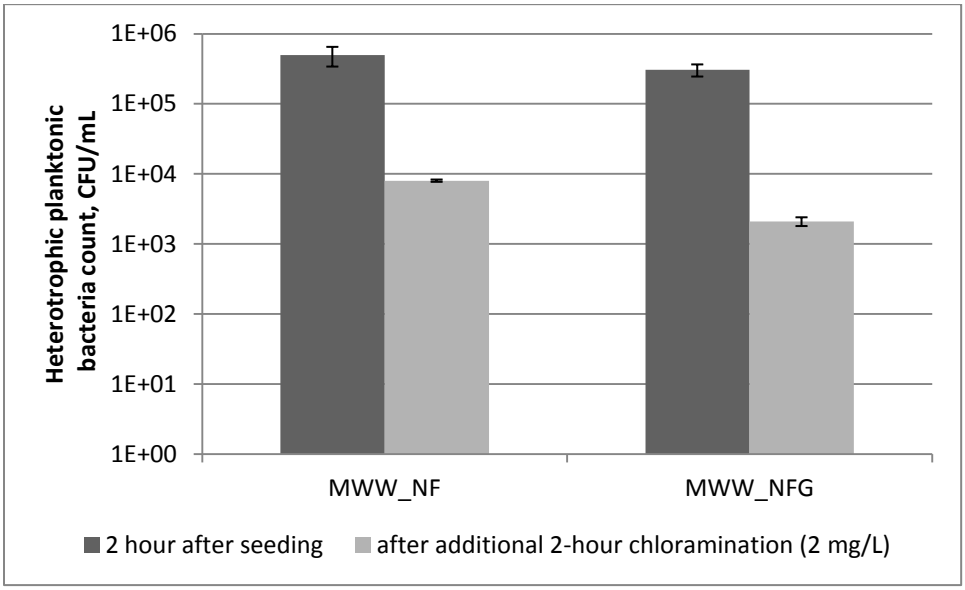


**Figure 4.1.** Planktonic heterotrophic bacteria plate counts 2 hours after seeding sterilized wastewater samples and after additional 2 hour-chloramination with 2 mg/L of pre-formed monochloramine.

After a 2-hour growth phase, 2 mg/L (MCA) was added to both MWW_NF and MWW_NFG samples to evaluate biocidal potential of MCA. Heterotrophic bacterial inactivation rates observed in the MWW_NF and MWW_NFG after 2-hour chloramination were 98.4 and 99.3%, respectively (Figure 4.1). Residuals measured throughout the test showed an overall decrease in biocide demand when TOC was removed by GAC adsorption. The total chlorine demand at the end of the test was 1.15 and 0.72 mg/L for MWW_NF and MWW_NFG,

respectively (Figure 4.2) while the ratio of monochloramine and the total chlorine residual in MWW_NF and MWW_NFG were 84.1 ± 6.3 % and 94.8 ± 3.3 %, respectively. Results from this test indicated that the removal of organics can reduce monochloramine demand. This observation agrees with findings from a previous study that evaluated the impact of organic matter removal on in-situ chloramination in drinking water distribution system (Chandy and Angels 2001). Furthermore, the hydrolysis and conversion of monochloramine to other chloramines were also slowed by TOC reduction.

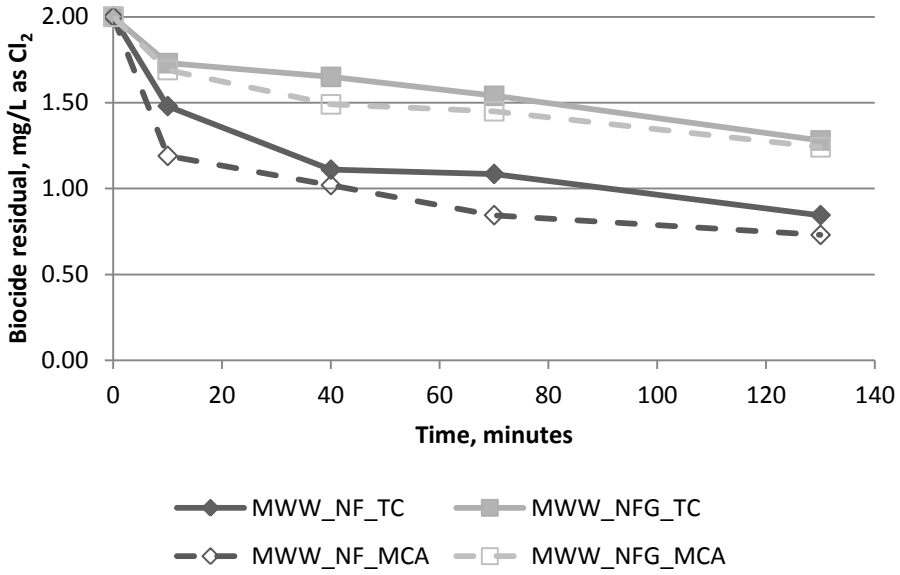


**Figure 4.2.** Total chlorine (TC) and monochloramine (MCA) residual during chloramination of MWW_NF and MWW_NFG.

Biological growth potentials in tertiary effluents were further examined with CoC 4 MWW, MWW_NF, and MWW_NFG in a bench-scale recirculating system to validate the findings of the batch tests under turbulent flow conditions. Results of the bench-scale recirculating tests without biocide addition are shown in Figure 4.3. It should be noted that the first sessile sample was taken 12 hours after the beginning of the test in order to have measurable sessile biological growth. Planktonic biological growth in all three types of CoC4 wastewaters

increased to 6 Log HPC ($10^6$ CFU/mL) after 4 hours. Concentrations of planktonic bacteria increased steadily in MWW but decreased slightly in MWW_NF and MWW_NFG from 4 to 12 hours, which can be explained by lower assimilable organic carbon and non-adsorable organic components left in these samples (Escobar et al., 2001). Therefore, planktonic biological growth in MWW_NF and MWW_NFG was hindered and led to a longer lag growth phase since the planktonic HPC measured after 24, 48, and 72 hours showed negligible differences among the three wastewater samples when planktonic biological growth reached stationary phases.

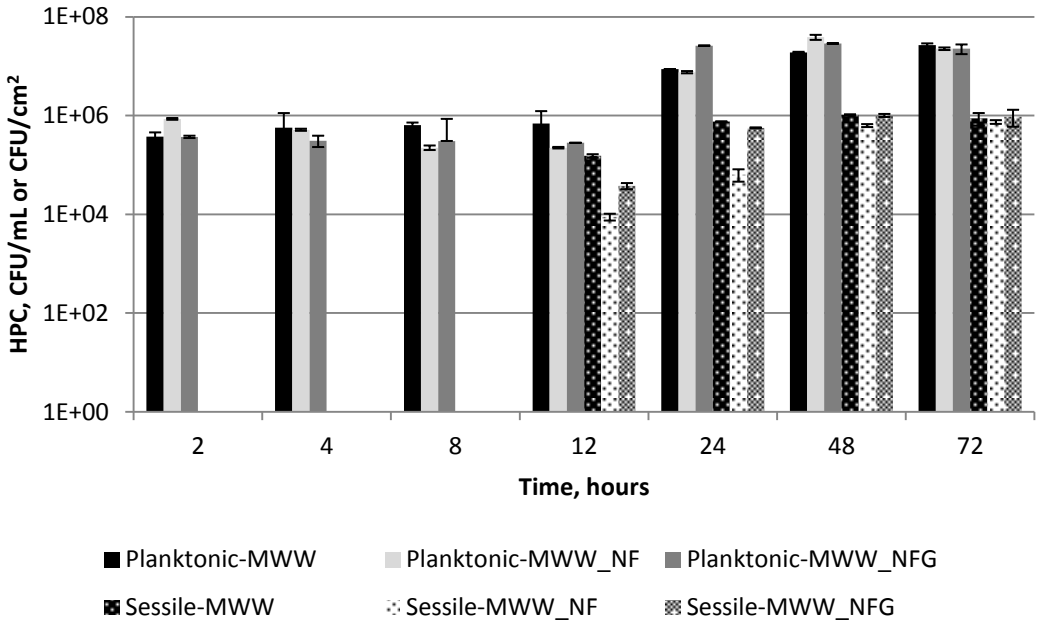


**Figure 4.3.** Planktonic and sessile HPCs in CoC 4 MWW_NF and MWW_NFG in bench scale recirculating system for three days without any biocide addition.

The growth rate of sessile bacteria in the first 12 hours was higher in secondary-treated MWW (0.99 $hr^{-1}$) than in the two tertiary-treated wastewaters (0.75 $hr^{-1}$ in MWW_NF and 0.87 $hr^{-1}$ in MWW_NFG). After that, sessile biological growth reached a stationary phase in all three wastewater samples and there were no measurement differences after 3 days. Furthermore, planktonic and sessile biological growth in all samples exceeded the control objectives for cooling systems ($10^4$ CFU/mL for planktonic bacteria and $10^5$ CFU/$cm^2$ for sessile bacteria) within 24 hours regardless of water quality.

These results indicated that no apparent correlation between the total planktonic and sessile biological growth and wastewater quality can be deduced from bench-scale recirculating systems.

### 4.3.2 Biocide demand and biocidal efficiency in tertiary treated municipal wastewater at 40 ℃.

A total chlorine residual between 3 to 4 mg/L and a Ct value of 450 mg-minute/L in the contact chamber is the minimum required Ct to achieve effective control of total coliform concentration in municipal wastewater treatment (Huitric et al., 2006). However, biological growth control objectives in recirculating cooling system is not as strict as in wastewater disinfection and thus the required Ct values and biocide doses are lower than those in wastewater treatment process.

Prior to conducting bench-scale recirculating tests, batch tests were conducted to determine optimal biocide dose required to achieve a given biocide residual at a prescribed contact time, pH, and temperature following the standard method (Method 4500-Cl G, APHA, 2012).

Table 4.3 shows biocide residual and biocidal efficiency of pre-formed monochloramine in CoC1 MWW_pH, MWW_NF, and MWW_NFG at 40℃ after 2 hours of contact time. This test differed from the biological growth potential tests in that the initial microorganism population was the one that was present in the original wastewater samples. The average initial planktonic HPC in 20 different samples of tertiary-treated MWW was $10^{6.33} \pm 10^{6.32}$ CFU/mL. Therefore, a biocidal efficacy above 99.5% had to be achieved to reach the planktonic biological growth control criterion in cooling water of $10^4$ CFU/mL. For the batch tests in the present study, a 2 mg/L initial monochloramine dose was required to achieve biological growth control criterion in MWW_pH, while only 1 mg/L initial monochloramine dose was required for the same outcome would be required to achieve 99.5% biocidal efficiency in MWW_NF and MWW_NFG. These results suggest that Ct values of 20, 20, and 72 mg-minute/L in MWW_pH, MWW_NF, and MWW_NFG, respectively.

Pre-formed monochloramine addition to the three tertiary-treated wastewaters resulted in much greater fraction of monochloramine in total chlorine residual in MWW_NF (89 ± 3%) and MWW_NFG (94 ± 6%) than in MWW_pH (78%). A previous study showed that keeping the water temperature at 40℃ greatly enhanced biocidal efficacy in MWW and resulted in the reduction of biocide required to reach biological control objectives by 25 to 50% (Chien et al., 2012b). Removal of organic matter from the secondary effluent also reduced biocide demand but there was no significant improvement in biocidal efficacy of MCA against heterotrophic microorganisms with a decrease in the concentration of organic constituents.

**Table 4.3.** Biocide demand, chlorine residuals, and biocidal efficacy after 2-hour contact time with unconcentrated tertiary treated municipal wastewaters at 40 ℃

| Biocide dose, mg/L as $Cl_2$ | MWW_pH | | MWW_NF | | MWW_NFG | |
|---|---|---|---|---|---|---|
| | TC[(1)] residual, mg/L as $Cl_2$ | Biocidal efficacy[(3)], % | TC residual, mg/L as $Cl_2$ | Biocidal efficacy[(4)], % | TC residual, mg/L as $Cl_2$ | Biocidal efficacy[(4)], % |
| 0.5 | 0.00 (0.00)[(2)] | 96.13 | 0.09 (0.00) | 99.40 | 0.20 (0.20) | 58.86 |
| 1 | 0.03 (0.00) | 97.84 | 0.17 (0.15) | 99.98 | 0.61 (0.58) | 99.99 |
| 2 | 0.18 (0.14) | 99.94 | 0.85 (0.73) | 99.98 | 1.28 (1.24) | 98.13 |
| 4 | 0.64 (0.51) | 99.98 | 2.46 (2.27) | 99.95 | 2.92 (2.45) | 99.99 |

(1) Total chlorine; (2): number in parenthesis indicates the monochloramine residual; (3) initial HPC: $10^{5.71}$ CFU/mL; (4) initial HPC: $10^{5.20}$ CFU/mL; (5) initial HPC: $10^{5.54}$ CFU/mL

### 4.3.3 Biological growth control using pre-formed monochloramine in bench-scale recirculating systems with MWW_NF and MWW_NFG

The effectiveness of pre-formed monochloramine against sessile biological growth in the bench-recirculating system was evaluated using the Ct values derived from batch tests as guidance. Liu et al. (2006) demonstrated that a turbulent flow regime can significantly enhance the formation of sessile bacteria on pipe surfaces, thereby resulting in biological growth that is much more difficult to control. Simoes et al. (2003) suggested that biological growth in turbulent flow is more resistant to biocides than that in laminar flow because of extracellular polymeric substances. Therefore, an MCA residual of 0.5-1.0 mg/L and a contact time of 60 minutes (Ct value of 30-60) were selected to control the biological growth in the recirculating system with CoC 4 MWW_NF. Contrary to the observations from batch tests, this test showed that both planktonic and sessile HPCs exceeded 6 log within 72 hours when MCA residuals were maintained at 0.98 ±0.79 mg/L as $Cl_2$ (data not shown). The most likely explanation for this behavior is that the recirculating

system was operated with concentrated wastewater compared to batch tests. Hence, the subsequent tests were conducted using an MCA residual between 2-3 mg/L as $Cl_2$.

Planktonic and sessile biological growth in the presence of a MCA residual of 2-3 mg/L as $Cl_2$ in CoC 4 MWW_NF and MWW_NFG is depicted in Figure 4.4. In the test with MWW_NF, with MCA residual of 2.29 ± 0.42 mg/L accounting for approximately 83% of the total chlorine residual (2.77 ± 0.50 mg/L of total chlorine as $Cl_2$), the planktonic and sessile bacteria populations were maintained below the accepted biological growth control criteria. This test demonstrated that maintaining monochloramine residual between 2-3 mg/L successfully controlled biological growth in CoC 4 MWW_NF with a dosing rate of 14.2 mg/L·day.

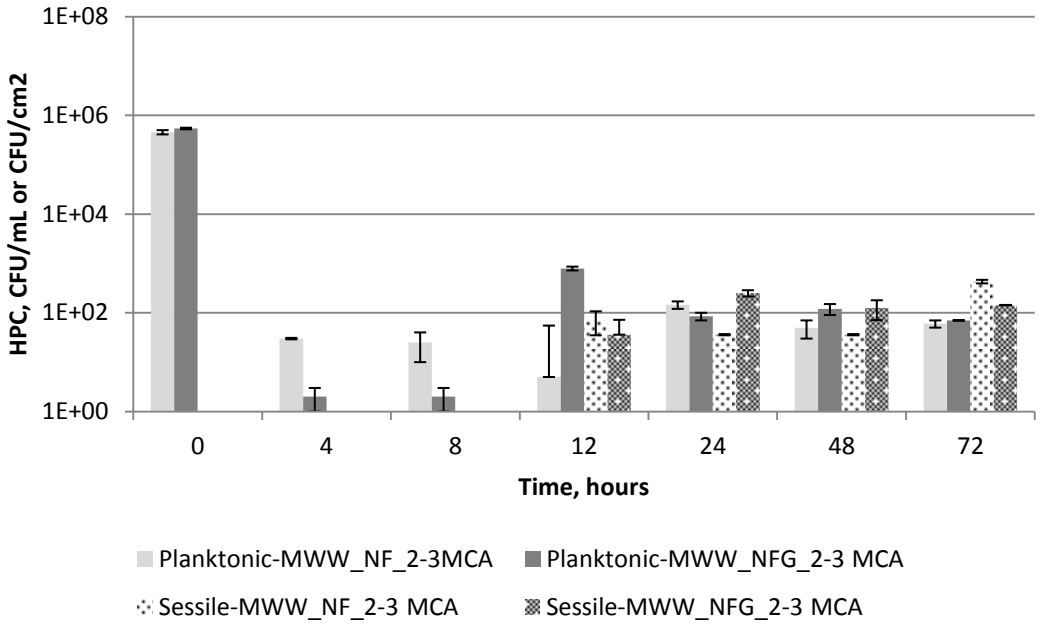


**Figure 4.4.** Planktonic and sessile HPCs in CoC 4 MWW_NF and MWW_NFG in bench scale recirculating system with MCA residual of 2-3 mg/L.

In the test with CoC 4 MWW_NFG, monochloramine residual (2.90 ± 0.55 mg/L of MCA) accounted for approximately 88% of the total chlorine residual (3.30 ± 0.65 mg/L of total chlorine as $Cl_2$) and both planktonic and sessile heterotrophic bacteria in the recirculating system

were maintained below the accepted biofouling control criteria. The dosing rate required to maintain a 2-3 mg/L monochloramine residual in CoC 4 MWW_NFG was 10.8 mg/L·day.

Comparison of the results from the bench scale recirculating system tests with CoC 4 MWW_NF and MWW_NFG suggests that the use of GAC adsorption slightly reduced the biocide dosing rate required to achieve a 2-3 mg/L MCA residual. Similar to the results observed in the batch tests, the fraction of monochloramine in the total chlorine residual did not increase significantly when TOC was reduced from 27 mg/L in CoC 4 MWW_NF to 10 mg/L in CoC 4 MWW_NFG. This observation is not consistent with those from a previous study of chloramination of natural waters, where the formation rates of organic chloramines were inversely proportional to the ratio of dissolved organic carbon to dissolved organic nitrogen in surface waters (Lee and Westerhoff, 2009).

### 4.3.4 Chloramination Efficacy in Pilot-Scale Experiments

#### 4.3.4.1 Impact of tertiary treatment alternatives on key recirculating water quality

Table 4.4 summarizes the key water quality parameters in recirculating cooling waters during pilot-scale tests with tertiary – treated MWW (data from the test with MWW are included here for comparison). Acidification did not show a significant reduction of TOC in MWW (9%) but increased the ammonia concentration to about 51 mg/L in the system through reduction of ammonia stripping. The use of nitrification and sand filtration treatments after secondary treatment reduced ammonia and TOC in MWW by 62% and 68%, respectively. Additional GAC treatment of MWW_NF reduced ammonia and TOC by 93% and 89%, respectively.

**Table 4.4.** Key water quality parameters of the recirculating water in the field tests

| Parameters | Unit | MWW | MWW_pH | MWW_NF | MWW_NFG |
|---|---|---|---|---|---|
| pH | | 8.42 | 7.46 | 7.75 | 8.09 |
| $NH_3$-N | mg/L | 8.02 | 50.95 | 3.07 | 0.58 |
| COD | mg/L | 284 | 364 | 171 | 40 |
| TOC | mg/L | 83.7 | 75.9 | 27.0 | 9.3 |
| Nitrate | mg/L | 18.7 | 22.0 | 22.2 | 20.7 |
| Alkalinity | mg/L | 227.3 | 74.3 | 71.8 | 112.5 |

**MWW**: Secondary treated municipal wastewater; **MWW_NF**: Secondary treated municipal wastewater plus nitrification and sand filtration; **MWW_NFG**; Secondary treated municipal wastewater plus nitrification, sand filtration, and GAC filtration.

Nitrate is commonly considered as an indicator of the reaction between monochloramine and natural organic matter in drinking water systems (Valentine, 1998). In this study, nitrate concentrations in cooling systems operated using MWW_pH and MWW_NF were were both slightly higher than that in MWW. However, none of the nitrate concentrations in the field tests were near the expected values (4-5 times of the original nitrate concentrations in the makeup waters shown in Table 4.1). A potential explanation for nitrate reduction in the cooling system is that it servesd as nutrient supply for algal and bacterial growth in the cooling tower. Reay et al. (1999) showed that nitrate consumption rate significantly increased together with the increase of water temperature (i.e., from 25 to 40 ℃) in batch systems.

Alkalinity in the CoC 4 recirculating treated wastewaters was dominated by bicarbonate in this study. Acidification reduced the total alkalinity in CoC4 MWW by 67%, while nitrification reduced the pH in CoC4 MWW_NF. However, GAC adsorption led to an increase in final pH in the recirculating system operated with CoC4 MWW_NFG as compared to the system operated with MWW_NF as makeup water. This observation agrees with previously observed increase in pH as a result of GAC treatment (Farmer et al., 1996).

#### 4.3.4.2 Pilot-scale tests with MWW_pH

In the pilot-scale test with MWW_pH, the monochloramine residual was maintained at 3.42 ± 4.38 mg/L as $Cl_2$ and the total chlorine residual averaged at 4.75 ± 6.34 mg/L for 30 days (Figure 4.5). Despite the variations in monochloramine residual, both planktonic and sessile HPCs were well-controlled in this test. On average, monochloramine accounted for 66% of total chlorine residual. The cooling system using MWW_pH was operated at pH 7.46 and ammonia concentration in the recirculating water was 51 mg/L as there was little ammonia stripping at this pH (Hsieh et al., 2012).

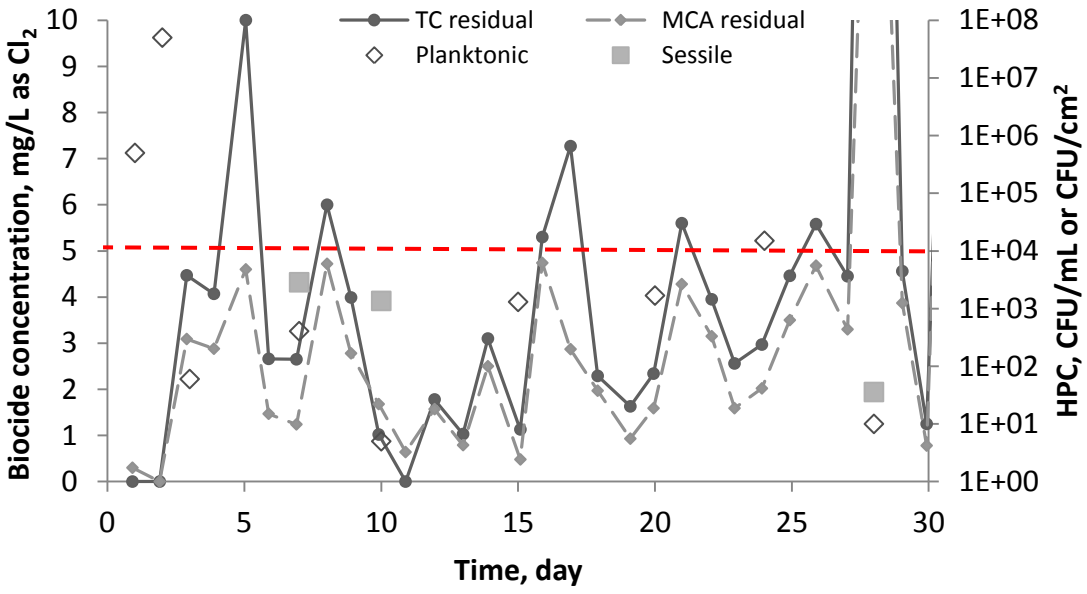


**Figure 4.5.** Total chlorine and monochloramine residual and planktonic and sessile bacterial count in pilot scale cooling tower (4 cycles of concentration) using MWW_pH. MCA residual was maintained at 3.42 ± 4.38 mg/L as $Cl_2$ and total chlorine residual was maintained at 4.75 ± 6.34 mg/L for 30 days

Hydrolysis of MCA to dichloramine at low pH was also observed in the tests with MWW_pH. During the first 15 days of the test when the pH was below 7.2, the presence of dichloramine was tracked using the FAS-DPD method (4500-Cl F, DPD-FAS titrimetric method, APHA, 2012). In contrast to the theoretical values suggested by Morris and Isaac (1983), dichloramine accounted for less than 10% of the total chlorine residual in this system. The findings support our previous observation that organic chloramines accounted for most of the non-monochloramine fractions of the total chlorine residual in concentrated secondary treated effluent at pH 8.5 (Chien et al., 2012b).

#### 4.3.4.3 Pilot-scale tests with MWW_NF

Target chloramine residual for the pilot-scale tests with MWW_NF was 2-3 mg/L as $Cl_2$ based on the biocide effectiveness observed in bench-scale recirculating system. Results of biocide residuals and planktonic and sessile HPCs in this test are shown in Figure 4.6. Monochloramine residual averaged 2.76 ± 1.10 mg/L as $Cl_2$ and the total chlorine residual averaged 3.16 ± 1.09 mg/L during a 30-day test. Monochloramine residual was maintained above 2 mg/L except on Day 23 and only 13% of MCA was converted to other chloramine forms due to the reduced presence of organic compounds.

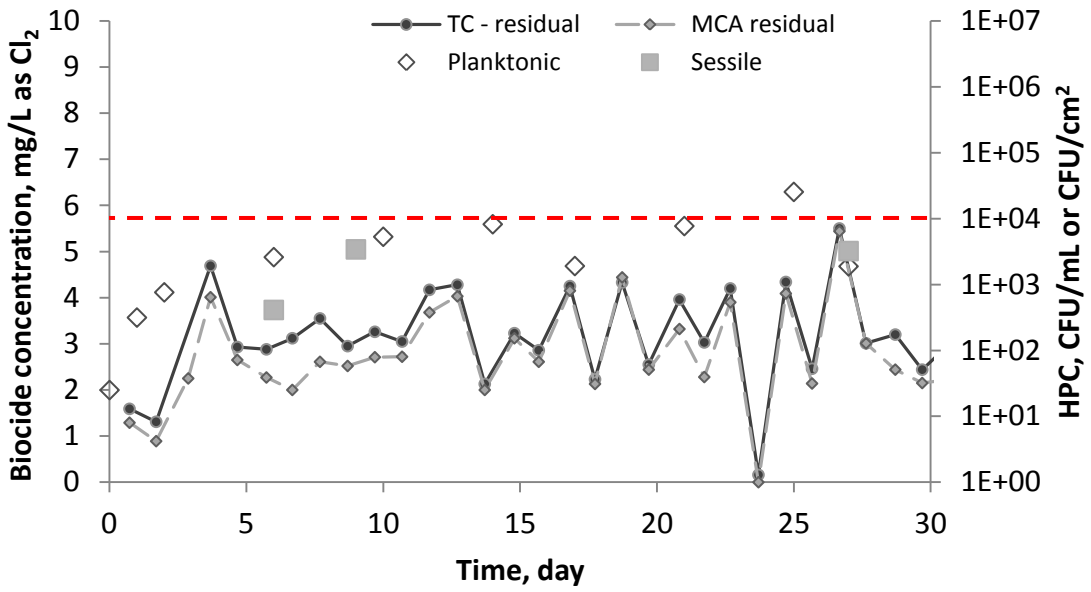


**Figure 4.6.** Total chlorine and monochloramine residual and planktonic heterotrophic and sessile bacterial count in pilot scale cooling tower (4 cycles of concentration) using MWW_NF. MCA residual was maintained at 2.76 ± 1.10 mg/L as $Cl_2$ and total chlorine residual was 3.16 ± 1.09 mg/L as $Cl_2$ for 30 days.

All four sessile HPC measurements were well below the accepted biofouling control criterion (i.e., $10^5$ CFU/cm$^2$). Only the planktonic sample on Day 24 showed an HPC level slightly above the control criterion due to the failure of the dosing equipment to maintain proper MCA residual one day prior to the sampling event. This test indicated that both planktonic and sessile biological growth were controlled below the accepted standards but clearly indicate that it is critical to maintain MCA residual above 2 mg/L at all times to ensure that these standards are not exceeded.

#### 4.3.4.4 Pilot-scale tests with MWW_NFG

Biocide residuals and HPC measurements for the cooling tower test with MWW_NFG are shown in Figure 4.7. The monochloramine residual averaged 2.23 ± 0.64 mg/L as $Cl_2$ and accounted for 86% of the total chlorine residual. Planktonic HPCs were above the biofouling control criterion of $10^4$ CFU/ml on Days 13, 17, and after Day 25, despite the fact that the MCA residuals were at reasonable levels on these days. The only sessile sample that exceeded the biofouling control criterion was on Day 10 but the replicate sessile sample collected on Day 17 did not reflect the same behavior. In summary, maintaining the MCA residual above 2 mg/L in the pilot-scale test with MWW_NFG was not able to restrain planktonic bacteria to below $10^4$ CFU/mL but was able to control sessile bacteria below $10^4$ CFU/cm$^2$ for a period of 30 days.

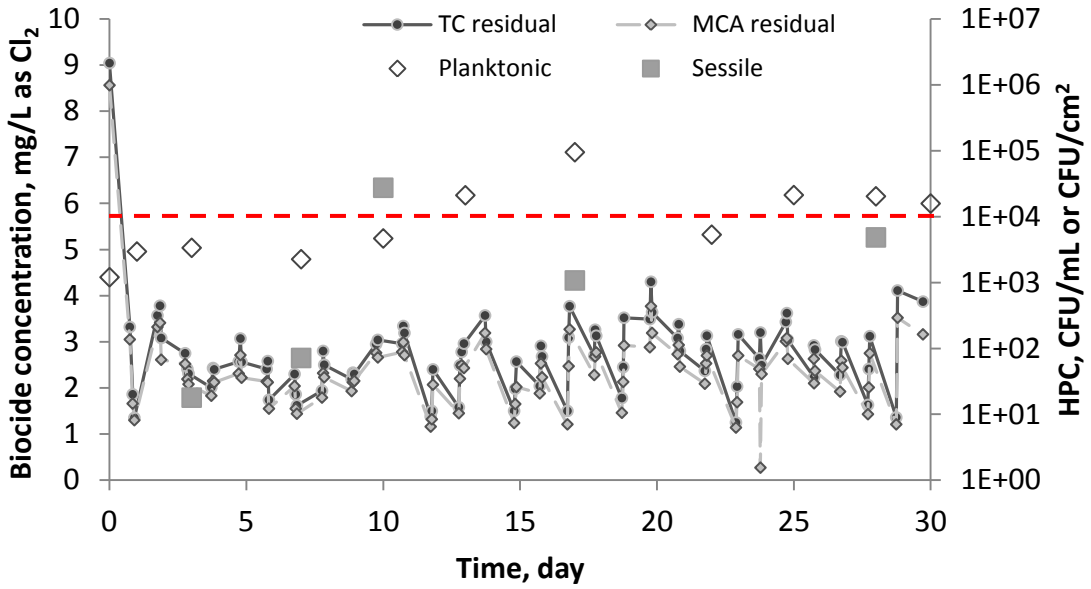


**Figure 4.7.** Total chlorine and monochloramine residual and planktonic and sessile bacterial count in a pilot scale cooling tower (4 cycles of concentration) using MWW_NFG. MCA residual was maintained at 2.23 ± 0.64 mg/L as $Cl_2$ and total chlorine residual was 2.62 ± 0.69 mg/L as $Cl_2$ for 30 days.

Meesters et al. (2003) showed that the reduction in biodegradable carbon content in bench-scale recirculating testing with synthetic process water resulted in a 30-40 fold decrease in bacterial population, but results of pilot-scale tests conducted in this study suggested the opposite behavior. It was observed that the recirculating cooling systems operated with MWW_NFG, which contained much less total organic carbon than MWW_NF, exceeded the cooling tower control criterion of $10^4$ CFU/cm$^2$ (Figure 4.7) with similar residual biocide.

A sessile sample collected after being immersed for 28 days in the pilot-scale system operated with MWW_NF revealed no mineral deposits on the stainless steel specimen. However, the testing with MWW_NFG resulted in mineral deposits on the sample immersed in that system for 28 days. The increase in pH as a result of GAC treatment increased the scaling potential and reduced the effectiveness of MCA to control biological growth.

#### 4.3.4.5 Comparison of pilot-scale tests with MWW_pH, MWW_NF, and MWW_NFG tests

Biocide usage results in of the pilot-scale tests with MWW, MWW, MWW_pH, MWW_NF, and MWW_NFG treated wastewaters are summarized in Table 4.5. Acidification of MWW lowered the total amount of biocide required to achieve biofouling control criteria by 18% compared to tests with MWW. Addition of nitrification and sand filtration to secondary effluent reduced monochloramine consumption by 30% while the addition of GAC treatment reduced biocide consumption by 45% compared to MWW. However, this reduction in MCA consumption in cooling towers using MWW_NFG may not be advantageous since a higher MCA residual above 2-3 mg/L is likely required to achieve proper biological growth control.

**Table 4.5.** Biocide dosing rate and consumption in the pilot-scale cooling system

| Water sample | $NH_2Cl$ residual, mg/L | Biocide dosing rate, g/day | Biocide consumption, mg/day·L | Biocide cost, USD/day·1000L |
|---|---|---|---|---|
| MWW | 3.16 ± 1.95 | 12.18 | 72.38 | 0.073 |
| MWW_pH | 3.42 ± 4.38 | 12.97 | 59.34 | 0.060 |
| MWW_NF | 2.76 ± 1.10 | 10.08 | 50.49 | 0.051 |
| MWW_NFG | 2.23 ± 0.64 | 8.25 | 40.00 | 0.041 |

In the tests with MWW_pH and MWW_NFG, a piece of drift eliminator having visible biomass growth was analyzed for *Legionella* species at the end of the experiment. Results indicate that *Legionella* species were not able to grow in the pilot-scale cooling systems fed with three type of wastewaters and treated with monochloramine over a period of one month.

## 4.4 SUMMARY AND CONCLUSIONS

This study evaluated the use of treated municipal wastewater in power plant cooling systems as makeup water, with a focus on understanding the influence of tertiary-treated wastewater quality on biological growth, the effectiveness of monochloramine in suppressing biological proliferation, and the impacts of water quality on the performance of monochloramine in recirculating cooling systems.

TOC reduction through tertiary municipal wastewater treatment hindered biological growth rate but did not affect the overall biological growth potential. Regardless of the TOC concentration in CoC 4 tertiary-treated wastewater, planktonic bacteria population reached exponential growth phase within 24 hours, while the sessile bacterial population exceeded the biofouling control criterion ($10^5$ CFU/$cm^2$) in bench-scale recirculating system at 40 ℃.

Pilot-scale experiments confirmed that biological growth in recirculating cooling systems using treated municipal wastewater can be controlled with pre-formed monochloramine as primary biocide. Monochloramine residual of about 3 mg/L as $Cl_2$ was required to meet the biological growth control criteria in the cooling systems using acidified secondary effluent as makeup. When secondary effluent was treated with nitrification and sand filtration, the required monochloramine residual to achieve desired biological growth control was reduced to 2-3 mg/L. In addition, monochloramine accounted for a larger fraction of total chlorine residual when compared to the system operated with secondary-treated municipal wastewater.

Pilot-scale testing was the best determinant of effective biocide doses. Both batch and bench-scale recirculating tests accurately predicted relative trends of biological growth and biocidal effectiveness as a function of water quality. However, bench-scale recirculating tests underestimated the biocide requirements in pilot-scale tests by as much as 4 to 6 times.

The findings of this study demonstrated the effectiveness of monochloramine in recirculating cooling system using treated municipal wastewater as cooling tower makeup. Nitrification and sand filtration was the optimal tertiary treatment for municipal wastewater to effectively use chloramination (pre-formed monochloramine) for biological growth control in this water resue application.

# 5.0 COMPREHENSIVE EVALUATION OF BIOLOGICAL GROWTH CONTROL BY CHLORINE-BASED BIOCIDES IN POWER PLANT COOLING SYSTEMS USING TERTIARY EFFLUENT

Oxidizing chemicals, i.e. sodium hypochlorite, pre-formed monochloramine, and chlorine dioxide, have been widely used in cooling systems to control biological growth. Recent studies have shown that treated municipal wastewater can be a reliable cooling water alternative to freshwater. However, elevated nutrient concentration and microbial population in wastewater lead to aggressive biological proliferation in the cooling system. Three chlorine-based biocides were evaluated for the control of biological growth in cooling systems using tertiary treated wastewater as makeup based on their efficiency, cost-effectiveness, and environmental and public health impacts. Optimal chemical regimens for achieving successful biological growth control were elucidated based on batch-, bench-, and pilot-scale experiments. Biocide usage and biological activity in planktonic and sessile phases were carefully monitored to understand biological growth potential and biocidal efficiency of the three disinfectants in this particular environment.

Water parameters, such as temperature, cycles of concentration, and ammonia concentration in recirculating water, critically affected the biocide performance in recirculating cooling systems. Bench-scale recirculating tests were shown to adequately predict the biocide residual required for a pilot-scale cooling system. The optimal residuals needed for proper

biological growth control were 1, 2-3, and 0.5-1 mg/L as $Cl_2$ for NaOCl, pre-formed $NH_2Cl$, and $ClO_2$, respectively. Cost analysis of these biocides was performed based on the results of pilot-scale experiments to provide relevant practical information for municipal wastewater reuse. The analysis showed that the use of NaOCl for biological growth control in power plant recirculating cooling systems using tertiary-treated wastewater as makeup was the most cost-effective.

## 5.1 INTRODUCTION

Increase in energy demand requires additional power generation capacity and improvement in the efficiency of operation. However, lack of freshwater needed for the cooling systems of thermoelectric power plants has led to problems in power plant operation and expansion in arid areas (Feeley and Ramezan, 2003; Dishneau, 2007). Reliable alternative water sources are critical for the future of power generation.

Treated secondary municipal wastewater is an obvious cooling water alternatives based on the proximity to its potential use, quantity, and consistent quality (Vidic and Dzombak, 2009). This impaired water is among the most promising alternative cooling water sources in the U.S. for power plant recirculating cooling systems (Li et al, 2011a). Previous studies demonstrated that secondary treated municipal wastewater subjected to nitrification and sand filtration (MWW_NF) results in optimal water quality to control corrosion (Hsieh et al., 2010; Choudhury et al., 2012), scaling (Li et al., 2011b; Liu et al., 2012), and biological growth (Chien et al., 2012c) when using this impaired water as the only makeup for recirculating cooling systems.

A recirculating cooling system is a warm and nutrient-rich environment ideal for growth of both planktonic and sessile bacteria. Biological growth (biofouling) is a common and most significant problem in the operation of cooling systems (Melo and Bott, 1997; Frayne, 1999, Flemming, 2002). Along with the favorable growth conditions available in the cooling system (e.g., elevated temperature, neutral pH, constant aeration), organic matter and nutrients present in tertiary-treated effluent are concentrated in the cooling systems, which make the biological growth control an even more challenging task.

Most microorganisms can form biofilm (Costerton et al. 1999) and are able to colonize on heat exchanger surface within 4~8 hours (Rossmoore, 1995). Sessile biological growth in cooling systems adversely impacts the efficiency of heat exchangers and promotes microbiologically induced corrosion (MIC) underneath the biofilm matrix (Characklis, 1990; Ludensky, 2005). This phenomenon can be further exacerbated when using impaired water as cooling tower makeup (Zaidi, 2006; Puckorius, 2003).

In addition, presence of *Legionella* species due to poor biological control in the recirculating water (Fraser et al., 1977; Edelstein, 1993; Yu, 2008) is of particular concern because of the potential for aerosol emissions from cooling towers. The Cooling Tower Institute (CTI) proposed that cooling tower operators monitor for *Legionella* regularly and suggested that planktonic heterotrophic bacteria count in the bulk water is maintained below $10^4$ CFU/mL and sessile heterotrophic bacteria count on surfaces are below $10^5$ CFU/cm$^2$ to reduce health and operational risks (CTI, 2008).

Sodium hypochlorite (NaOCl), monochloramine ($NH_2Cl$), and chlorine dioxide ($ClO_2$) are known agents for biological growth control in recirculating cooling towers using freshwater (Kim et al., 2002; Ludensky, 2005). Several studies evaluated the use of treated municipal wastewater as cooling tower makeup in power plants and pointed out the importance of controlling biological growth in the cooling system by using these oxidizing chemicals (Adams et al., 1980; Selby et al., 1996, Chien et al., 2012b).

Grant and Bott (2005) suggested that only doses resulting in sufficient biocide residual can succeed in biological growth control. However, none of the previous studies provide sufficient detail to demonstrate the effectiveness of these biocides when using tertiary treated wastewater in recirculating cooling systems. Besides the biocidal effectiveness and demand, it is also important to understand the cost of appropriate biological growth control.

The specific objectives of this study were: (1) to evaluate the effectiveness of NaOCl, $NH_2Cl$, and $ClO_2$ for the control of biological growth in concentrated MWW_NF under well-controlled laboratory conditions; (2) to examine the effectiveness of NaOCl, $NH_2Cl$, and $ClO_2$ to control planktonic and sessile biological growth in recirculating cooling systems using MWW_NF as makeup water at 4-5 cycles of concentrations; (3) to evaluate the potential of NaOCl, $NH_2Cl$, and $ClO_2$ to control biological growth, including *Legionella pneumophila* in pilot-scale recirculating cooling tower systems; and (4) to determine the cost of using NaOCl, $NH_2Cl$, and $ClO_2$ for biological growth control.

## 5.2 MATERIALS AND METHODS

Tertiary treated wastewater samples were collected from Franklin Township Municipal Sanitary Authority (FTMSA) in Murrysville, Pennsylvania. The main wastewater treated in their 4.9 MGD facility is municipal sewage and a small amount of urban runoff. The water characteristics of MWW_NF are shown in Table 5.1. This wastewater treatment facility incorporates primary sedimentation, aerobic biological trickling filters, secondary clarification, nitrification, sand filtration, and UV disinfection. Samples were collected after sand filtration and prior to UV disinfection.

**Table 5.1.** Key water quality parameters tertiary treated wastewater in Franklin Township Municipal Sanitary Authority, Murrysville, PA.

| Parameters | Unit | Value | Detection limit |
|---|---|---|---|
| Ca | mg/L | 39.7 | 5 |
| Cu | mg/L | 0.17 | 0.25 |
| Fe | mg/L | 0.31 | 0.1 |
| Mn | mg/L | 9.8 | 5 |
| pH | - | 6.7 | |
| $NH_3$-N | mg/L | 1.42 | 0.01 |
| BOD | mg/L | 5.8 | 1 |
| COD | | 34.0 | 1 |
| Cl | mg/L | 174 | 10 |
| $NO_3$-N | mg/L | 12.1 | 0.1 |
| $SO_4$ | mg/L | 57.8 | 1 |
| Total P | mg/L | 7.16 | 0.01 |
| Total Alkalinity | mg/L as $CaCO_3$ | 34.0 | 5 |
| TOC | mg/L | 8.7 | 1 |
| TSS | mg/L | 20.8 | 5 |
| TDS | mg/L | 474 | 10 |
| Conductivity | µs/cm | 870 | 10 |

### 5.2.1 Wastewater sample preparation

Wastewater samples collected from FTMSA were transported to the laboratory and processed within three days of collection. The planktonic heterotrophic bacteria count in 20 different samples averaged $10^{6.33} \pm 10^{6.32}$ CFU/mL. Thus, a minimum inactivation rate of 99.5% would be

required to achieve the target biological growth criterion developed by CTI (i.e. $10^4$ CFU/mL). Wastewater samples were concentrated to four cycles of concentration (CoC4) by evaporation at 40 ℃. A fine bubble diffuser was used to provide gentle aeration throughout the evaporation process to simulate ammonia stripping in recirculating cooling systems. Concentrated samples were used in the batch and bench-scale tests within 24 hours.

In pilot-scale tests, tertiary treated effluent was stored in 75-gallon HDPE tanks to serve as cooling tower makeup source. Details about the pilot-scale units are provided in Chien et al., (2012a). The makeup tanks were treated with pre-formed monochloramine at 1 mg/L to represent fresh tertiary effluents discharged from municipal wastewater treatment works. Planktonic heterotrophic bacteria in the recirculating water and in the makeup water were measured every 3-4 days during the pilot-scale tests. The average planktonic HPCs in the makeup water tank in all three tests was $10^{.4.04} \pm 10^{4.61}$ CFU/mL.

### 5.2.2 Chemical preparation and residual analysis

Preparation, use, and analysis of sodium hypochlorite and monochloramine are described by Chien et al. (2012 b, c). Chlorine dioxide stock solution was prepared using a small-scale chlorine dioxide generator (Envirox H1000SRE, Nalco Company, Naperville, IL). Chlorine dioxide concentration in the liquid stock solution varied from 300 and 500 mg/L depending on the quality of sodium chlorite stock solution. Chlorine dioxide ($ClO_2$) residuals were measured using a Hach DR/890 portable datalogging colorimeter (Hach, Loveland, CO) following the Indophenol method 10171 and 10126 (Hach, Loveland, CO).

### 5.2.3 Biological analysis

Water samples were cultured for planktonic bacteria counts following the spread plate count method (Method 9215 C. Spread Plate Method, APHA, 2012). A standard plate count agar (Fisher Scientific, USA) was used as the culture medium and the cultured samples were incubated for at least 48h at 35℃ to derive most probable numbers (MPN) of colony forming units. Circular stainless steel coupons (5.61 $cm^2$ in area) were used to monitor sessile biological growth as described by Chien et al. (2012b, c). Water samples were analyzed every week for Legionella species by the Special Pathogen Laboratory (Pittsburgh, PA). At the end of the field test, a 2x2 $cm^2$ piece of drift eliminator from each pilot-scale system having visible biomass accumulation was also analyzed for *Legionella*.

### 5.2.4 Experimental design

Evaluation of biocidal effectiveness and efficiency followed similar procedures developed previously by Chien et al. (2012b, c). The three-stage evaluation process was employed to provide side-by-side comparison of the chosen biocides at 40 ℃ in batch-, bench-, and pilot-scale tests. Batch experiments were designed to evaluate planktonic biological growth and biocide performance under static, well-controlled conditions. It should be noted that breakpoint chlorination tests were conducted in parallel where the first batch reactor was dosed with 1 mg/L NaOCl gradually to achieve breakpoint chlorination, while the second batch reactor received a slug dose of NaOCl required for breakpoint chlorination. The bench-scale recirculating system was used to study sessile biological growth and biocidal inactivation efficacy under the influence of hydrodynamic forces similar to those observed in full-scale cooling systems. A pilot-scale

cooling system equipped with both cooling and heating sessions was assembled to study biological growth control when using treated wastewaters as cooling tower makeup under realistic process conditions (Chien et al., 2012a).

Cost analysis for the use of three biocides in a full-scale cooling system was based on the dosing rate of each biocide obtained from the pilot-scale studies that was extrapolated to a full scale 550MW power plant cooling system requiring 28.8 million liters per day (7.5 MGD) (NETL, 2008) of MWW_NF with consistent quality.

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Biocide demand and biocidal efficiency in tertiary treated municipal wastewater at 40 ℃.

Table 5.2 shows the biocide demand and biocidal efficiency of sodium hypochlorite, monochloramine, and chlorine dioxide in raw MWW_NF at 40 ℃. It should be noted that Ct values were calculated using the residuals measured after 130 minutes while heterotrophic bacteria were cultured from samples collected after 120 minutes. Breakpoint chlorination was first evaluated in batch tests and it was determined that a $Cl_2$ : N as TKN weight ratio of 7.7 was required to consume 3.0 mg/L TKN (0.74 mg/L of $NH_3$-N plus organic nitrogen) in the unconcentrated MWW_NF sample at room temperature. Although the ammonia concentration in the MWW_NF was fairly consistent, records show that the average ammonia concentration was 1.42 mg/L as N and that the largest recorded value among 20 samples tested in this study was 3.4 mg/L. Therefore, even higher dose of NaOCl may be required to achieve free chlorine residual if the wastewater is not fully nitrified.

LeChevallier et al. (1988) showed that a Ct value of 3.3 mg/L·min was required to achieve 99% inactivation of common heterotrophic bacteria at 1-2 ℃ in chlorine demand-free water. However, the relatively high water temperature in this study resulted in higher chemical reactivity and rapid decomposition of free chlorine residual. Even the initial NaOCl dose of 4 mg/L above the breakpoint chlorination resulted in no measurable residual after a contact time of two hours. Although there was no residual left in the batch reactor, planktonic HPCs analyses showed an averaged 99.99% inactivation rate regardless of the amount of NaOCl added beyond breakpoint chlorination.

**Table 5.2.** Biocide demand and biocidal efficiency after 2 hour contact time with MWW_NF at 40 ℃

| Biocide | Dose, mg/L | 2-hr biocide residual, mg/L | 2-hr biocide demand, mg/L | Biocidal efficiency (%) | | | Ct, mg/L·min |
|---|---|---|---|---|---|---|---|
| | | | | Initial HPC, CFU/ml | 30 mins | 2 hrs | |
| **NaOCl** | **0.5** | 0.00[(1)] | 0.49 | $10^{5.48}$ | 99.99 | 99.99 | - |
| | **1** | 0.00 | 0.99 | | 99.99 | 99.99 | - |
| | **2** | 0.00 | 1.96 | | 99.99 | 99.99 | - |
| | **4** | 0.00 | 3.97 | | 99.99 | 99.99 | - |
| **In-situ formed $NH_2Cl$** | **0.5** | 0.00[(2)] | 0.35 | $10^{5.81}$ | 98.12 | 99.67 | - |
| | **1** | 0.00 | 0.85 | | 99.97 | 99.99 | - |
| | **2** | 0.00 | 1.85 | | 99.94 | 99.99 | - |
| | **4** | 0.22 | 3.63 | | 99.99 | 99.99 | 28.6 |
| **Pre-formed $NH_2Cl$** | **0.5** | 0.09[(3)] | 0.11 | $10^{5.20}$ | 91.98 | 99.40 | 11.7 |
| | **1** | 0.17 | 0.54 | | 99.98 | 99.98 | 22.1 |
| | **2** | 0.85 | 0.86 | | 99.92 | 99.98 | 110.5 |
| | **4** | 2.46 | 1.25 | | 99.71 | 99.95 | 319.8 |
| **$ClO_2$** | **0.5** | 0.07[(4)] | 0.20 | $10^{5.36}$ | 81.12 | 50.90 | 9.1 |
| | **1** | 0.14 | 0.63 | | 96.18 | 99.19 | 18.2 |
| | **2** | 0.12 | 1.65 | | 99.20 | 99.78 | 15.6 |
| | **4** | 0.13 | 3.64 | | 99.82 | 99.94 | 16.9 |

Note: (1) free chlorine residual as $Cl_2$; (2) total chlorine residual as $Cl_2$; (3) monochloramine residual as $Cl_2$; (4) chlorine dioxide as $Cl_2$

Batch tests with MWW_NF were also conducted to evaluate the effectiveness of in-situ formed monochloramine. Theoretically, the ammonia concentration in the wastewater should be sufficient to form total combined chlorine residual as inorganic chloramines, e.g. $NH_2Cl$, $NHCl_2$, etc. (Asano and Levine, 1998). However, NaOCl dosage below 2 mg $Cl_2$/mg $NH_3$-N (NaOCl dose below 4 mg/L) was unable to provide any combined chlorine residual within the contact time of 2 hours. High temperature may have driven the $OCl^-$ to oxidize compounds other than ammonia as previous studies have shown that the reaction of NaOCl with specific organic compounds was greatly enhanced by the increase in temperature (Abou-Rass and Oglesby, 1981; Sirtes et al., 2005). Chlorine demand in these tests with MWW_NF was similar to that observed for secondary treated municipal wastewater (Chien et al., 2012b) regardless of the improved quality of wastewater used in this study. Biocidal efficiency observed under these conditions was similar to that observed for breakpoint chlorination where a Ct value of 28.6 mg/L·min was able to achieve almost 99.9% HPC inactivation.

As shown in Table 5.2, the use of pre-formed $NH_2Cl$ in MWW_NF resulted in a reliable residual maintenance. An initial $NH_2Cl$ dosage of 1.0 mg/L was required to achieve 99.5% inactivation rate with a Ct value of 22.1 mg/L·min. This Ct value was lower than that required for 99% inactivation of heterotrophic bacteria in chlorine-demand free water at 1-2 ℃ but it was within the range of Ct values (15-72 mg/L·min) required to achieve 99.9% inactivation of common heterotrophic bacteria in drinking water at 25 ℃ (LeChevallier et al., 1988, 1990). This result confirms the previous finding that that an increase in water temperature greatly enhances the reactivity of $NH_2Cl$ in treated municipal wastewater (Chien et al., 2012b).

Chlorine dioxide residual was consistently observed in MWW_NF after 2 hours of contact time in all four batch tests conducted in this study. It is interesting to note that $ClO_2$ residual remained the same regardless of the increase of $ClO_2$ dosage above 1 mg/L. An initial dosage of 2 mg/L $ClO_2$ corresponding to Ct value of 15.6 mg/L·min was required to achieve the target 99.5 inactivation of HPCs in two hours. A Ct value of 9.1 mg/L·min was unable to achieve target inactivation of HPCs in MWW_NF, while a 50 times lower Ct value was shown to be sufficient to remove 99% of HPCs in chlorine-demand free water at 1-2 ℃ (LeChevallier et al., 1988). Stampi et al. (2002) also observed that the inactivation of total HPCs was lower than that of specific coliforms present in the secondary effluent.

### 5.3.2 Impact of cycles of concentration on biocidal efficiency and biocide residual in tertiary treated municipal wastewater at 40 ℃

Batch tests with slug biocide dosages were conducted in four times concentrated (CoC 4) MWW_NF with a target initial biocide dose equal to four times the dose required in the tests with unconcentrated MWW_NF. The initial dosages for NaOCl, $NH_2Cl$ and $ClO_2$ were 8 mg/L as NaOCl, 4 mg/L as $NH_2Cl$, and 8 mg/L as $ClO_2$, respectively. A dose of 9.6 mg/L of NaOCl was added to reach breakpoint chlorination in CoC 4 MWW_NF.

Figure 5.1 shows biocide residual in each test during a 2-hour experiment. The Ct values for breakpoint chlorination, in-situ formed $NH_2Cl$, preformed $NH_2Cl$, and chlorine dioxide in these tests were 16.3, 85.2, 153.4, and 64.4 mg/L·min, respectively. Biocide residual in the case of in-situ formed $NH_2Cl$ and $ClO_2$ had a significant drop within the first 10 minutes. On the other hand pre-formed $NH_2Cl$ had a much slower and gradual decrease in biocide residual, while 1 mg/L free chlorine residual after breakpoint chlorination gradually diminished within 40 minutes from the beginning of the test.

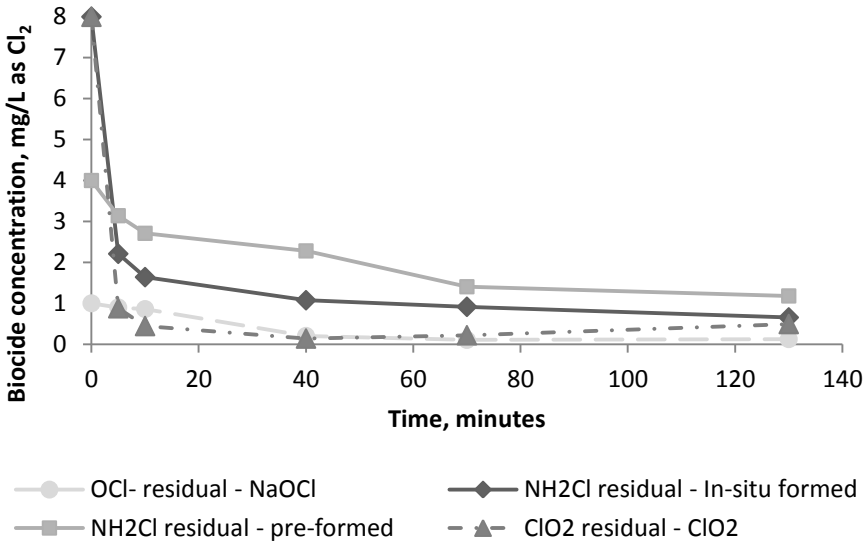


**Figure 5.1.** Biocide residuals in four times concentrated (CoC4) MWW_NF during batch tests at 40℃.

Although the use of pre-formed $NH_2Cl$ appears to be the most promising biocide with respect to maintaining the biocide residual in the wastewater, results of the biocidal efficiency analysis shown on Figure 5.2 suggest that only 1 mg/L NaOCl after breakpoint chlorination could achieve 99.5% (about 3 log) inactivation rate in CoC 4 MWW_NF. This result indicates that the initial biocide dosage required to achieve 99.5% HPC inactivation in concentrated wastewater, e.g. CoC 4 MWW_NF is much greater than that calculated based on a simple increase in cycles of concentration.

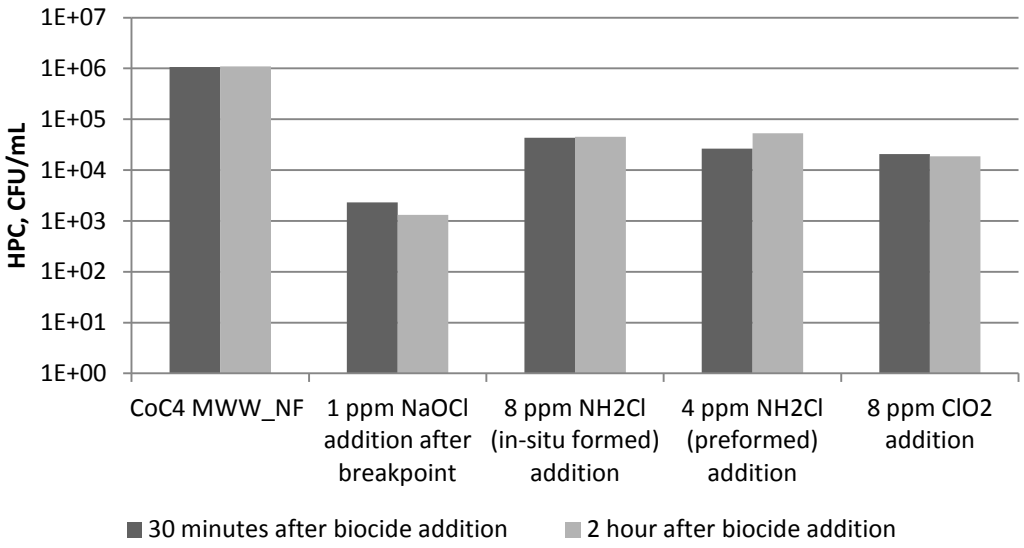


**Figure 5.2.** Biocidal efficiency of chlorine-based biocides against planktonic heterotrophic bacteria in four times concentrated (CoC4) MWW_NF in batch tests at 40℃.

### 5.3.3 Biological growth control in bench-scale recirculating system with CoC 4 MWW_NF

The effectiveness of different biocides in controlling biological growth was further tested in a bench-scale recirculating system designed to simulate temperature, flow velocity and water quality similar to those in a full-scale recirculating cooling systems. Concentrated MWW_NF was aerated in these tests and the average pH in all three tests was 8.4 ± 0.05. The initial planktonic HPCs in the untreated CoC 4 MWW_NF were $10^{5.76} \pm 10^{5.26}$ CFU/mL. The bench-scale test lasted for 72 hours and the recirculating system was treated with periodic biocide dosing to maintain a desired biocide residual. Planktonic HPCs were cultured at 4, 8, 12, 24, 48, and 72 hours and sessile HPCs were cultured after 12, 24, 48, and 72 hours. Planktonic and sessile HPCs profiles in these experiments are shown in Figure 5.3.

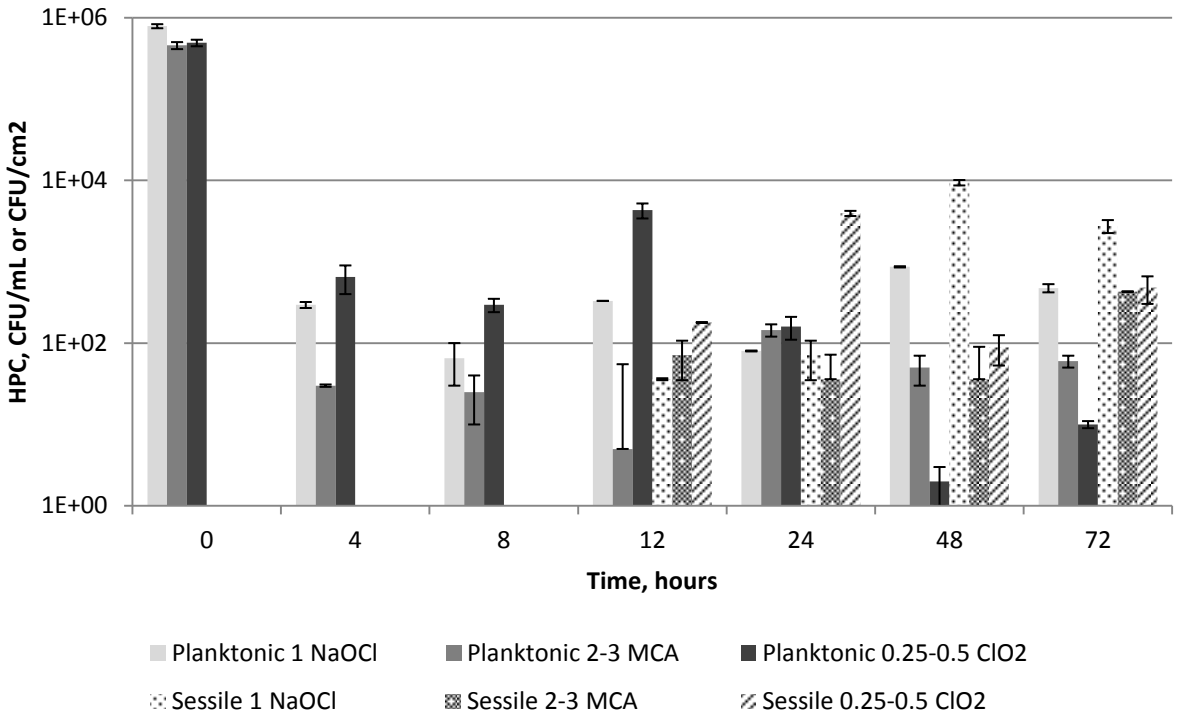


**Figure 5.3.** Effectiveness of NaOCl, $NH_2Cl$, and $ClO_2$ against planktonic and sessile HPCs in bench scale recirculating system operated with CoC 4 MWW_NF at 40°C.

A recirculating cooling system operated with surface water is usually treated by maintaining a free chlorine residual between 0.5-1 mg/L (CTI, 2008). The same criterion was adopted in this study that evaluated the use of MWW_NF as makeup. Since the initial inorganic ammonia concentration in CoC MWW_NF was 0.09 mg/L as $NH_3$-N, $NH_2Cl$ was only detected in the system during the early stages of the test (i.e., until the breakpoint chlorination was achieved). The free chlorine residual was 1.27 ± 0.75 mg/L as $Cl_2$ after reaching the breakpoint chlorination and sodium hypochlorite was added to the system at a rate of 1.10 mg/L per hour (i.e., total mass of biocide divided by total volume of makeup water added to the system during the entire test) to maintain this residual. Planktonic HPCs decreased from $10^{5.89}$ to below $10^4$ CFU/mL after four hours and remained below the control criterion until the end of the experiment. The analysis of sessile HPC indicated that biofilm formation was also controlled below $10^5$ CFU/cm$^2$ in the presence of 1.27 mg/L free chlorine residual.

Previous work has shown that $NH_2Cl$ residual of 3 mg/L can achieve good biological growth control when using secondary treated wastewater as cooling tower makeup (Chien et al., 2012b). A slightly lower target $NH_2Cl$ residual of 2-3 mg/L was used in this study since the tertiary effluent had better water quality. Monochloramine residual (2.29 ± 0.42 mg/L of $NH_2Cl$) accounted for approximately 83% of the total chlorine residual (2.77 ± 0.50 mg/L as $Cl_2$). Pre-formed monochloramine was added to the system at a rate of 0.59 mg/L per hour to maintain the $NH_2Cl$ residual in CoC 4 MWW_NF. Both planktonic and sessile HPCs were maintained below the control criteria of $10^4$ CFU/mL or $10^5$ CFU/cm$^2$, respectively throughout the experiment.

At present, there is no clear standard indicating the required $ClO_2$ residual for biological growth control in recirculating cooling tower systems. A widely accepted industrial criterion for *Legionella* control in recirculating institutional water system is to maintain $ClO_2$ residual

between 0.5-0.7 mg/L (Zhang et al., 2009). Therefore, a $ClO_2$ residual between 0.25-0.5 mg/L as $Cl_2$ in recirculating system was adopted in this test. The $ClO_2$ residual was 0.27 ± 0.12 mg/L as $Cl_2$ throughout the test. The dosing rate required to maintain this $ClO_2$ residual in CoC 4 MWW_NF was 1.04 mg/L per hour and was successful in controlling both planktonic and sessile HPCs in CoC 4 MWW_NF below the desired control criteria. Table 5.3 summarizes the biocide residual, biocide dosing rate, and results of biological growth control for selected biocides.

**Table 5.3.** Biocide dosing rates, biocide residuals, and biocidal effectiveness of selected biocides in bench-scale recirculating using CoC4 MWW_NF at 40 ℃

| Biocide | Dosing rate, mg/L-hr | Biocide residual, mg/L | Results |
|---|---|---|---|
| **NaOCl** | 1.10 | 2~3 as TC | Both planktonic and sessile biological growth were well controlled |
| **Pre-formed $NH_2Cl$** | 0.59 | 2~3 as MCA | |
| **$ClO_2$** | 1.04 | 0.25~0.5 as ClO2 | |

### 5.3.4 Biocidal Efficacy in Pilot-scale Experiments with CoC 4-5 MWW_NF

Pilot-scale experiments were conducted to confirm the findings from bench scale studies under more realistic conditions. The pilot scale experiment focused on the biocidal effectiveness against HPCs and *Legionella pneumophila* based on the optimal dosages obtained from bench-scale tests. Chemical regimes used for corrosion and scaling control are described by Choudhury et al. (2012) and Liu et al. (2012).

Effectiveness of sodium hypochlorite to control biological growth in pilot-scale cooling tower is shown in Figure 5.4. Free chlorine residual in this test was maintained at 1.99 ± 1.80 mg/L as $Cl_2$, while monochloramine residual averaged 0.09 ± 0.02 mg/L as $Cl_2$. The formation of $NH_2Cl$ was limited due to low initial ammonia concentration (0.75±0.25 mg/L) and effective ammonia stripping in the recirculating cooling system (Hsieh et al., 2012). On average, free chlorine residual accounted for 32 ± 20 % of total chlorine residual. Although NaOCl was dosed into the cooling water reservoir at similar rate as in the bench scale study (1.2 mg/L·hr of NaOCl), organic matter in MWW_NF resulted in conversion of more than 60% of NaOCl to organic chloramines. Planktonic HPCs in recirculating water were below the target criterion of $10^4$ CFU/mL throughout the test. The 10-day and 28-day sessile samples were approaching the sessile biological growth control criteria of $10^5$ CFU/cm$^2$ because the concentration of free chlorine was quite low in the period preceding these sampling events.

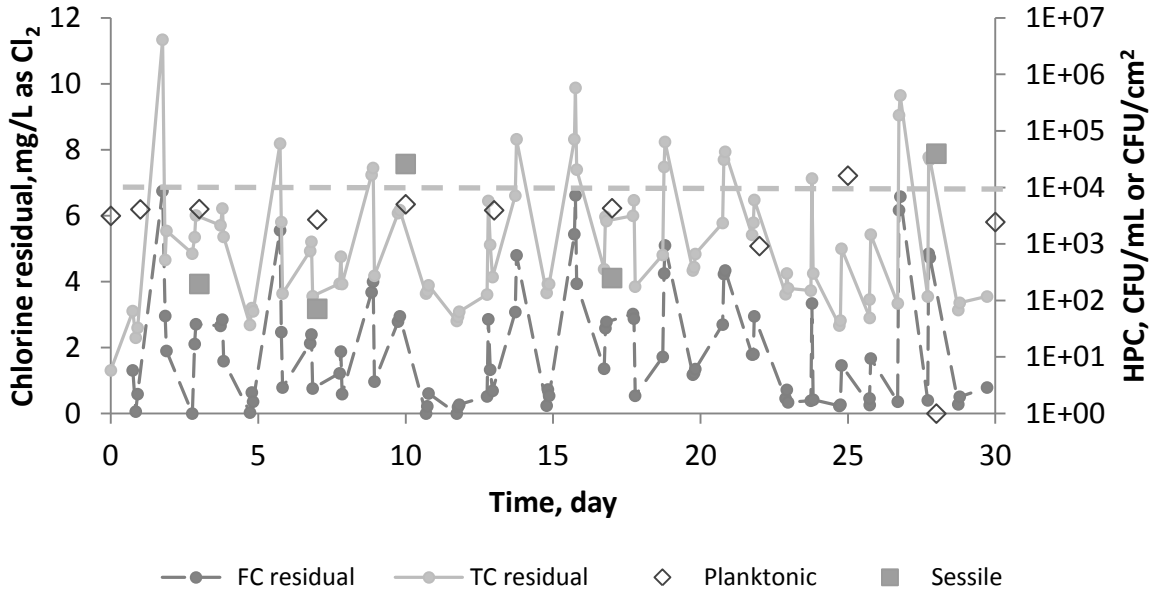


**Figure 5.4.** Biocide residual and HPCs in recirculating cooling system with chlorination and MWW_NF. Dashed line indicates the planktonic biological growth control criteria, $10^4$ CFU/mL.

Effectiveness of pre-formed $NH_2Cl$ for biological growth control is shown in Figure 5.5. Previous studies (Chien et al., 2012b; Vidic et al., 2009) demonstrated that the use of pre-formed $NH_2Cl$ is suitable for biological growth control in cooling towers using secondary treated municipal wastewater as makeup. In this test, $NH_2Cl$ residual was maintained at 2.76 ± 1.10 mg/L as $Cl_2$ for 30 days. On average, the $NH_2Cl$ residual accounted for 85% of total chlorine residual (3.16 ± 1.11 mg/L) throughout the test. Planktonic HPCs results were mostly below $10^4$ CFU/mL except for one sample on Day 26 because nearly no $NH_2Cl$ residual was detected in the system one day prior to sampling. Among the four sessile samples taken during the 30-day period, only the last sample showed the biofilm growth that approached the control criterion of $10^5$ CFU/cm$^2$. In general, sessile HPCs were well controlled to at least 1-log below the CTI criterion throughout the test.

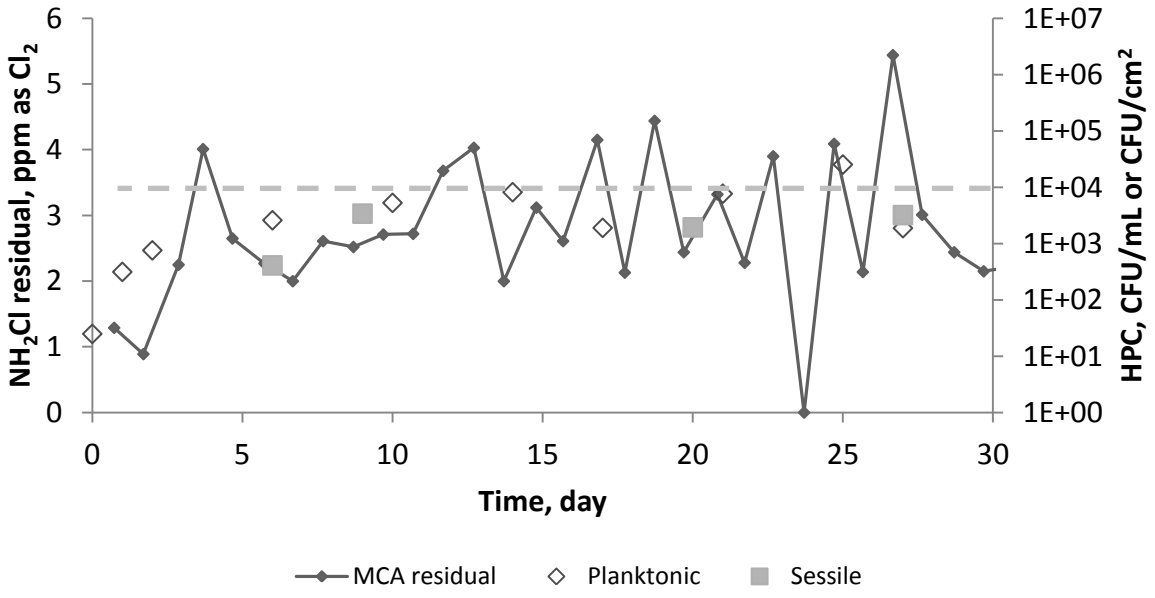


**Figure 5.5.** Biocide residual and HPCs in recirculating cooling system with chloramination and MWW_NF. Dashed line indicates the planktonic biological growth control criteria, $10^4$ CFU/mL.

Biological growth control with $ClO_2$ is illustrated in Figure 5.6. Chlorine dioxide residual averaged at 0.41 ± 0.16 mg/L as $Cl_2$ throughout the experiment. In the first 10 days of test, the $ClO_2$ was maintained between 0.25 and 0.5 mg/L and it was observed that planktonic HPCs frequently exceeded the control criterion. The target residual concentration was then increased to 0.5-1.0 mg/L $ClO_2$ for the remaining test period. This adjustment resulted in much better control of sessile biological growth, which was reduced from $10^{4.5}$ to below $10^2$ CFU/cm$^2$ on day 28.

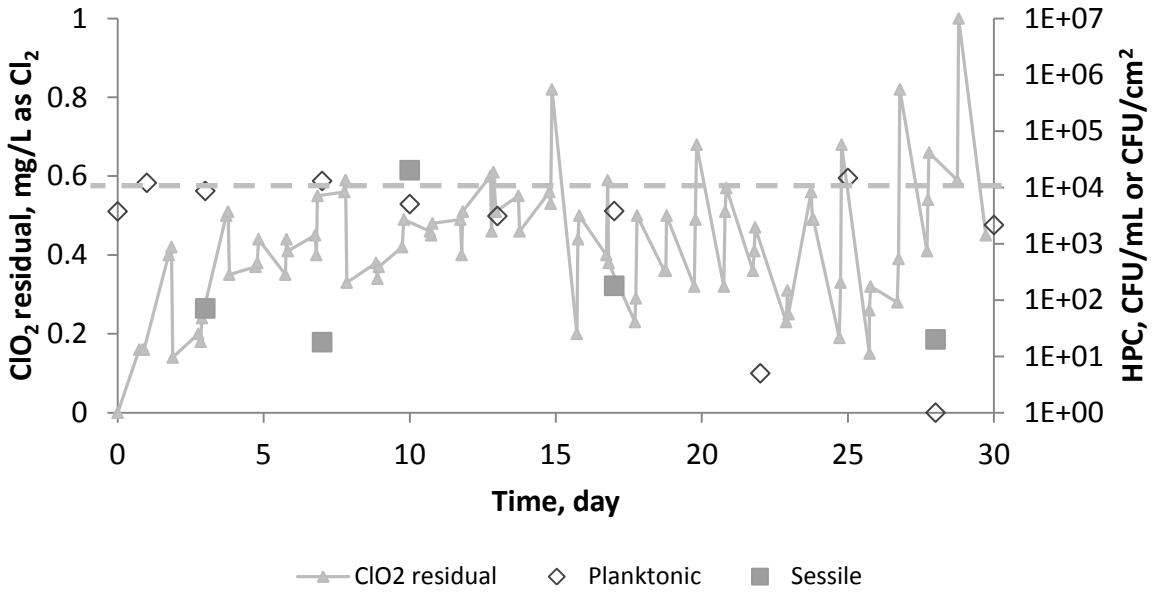


**Figure 5.6.** Biocide residual and HPCs in recirculating cooling system with chlorine dioxide and MWW_NF. Dashed line indicates the planktonic biological growth control criteria, $10^4$ CFU/mL.

Recirculating cooling water samples from pilot-scale systems were sent weekly to the Special Pathogen Laboratory (Pittsburgh, PA) for *Legionella* analysis. Pieces of drift eliminator and packing having visible microbial-deposit were also analyzed for *Legionella* at the end of the test. Regardless of the type of biocide used, all samples were negative for Legionella indicating that this opportunistic pathogen was not able to grow in the pilot-scale cooling systems fed with MWW_NF and with continuous biocide addition over a period of 30 days.

### 5.3.5 Economic Analysis

Economic analysis was conducted based on the biocide usage observed in pilot-scale tests with MWW_NF as makeup. Biocide dosing rate was calculated by multiplying the volume of biocide stock solution consumed daily and biocide concentration in the stock solution. The biocide dosing rate was then normalized by daily makeup water volume to estimate the overall cost required for large scale cooling systems based on the chemical unit costs obtained from manufacturers. Table 5.4 lists the biocide dosing rates, chemical unit costs, and estimated daily costs for all three biocides. Sodium hypochlorite was the most cost-effective biocide, while pre-formed monochloramine was the most expensive because it required more than twice the amount of NaOCl. The high biocide unit cost of $ClO_2$ reflects the cost of more complicate production process and the value of chemicals required for $ClO_2$ generation.

**Table 5.4.** Biocide residual, dosing rate, and biocide consumption in MWW_NF tests

| Biocide | Biocide residual (mg/L) | Biocide dosing rate (g/day) | Biocide dose per liter makeup (g/L-day) | Unit cost for biocide (USD/kg) [4] | Estimated daily cost per $10^6$L makeup (USD/day)[5] | Estimated annual cost for 550 MW power plant (28.8 LGD) (USD/yr)[5] |
|---|---|---|---|---|---|---|
| **NaOCl** | 1.99±1.80[1] | 5.75 | 0.028 | 0.99 | 28 | 294,336 |
| **$NH_2Cl$** | 2.76±1.10[2] | 10.08 | 0.050 | 1.01 | 51 | 546,112 |
| **$ClO_2$** | 0.41±0.16[3] | 1.17 | 0.006 | 6.61 | 40 | 420,480 |

(1) residual as free chlorine; (2) residual as monochloramine; (3) residual as chlorine dioxide; (4) dollar value in 2009 obtained from Puckorius & Associates, Inc., Crown Solutions, and Eka chemicals, Inc.;(5) dollar value in 2009

## 5.4 SUMMARY AND CONCLUSIONS

The primary objective of this study was to investigate the effectiveness of sodium hypochlorite, pre-formed monochloramine, and chlorine dioxide as biocides to control biological growth in recirculating cooling systems employing tertiary treated municipal wastewater as sole makeup water. Secondary objective of this study focused on cost for different biocides needed to achieve proper biological growth control.

Water parameters, such as temperature, cycles of concentration, and ammonia concentration of recirculating water, critically affected the biocide performance in the cooling systems. Laboratory batch studies confirmed improvement in biocidal effectiveness of all three biocides in the tertiary treated municipal wastewater with an increase in temperature. A linear increase in the initial biocide dosage with an increase in cycles of concentration of wastewater was not adequate to control the planktonic biological growth regardless of the type of biocide used. Variable ammonia concentrations in pilot-scale cooling systems resulted in occasionally more aggressive sessile biological growth.

Optimal biocide dosing schemes required to achieve adequate biological growth control were evaluated in bench- and pilot-scale tests. Bench-scale studies in a recirculating system with continuous biocide addition indicated that all three biocides could achieve biological growth control criteria for 72 hours despite periodic addition of fresh microorganisms and nutrients. Pilot-scale tests were conducted using the optimal biocide dosing and residuals determined from bench-scale tests. The studies revealed that the biocide dosing rates established in bench-scale tests did not adequately reflect the biocide dosages required to maintain target residuals in larger recirculating cooling systems. The optimal residuals of NaOCl, $NH_2Cl$, and $ClO_2$ to achieve recommended biological growth criteria were 1, 2-3, and 0.5-1.0 mg/L as $Cl_2$, respectively. Free chlorine was the most cost-effective disinfectant for recirculating cooling systems using tertiary treated municipal wastewater (MWW_NF).

Pilot-scale tests also revealed complete absence of *Legionella pneumophila* from the system, which ensures the safety of those who work or live around a recirculating cooling systems using tertiary treated municipal wastewater as makeup.

# 6.0 SUMMARY, CONCLUSIONS AND FUTURE WORK

## 6.1 SUMMARY AND CONCLUSIONS

This study evaluated the use of treated municipal wastewater in power plant cooling systems as makeup water, with a focus on understanding the kinetics, effectiveness, and mitigation of biological growth using chlorine-based biocides. The specific objectives of this study were to: 1) develop a methodology for evaluating the biological growth under realistic conditions by employing a pilot-scale recirculating cooling tower; 2) determine the effectiveness of pre-formed monochloramine in recirculating cooling systems using secondary treated municipal wastewater; 3) determine the impact of tertiary treatments on performance of pre-formed monochloramine in recirculating cooling systems 4) conduct comprehensive evaluation of the applicability of three chlorine-based biocide, i.e. sodium hypochlorite, monochloramine, and chlorine dioxide, under process conditions relevant to cooling system operation in both lab-scale and pilot-scale systems. The main findings were summarized in the following four sections with respect to the four objectives described above.

### 6.1.1 Design of pilot-scale cooling system for evaluating biological growth control under realistic conditions.

A pilot-scale cooling tower was designed for testing different scaling, corrosion, and biofouling control strategies for potential use of treated municipal wastewater in full-scale recirculating cooling systems. The system integrated the core operating conditions in real power plant cooling systems with corrosion/scaling/biofouling monitoring system. It was demonstrated that the pilot-scale cooling system can be useful for evaluating of different chemical regimes under varying operating conditions in a cooling system with makeup water of complex quality.

### 6.1.2 Use of secondary treated municipal wastewater as cooling tower makeup

Chloramination of recirculating cooling systems using secondary treated municipal wastewater as makeup was identified as a successful biological growth control strategy based on the results of planktonic and sessile heterotrophic bacteria and *Legionella* culturing. Pre-formed monochloramine was found to be more effective than in-situ formed chloramines in controlling biological growth. Ammonia variation in the treated municipal wastewater was found to significantly affect the effectiveness of in-situ monochloramine formation as a biofouling control strategy. Both bench- and pilot- scale recirculating tests demonstrated that it was difficult to achieve requisite biocidal efficacy by the addition of sodium hypochlorite when the ammonia concentration in the cooling water was low.

Pilot-scale testing indicated that maintaining a total chlorine residual at 3 - 4 mg/L and relying on in-situ formed monochloramine was still insufficient to control both planktonic and sessile biological growth. Maintaining a total chlorine residual at 3 – 4 mg/L (monochloramine

residual above 3 mg/L) as $Cl_2$ by the addition of pre-formed monochloramine was effective in controlling planktonic and sessile biological growth to desired levels. The higher dosing requirement observed in pilot-scale studies was due to greater variability in the operating conditions relative to the bench-scale testing.

### 6.1.3 Complete absence of *Legionella pneumophila* was observed in the pilot-scale tests using secondary treated municipal wastewater as cooling tower makeup. This finding ensures the safety of those who work or live around a recirculating cooling systems using this impaired water as makeup.Impact of tertiary treatment on the effectiveness of pre-formed monochloramine

Although the use of secondary treated effluent as cooling tower makeup was feasible with respect to biological growth control, severe scaling formation was found to make this option less preferable for real application. Therefore, the applicability of monochloramine was evaluated in cooling systems using secondary effluent subjected tertiary treatment as cooling tower makeup.

The use of different tertiary treatments was determined to have limited influence on biological growth potential (e.g. planktonic and sessile heterotrophic bacterial growth) and biocidal efficiency of monochloramine in treated municipal wastewater. Direct comparison of biological growth between MWW_NF and MWW_NFG indicated that TOC reduction through tertiary municipal wastewater treatment can hinder biological growth rate but does not affect the overall biological growth potential.

Applying tertiary treatment to secondary effluent can critically affect the stability of monochloramine residual in the recirculating cooling water. The amount of monochloramine required to restrain biological growth was significantly reduced when secondary effluent was

treated with nitrification and sand filtration (MWW_NF) prior to use as cooling tower makeup. Although MWW_NF subjected to GAC adsorption resulted in better water quality, further improvement in monochloramine stability and biocidal efficiency was quite limited.

It was determined that nitrification and sand filtration represent optimal tertiary treatment to effectively use pre-formed monochloramine for biological growth control in recirculating cooling systems. Monochloramine residual required to achieve proper biological growth control was reduced to 2-3 mg/L and the required dosing rate was reduced by 30% compared to secondary treated municipal wastewater.

Similar to the results observed in tests using secondary effluent, complete absence of *Legionella pneumophila* was observed in the pilot-scale tests. This finding ensures the safety of those who work or live around a recirculating cooling systems using either secondary or tertiary treated municipal wastewater as makeup.

### 6.1.4 Comprehensive evaluation of chlorine, monochloramine, and chlorine dioxide for the control of biological growth

With the improved water quality and promising performance observed in tests with chloramination, additional testing was carried out to evaluate the applicability of common chlorine-based biocides in recirculating cooling systems using tertiary treated effluent. The extended study focused on the effectiveness of sodium hypochlorite, pre-formed monochloramine, and chlorine dioxide as primary biocides to control biological growth.

Optimal chemical regimes for biological growth control were determined using the systematic analysis developed in this study. Pilot-scale tests showed that optimal residual of NaOCl, $NH_2Cl$, and $ClO_2$ to achieve recommended biological growth criteria were 1, 2-3, and 0.5-1.0 mg/L as $Cl_2$, respectively.

Cost analysis was conducted to provide additional guidance to utilities considering the use of municipal wastewater for recirculating cooling systems. Among the three biological growth control strategies, use of sodium hypochlorite was the most cost-effective when using tertiary treated effluent as cooling tower makeup. Chemical cost in the case of $NH_2Cl$ was driven by the high biocide residual requirement. Despite having the lowest dose requirement for appropriate biological growth control, $ClO_2$ still exhibited higher cost compared to monochloramine.Both batch and bench-scale recirculating tests accurately predicted relative trends of biological growth and biocidal effectiveness as a function of water quality. However, laboratory tests underestimated the biocide requirements in pilot-scale tests by as much as 4 to 6 times. The increase in cycles of wastewater concentrations in the recirculating cooling systems resulted in a non-linear increase in the initial biocide dosage required to control the planktonic biological growth.

### 6.1.5 Overall findings

In summary, use of the treated municipal wastewater in recirculating cooling system was found to be feasible with respect to biological growth control by maintaining proper biocide residual. Monochloramine was determined to be as effective as other chlorine-based biocides in recirculating cooling systems using treated municipal wastewater. Secondary treated effluent subjected to nitrification and sand filtrations posed a preferable water quality and significantly decrease the biocide dose required for proper biological growth control.

## 6.2 KEY CONTRIBUTIONS

This study contributes to a better understanding of the kinetics, effectiveness, and mitigation of biological growth in the power plant cooling systems using treated municipal wastewater. The pilot-scale system developed in this study provides a convenient and reliable system to study the biological growth, scaling, and corrosion under realistic process conditions. This system can also help to guide the use of biocides for effective control of biological growth control in wastewater reuse applications for thermoelectric power plant cooling systems.

The original contributions of this study include: 1) design and assembly of a transportable pilot-scale system to evaluate major challenges associated with water quality in recirculating cooling systems; 2) identifying pre-formed monochloramine as an effective and reliable biocide for biological growth in cooling systems using secondary effluent as makeup; 3) scientific evidence and understanding based on laboratory and pilot-scale studies of the biocidal effectiveness of pre-formed monochloramine in three types of tertiary treated municipal

wastewaters as makeup for power plant cooling; 4) identifying nitrification and sand filtration as optimal tertiary treatment for wastewater reuse with respect to biological growth control; and 5) discovery that sodium hypochlorite was the lowest cost biocide for cooling systems employing tertiary treated effluent as makeup.

## 6.3 FUTURE DIRECTIONS

This study points to a promising future for wastewater reuse in power plant cooling systems with respect to biological growth control. To broaden the scope of the work in the areas of evaluation and mitigation of microbiological activities, several directions for future work are suggested below.

Developing a biocide consumption model in recirculating cooling system would be helpful to evaluate the actual biocide usage under realistic conditions. Preliminary results of the chlorine and monochloramine consumptions in a batch reactor showed that parallel first order model can best simulate the combined chlorine residuals under static and well controlled conditions (Appendix A and B). However, the batch reactor did not consider the effects of hydrodynamic forces, exposure to metal/plastic materials, and air stripping in full-scale recirculating cooling systems.

Sessile biological growth on stainless steel specimen was found to be less severe in comparison to that on the plastic packing material. An average 3% weight gain on packing material was observed in the field tests. Cases show that severely fouled packing could lead to a collapse of the interior structure and affect the energy generating efficiency. Therefore, biological growth tendency on different materials (i.e. PVC, copper, etc.) should be studied to understand the overall biological growth control in cooling systems using treated municipal wastewater.

The fate of inorganic nitrogen in the recirculating cooling system can be further studied to better understand whether the use of monochloramine can lead to abrupt variation of nitrate concentrations in open loop recirculating cooling system. The mass balance of nitrate concentration attempted for the pilot-scale tests at 4-6 CoC was not adequate. It is not clear whether nitrate is consumed through oxidization or denitrification. By closely monitoring the ammonia, nitrite, nitrate, and TKN concentrations in sterilized wastewater, the consumption through oxidation can be determined. Bacterial phenotyping for denitrifying bacteria in the recirculating water can be employed to exclude the occurrence of biological denitrification.

Depending on the final disposal alternative for the blowdown (i.e. surface water, wastewater treatment works, etc.), it may be required to dechlorinate the blowdown in order to meet the NPDES permit. Therefore, a study of the disinfection byproducts should focus on identifying and quantifying the major byproducts for each disinfectant evaluated in this study. This would be helpful for subsequent life cycle assessment that needs to include environmental and health impacts.

Additional study is required to determine whether the *Legionella* species were out-competed by heterotrophic bacteria or were specifically controlled by monochloramine in recirculating cooling systems using treated municipal wastewater as makeup. The outcome of

this study will help to understand how the *Legionella* growth was limited when treated municipal wastewater was used and provide additional assurance against potentially dangerous aerosol emissions.

# APPENDIX A

# KINETIC MODEL OF CHLORINE CONSUMPTION IN BATCH SYSTEMS

## A.1 APPROACH

Breakpoint chlorination is undoubtedly the most effective biocide process used in various industrial applications. However, emerging issues of public health related to exceeding chlorination byproducts have somewhat affected the breakpoint chlorination applications in practice. Our recent work has shown that chloramination with pre-formed monochloramine can achieve similar biocidal effectiveness as breakpoint chlorination in highly concentrated treated wastewater and can be more efficient regarding the overall chemical usages.

In order to improve understanding of the residual chlorine decomposition, data gathered from laboratory experiments were fitted with five different chlorine decay models. These models derived from the kinetic studies could provide valuable information for planning disinfection in wastewater reuse applications. However, it should be noted that the conclusions should be considered representative of only bulk chemical decay under specific conditions and that other environmental factors may have to be evaluated separately.

## A.2 METHODS

The decay of free and combined chlorine in three different tertiary treated municipal wastewaters was evaluated in the laboratory. For each combination of wastewater type and biocide at room temperature or at 40 ℃, a total of 16 data points were used to derive the reaction rate constant and the fraction of less reactive components indicated by each fitting model.

Five different biocide decay models (Table A.1) were used to simulate the biocide decomposition rate in a closed batch system. It has been known that the effectiveness of chlorine dosing critically depends on the type and fraction of available chlorine. Therefore, both total chlorine residual and monochloramine residual were fitted into each model to obtain information about the fate of different forms of chlorine in these waters.

**Table A.1.** Summary of candidate rate laws for biocide decay fitting

| Type | $f(C_o, t)$ (Equation 2) | Adjustable parameters |
|---|---|---|
| First order decay | $C_o \exp(-kt)$ | $k$ |
| Power law decay ($n^{th}$ order) | $(kt(n-1) + (1/C_o)^{n-1})^{-(1/n-1)}$ | $k$, $n$ |
| First order decay with stable component | $C^* + (C_o - C^*) \exp(-kt)$ | $k$, $C^*$ |
| Power law decay with stable component ($n^{th}$ order) | $C^* + (kt(n-1) + (1/(C_o - C^*)^{n-1})^{(1/n-1)}$ | $k$, $n$, $C^*$ |
| Parallel first order decay | $C_o x \exp(-k_1 t) + C_o (1-x) \exp(-k_2 t)$ | $k_1$, $k_2$, $x$ |

Source: Haas, C.N. and Karra, S.B., Kinetics of wastewater chlorine demand exertion, Journal WPCF, Vol. 56, Number 2, pp 170-173

From the comparison of coefficients of determination and standard deviation of residuals, it was found that a parallel first-order decay model provided the best fit for determining total chlorine demand in all three types of wastewaters. The parallel first order decay model assumes that the overall decay proceeds through two independent first order reactions. Accordingly, a number of fast reactions lead to the formation of reaction products that can be differentiated in two groups. The first fraction includes the reactions with reducing reagents (e.g., inorganic

reductants and common organic matter) that reduce hypochlorite to a final product (e.g. chloride ion). The second group involves the formation of chlorinated products which maintain oxidative potential (e.g. inorganic chloramines). Therefore, the total disinfectant concentration includes these products in addition to un-reacted hypochlorite.

After these initial fast reactions, the remaining disinfectant species, at $C_0$ concentration, can be separated into two fractions from a kinetic point of view: (1) a higher reactive fraction, whose concentration is expressed as $xC_0$, which includes stronger oxidizing agent such as hypochlorite, and (2) a slower reactive fraction with concentration expressed as $(1-x)\ C_0$, which contains other disinfectant chlorinated species (e.g. $NH_2Cl$) not included in the previous fraction. Note that x is limited to a range between 0 and 1.

Table A.2 summarizes the water quality from studies conducted by Hass and Karra (1984), March et al. (2005), and this study. Unfortunately, only nitrogen species and pH were provided by Haas and Karra (1984), and no data on grey water quality were reported by March et al. (2005). It was observed that MWW used in this study had slightly lower pH and higher ammonia concentration in comparison to the three MWW waters described by Hass and Karra (1984). The average nitrate concentration in our study was within the range shown by Hass and Karra.

Treated secondary effluent from the Peoria plant represents a combination of domestic and industrial wastewaters treated with a high-rate activated sludge process. The one from Morton was mainly domestic wastewaters from a stabilization plant comparable to a standard-rate activated sludge plant. The last one from Washington was domestic wastewater from a standard-rate trickling filter unit.

**Table A.2.**Water characteristics from three studies on the fate of chlorine species in MWW

| Source | pH | Ammonia N (mg/L) | Nitrate N (mg/L) | Organic N (mg/L) | Reference |
|---|---|---|---|---|---|
| Peoria (MWW) | 7.4-7.7 (7.5) | 7.1-19.4 (10.5) | 0.1-0.4 (0.3) | 2.6-9.8 (4.2) | Hass and Karra (1984) |
| Morton (MWW) | 7.4-7.6 (7.6) | 0.3-2.0 (1.4) | 5.7-12.2 (9.5) | 1.4-3.4 (2.5) | Hass and Karra (1984) |
| Washington (MWW) | 7.4-8.0 (7.8) | 6.3-9.4 (7.2) | 6.4-16.7 (9.3) | 0.1-0.6 (0.4) | Hass and Karra (1984) |
| Grey water from hotel | None available | | | | March et al (2005). |
| FTMSA (MWW) | (7.1) | (21.0) | (3.6) | N/A | This study |
| FTMSA (MWW_NF) | (6.8) | 0.3-1.2 (0.78) | 7.5-16.4 (11.2) | N/A | This study |
| FTMSA (MWW_NFG) | (7.9) | 0.2-0.8 (0.4) | 1.5-19.7 (11.8) | N/A | This study |

Note: (#) indicates the average value

The observed $k_1$, $k_2$, and x values by Hass and Karra (1984) are summarized in Table A.3. As described above, $k_1$ represents the first order decay coefficient for more reactive chlorine form and $k_2$ represents the first order decay coefficient of less reactive chlorine form in the wastewater sample. For the cases of treated domestic wastewaters, the standard error (the standard deviation of the differences between the predicted and observed chlorine residual) was 0.13 to 0.31 mg/L. The correlation coefficients indicate that the use of parallel first order decay models yielded a good fit to the experimental data in different types of secondary effluents and grey waters.

**Table A.3.** Parameters of parallel first order decay models from previous studies.

| Source | $k_1$ ($Min^{-1}$) | $k_2$ ($Min^{-1}$) | x | Correlation coefficient | Standard error (mg/L) |
|---|---|---|---|---|---|
| Peoria (MWW) | 1.01-1.42 | 0.002-0.004 | 0.170-0.344 | 0.943-0.999 | 0.366-0.850 |
| Morton (MWW) | 0.74-1.06 | 0.001-0.005 | 0.115-0.645 | 0.856-0.999 | 0.140-1.628 |
| Washington (MWW) | 0.79-1.25 | 0.001-0.002 | 0.157-0.220 | 0.999-0.999 | 0.134-0.307 |
| Grey water from hotel | N/A | N/A | N/A | 0.993 | 0.7 |

## A.3 RESULTS AND DISCUSSION

Results of this study are shown in graphical form in terms of residual biocide concentration in different types of treated wastewaters. Only the results of MWW+NaOCl and MWW+MCA were shown in this chapter and detailed information about model fitting for each biocide and wastewater combination is described in Appendix B. Among the four different initial dosage tested in this study (i.e., 0.5, 1, 2, and 4 mg/L of NaOCl as $Cl_2$), only the results for the initial biocide concentration of 4 mg/L are displayed below. Figure A.1 and Figure A.2 show the measured total chlorine residuals in MWW versus the curves generated from different fitting models. It should be noted that first-order decay with stable component and power law decay with stable component models were not included in Figure A.1 due to insufficient data of monochloramine and other chloramine residuals. The first-order decay model results compare well with the parallel first-order decay model results in estimating the total chlorine residual.

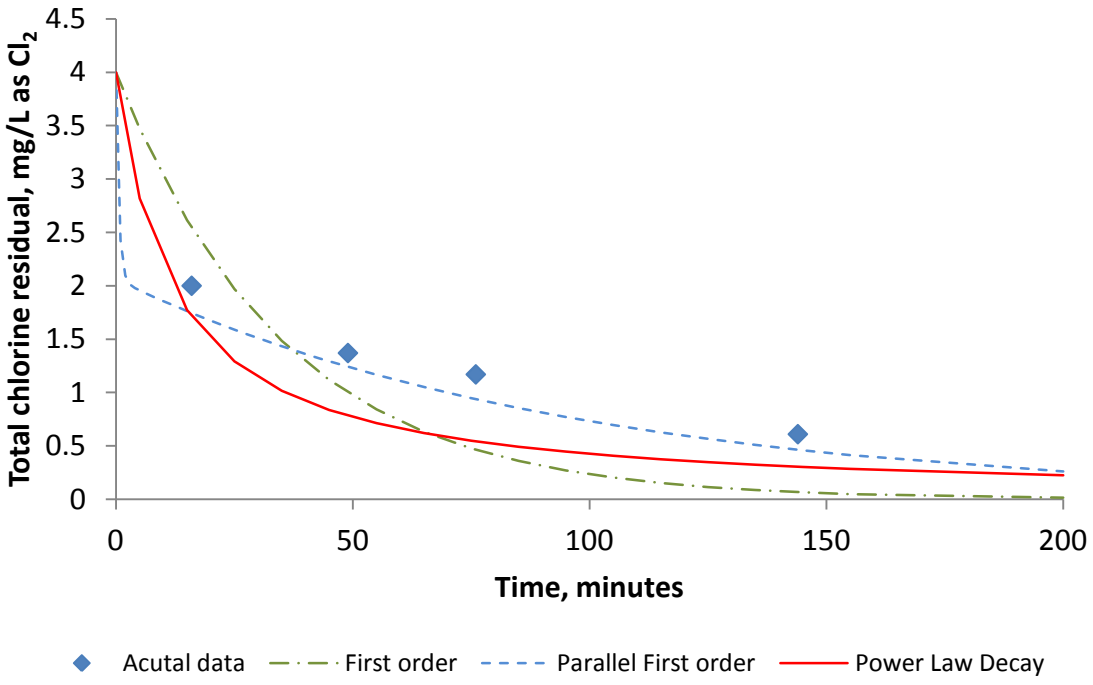


**Figure A.1.** Actual versus total chlorine residual estimated by different consumption models when adding 4 mg/L of NaOCl into 200 mL MWW at 40℃.

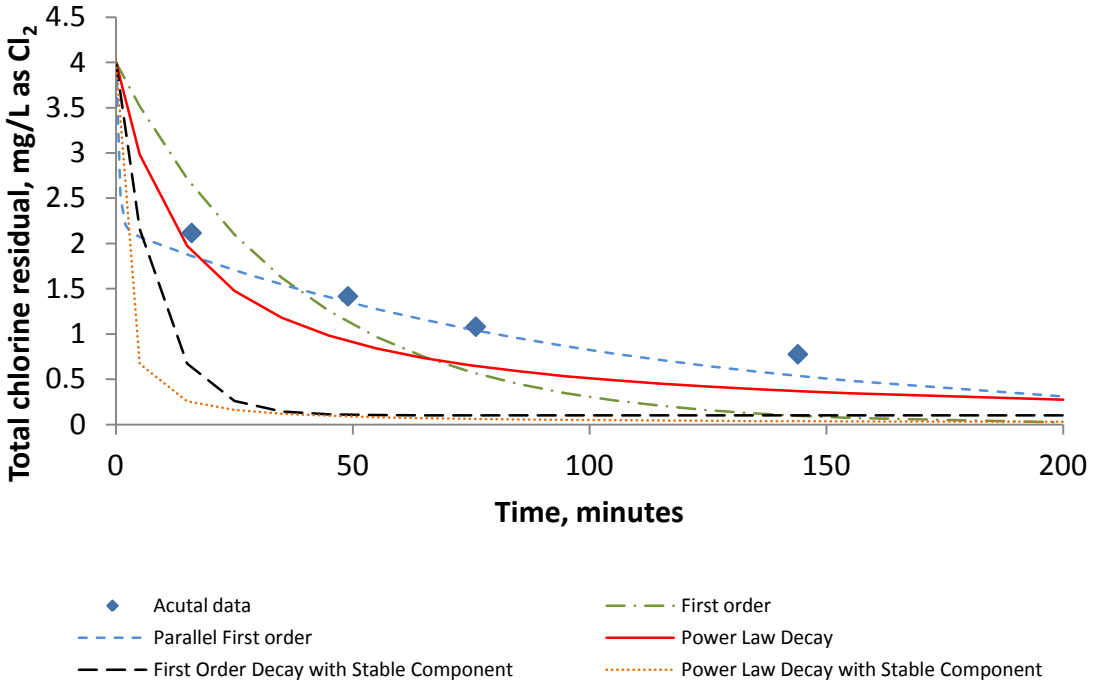


**Figure A.2.** Actual versus total chlorine residual estimated by different consumption models when adding 4 mg/L of pre-formed MCA into 200 mL MWW at 40℃.

Table A.4 summarizes the model fitting parameters for all five models when using NaOCl as a biocide for wastewater. The correlation coefficient was calculated by correlating actual values with simulated values, and the standard error indicates the difference between the two values. Modeling with first order decay and power law decay with stable components was not included in all cases since the major stable component, assuming monochloramine, was not determined. It was observed that the parallel first order decay model was the best fitting model based on correlation coefficient and standard error.

As described above, $k_1$ and $k_2$ represent the fast and slow reactive components of total chlorine residuals, respectively, and factor x represents the ratio of the fraction of rapidly decomposing species to that of the slowly decomposing species. Hass and Karra (1984) showed that 10-40% of chlorine applied to MWW decayed with a first order rate constant of 1 $min^{-1}$ in MWW, and the first order rate constant for the decomposition of the slow decaying fraction, $k_2$, was in good agreement with the rate constant for organic and inorganic chloramines. However, in our study with sodium hypochlorite in MWW at room temperature, only 7% of applied chlorine decayed at a much faster rate of 1.77 $min^{-1}$, while the slower decay rate was 0.002 min-1, similar to Hass and Karra's observation.

The fraction of fast decaying chlorine (factor x) at room temperature increased with improved wastewater quality. It was observed that factor x increased significantly from secondary effluent to tertiary effluent but remained similar when advanced GAC treatment was applied. That is to say, formation of stable chloramines, assuming mainly monochloramine, decreased when the major ammonia component was removed from the wastewater.

As the water temperature was increased, the slower decay rates increased 3-5 fold in all three water samples but fast decay rates decreased, especially in cases of MWW_NF and MWW_NFG. It was observed that fast decay rates increased when water quality improved. However, this observation contradicted the findings of Powell et al. (2000), where chlorine decay rate dramatically decreased together with TOC removal. Similar fast decay rates were observed in all three water samples at 40 ℃ because the kinetics of chlorine decay rate is more temperature sensitive. However, there is no clear explanation for higher fast decay rate observed with improved water quality at room temperature.

**Table A.4.** Model parameters for fitting of NaOCl biocide decay in three different wastewaters using five different fitting models.

| Wastewater type | Model | Temp (℃) | $k_1$ ($Min^{-1}$) | $k_2$ ($Min^{-1}$) | x | Correlation coefficient | Standard error (mg/L) |
|---|---|---|---|---|---|---|---|
| MWW | Parallel first order | 23 | 1.767 | 0.002 | 0.074 | 0.995 | 0.268 |
| | | 40 | 1.610 | 0.010 | 0.485 | 0.964 | 0.190 |
| | First order | 23 | 0.003 | - | - | 0.991 | 0.258 |
| | | 40 | 0.028 | - | - | 0.826 | 0.377 |
| | Power law decay (n=2) | 23 | 0.001 | - | - | 0.988 | 0.308 |
| | | 40 | 0.021 | - | - | 0.760 | 0.390 |
| MWW_NF | Parallel first order | 23 | 2.289 | 0.006 | 0.312 | 0.978 | 0.258 |
| | | 40 | 1.618 | 0.018 | 0.551 | 0.971 | 0.121 |
| | First order | 23 | 0.013 | - | - | 0.917 | 0.360 |
| | | 40 | 0.054 | - | - | 0.822 | 0.266 |
| | Power law decay (n=2) | 23 | 0.007 | - | - | 0.892 | 0.432 |
| | | 40 | 0.043 | - | - | 0.752 | 0.290 |
| MWW_NFG | Parallel first order | 23 | 3.271 | 0.002 | 0.303 | 0.986 | 0.218 |
| | | 40 | 1.608 | 0.008 | 0.495 | 0.947 | 0.273 |
| | | 40 | 1.608 | 0.008 | 0.223 | 0.985 | 0.242 |
| | First order | 23 | 0.007 | - | - | 0.938 | 0.350 |
| | | 40 | 0.025 | - | - | 0.788 | 0.455 |
| | | 40 | 0.012 | - | - | 0.952 | 0.290 |
| | Power law decay (n=2) | 23 | 0.003 | - | - | 0.918 | 0.401 |
| | | 40 | 0.017 | - | - | 0.715 | 0.484 |
| | | 40 | 0.006 | - | - | 0.928 | 0.404 |
| | First order with stable component | 23 | 0.007 | - | - | 0.938 | 0.348 |
| | | 40 | 0.025 | - | - | 0.780 | 0.456 |
| | | 40 | 0.012 | - | - | 0.952 | 0.291 |
| | Power law decay with stable component | 23 | 0.003 | - | - | 0.918 | 0.401 |
| | | 40 | 0.018 | - | - | 0.701 | 0.494 |

Note: Values in red color represent correlation coefficients that are below 0.9

Table A.5 summarizes the model fitting parameters of all five models when for using MCA as biocide for wastewater. It was observed that the parallel first order decay model was the best fitting model based on correlation coefficient and standard error. However, the fast and slow decay rate coefficients did not show any consistency with temperature and water quality. In addition, results indicate that the first order decay model can estimate accurately the MCA consumption in a batch system. Further work is required to conclude the consumption rate study of MCA in different wastewaters.

**Table A.5.** Model parameters for combination of three different wastewater and MCA with all 5 models in each fitting model

| Wastewater type | Model | Temp (℃) | $k_1$ ($Min^{-1}$) | $k_2$ ($Min^{-1}$) | x | Correlation coefficient | Standard error (mg/L) |
|---|---|---|---|---|---|---|---|
| MWW | Parallel first order | 23 | 1.884 | 0.006 | 0.239 | 0.988 | 0.240 |
| | | 40 | 1.610 | 0.010 | 0.456 | 0.982 | 0.136 |
| | First order | $23^{I}$ | 0.010 | - | - | 0.953 | 0.295 |
| | | $40^{I}$ | 0.026 | - | - | 0.876 | 0.335 |
| | | $23^{II}$ | 0.009 | - | - | 0.962 | 0.274 |
| | | $40^{II}$ | 0.033 | - | - | 0.790 | 0.388 |
| | Power law decay (n=2) | $23^{I}$ | 0.005 | - | - | 0.932 | 0.393 |
| | | $40^{I}$ | 0.017 | - | - | 0.836 | 0.329 |
| | | $23^{II}$ | 0.004 | - | - | 0.945 | 0.372 |
| | | $40^{II}$ | 0.024 | - | - | 0.732 | 0.385 |
| | First order with stable component | 23 | 0.003 | - | - | 0.996 | 0.086 |
| | | 40 | 0.128 | - | - | 0.995 | 0.064 |
| | Power law decay with stable component | 23 | $5x10^{7}$ | - | - | 0.999 | 0.048 |
| | | 40 | 0.253 | - | - | 0.994 | 0.066 |
| MWW_NF | Parallel first order | 23 | 0.004 | 0.087 | 0.793 | 0.996 | 0.131 |
| | | 40 | 0.005 | 0.005 | 0.265 | 0.982 | 0.267 |
| | First order | 23 | 0.007 | - | - | 0.982 | 0.188 |
| | | 40 | 0.005 | - | - | 0.987 | 0.257 |
| | Power law decay (n=2) | 23 | 0.003 | - | - | 0.972 | 0.267 |
| | | 40 | 0.002 | - | - | 0.971 | 0.358 |
| MWW_NFG | Parallel first order | 23 | 0.001 | 0.001 | 0.926 | 0.998 | 0.082 |
| | | 40 | 1.926 | 0.003 | 0.115 | 0.999 | 0.058 |
| | First order | 23 | 0.001 | - | - | 0.998 | 0.082 |
| | | 40 | 0.004 | - | - | 0.994 | 0.120 |
| | Power law decay (n=2) | 23 | $3x10^{-4}$ | - | - | 0.998 | 0.079 |
| | | 40 | 0.002 | - | - | 0.992 | 0.151 |

Note: Values in red color represent correlation coefficients that are below 0.9; I: Modeling for total chlorine demand; II: Modeling for monochloramine demand.

## A.4 SUMMARY AND CONCLUSIONS

- The parallel first order decay model provided the best fit (based on correlation coefficients and standard deviations between observed and predicted values) to the observed total chlorine residuals for cases of using NaOCl and MCA to treat three types of treated municipal effluents.
- In the case of NaOCl addition to MWW, MWW_NF, and MWW_NFG, increase in temperature resulted in a decrease in $k_1$ but an increase in $k_2$ and the fraction of fast reacting species, x. Slow decay rate $k_2$ increased since higher temperature leads to an increase in reactivity. The increase in x fraction can be explained by the increase in the overall reaction rate. However, it is difficult to explain the decrease in $k_1$ with an increase in temperature.
- Another interesting finding is that the x fraction depends on water quality. In MWW, x was only 0.07, while it was closer to 0.3 in MWW_NF and MWW_NFG. This finding can be explained by the fact that a large portion of free chlorine rapidly reacted with ammonia in MWW to form chloramines, which are more stable chlorine forms that react more slowly in solution. On the other hand, there was less ammonia available in MWW_NF and MWW_NFG and a larger fraction of added chlorine remained as faster reacting free chlorine.

# APPENDIX B

## KINETIC MODEL OF MONOCHLORAMINE CONSUMPTION IN SECONDARY EFFLUENT IN A BATCH REACTOR

Chloramine decay is a critical issue for the use of monochloramine as a major biocide for biological growth control of microorganisms in industrial applications. Several studies have proposed models based on auto-decomposition of monochloramine or oxidation with other components, such as NOM, nitrite, etc. (Valentine and Javfert, 1988; Valentine et al, 1998; Bone, 1999). However, these studies focused on chloramine decay in surface water and drinking water, which have less organic components and significantly better water equality than treated municipal effluent. In addition, these kinetic models do not provide insight into chloramine consumption for wastewater treatment.

In wastewater biocontrol, oxidizing agents are consumed through several mechanisms, such as 1) reaction with organic matter including oxidation of functional groups, electrophilic substitution, etc., 2) conversion to organic chloramines, 3) reaction with trace metals, or 4) other materials and processes. Hass and Karra (1984) proposed a different approach for chlorine consumption modeling in secondary effluent by simplifying the decomposition kinetic into two first order decay rates. The parallel first order model was shown to be useful in estimating

chlorine consumption in waters with high organic content (e.g., grey water) in a recent study by March et al. (2005). The objective of this study is to determine if the parallel first order model can be used to describe chloramine consumption in secondary treated municipal wastewater.

## B.1 APPROACH

In previous chapter, the decay of free and combined chlorine in three different treated municipal wastewaters was demonstrated. It was observed that parallel first order decay model provided the best fit (based on correlation coefficients and standard deviations between observed and predicted values) to the observed total chlorine residuals for cases of using pre-formed monochloramine to treat three types of treated municipal effluents.

In order to determine that this finding is not location-specified, batch tests were conducted using secondary treated wastewater samples collected from five different municipal wastewater treatment plants in greater Pittsburgh area: Franklin Township Municipal Sanitary Authority (FTMSA), City of Jeannette Municipal Authority Sewage Treatment Plant (COJMA), Allegheny Valley Joint Sewage Authority (AVJSA), Municipal Sanitary Authority of New Kensington (MSANK), and North Huntingdon Township Municipal Authority (NHTMA). Detailed information about each treatment facility is provided below together with key wastewater characteristics.

## B.2 CHARACTERISTICS OF WASTEWATER SAMPLES

The following section will briefly introduce each water treatment facility chosen for this study. It should be noted that only wastewater treatment processes will be described.

FTMSA is a tertiary treatment facility consisting of grit removal, primary clarification, aerobic biological treatment using trickling filters, secondary clarification, nitrification, shallow bed sand filtration and disinfection using ultraviolet (UV) technology. Permitted capacity of this facility is 4.9 MGD and the average flowrate is 3.4 MGD. This facility has only sanitary and combined sewers and the major portion of sewage comes from municipality. In order to have comparable water quality among different samples used in this study, water samples from FTMSA were collected after secondary clarification and before nitrification, sand filtration and UV disinfection.

COJMA is a secondary treatment facility consisting of grit removal with pulverization, primary clarification, aeration, final clarification, reaeration, chlorination, and UV disinfection. This facility is capable of treating 3.3 MGD of municipal wastewater from several combined sewers. Water samples were collected from water channel between reaeration tank and UV disinfection chamber.

AVJSA is an activated sludge secondary treatment facility consisting of pulverization comminutor, vortex grit removal, primary clarification, aeration, final clarification (flocculation), and chlorination. This facility has a design capacity of 5.5 MGD and annual average flowrate of 4.0 MGD. Majority of wastewater sources are from municipality and are conveyed through combined sewers. Water samples were collected from final clarifier due to limited access to the channel between final clarifier and chlorination chamber.

MSANK is an aerobic biological treatment facility consisting of grit removal, primary clarification, activated sludge, secondary clarification, and chlorine disinfection. The current permitted hydraulic capacity of the facility is 6 MGD and an average flowrate is 4.6 MGD. The wastewater collecting system consists of combined and separate sanitary sewers connected to four municipalities nearby. Water samples were collected from the open channel between secondary clarifier and chlorination chamber.

NHTMA is an aerobic biological treatment facility consisting of grit removal, primary clarification, rotary biological contactor, final clarification, and chlorine disinfection. Current average flowrate is 3.3 MGD and majority of wastewater influent is from the City of New Huntington and six nearby municipalities through combined sewers. Water samples were collected from water channel before the chlorination chamber.

Water samples were collected between December 2011 and February 2012 on days with zero to low precipitation to prevent influence of overflow storm water. Table B.1 shows the major parameters measured in this study, including pH, ammonia, chemical oxygen demand, chloride, nitrate, total and carbonate alkalinity, total organic carbon, total suspended solids, total dissolved solids, and conductance. Ammonia and chloride concentrations, conductivity and pH were monitored using electrodes (YO-27502-00, Cole-Parmer; S98242-17ND, Fisher-Scientific; 13636AP75A, Fisher-Scientific; WD-35614-20, Oakton). Nitrate and COD concentrations were measured using Hach DR890 portable colorimeter (Method 8039 and 8000, Hach, USA). Alkalinities, TSS, and TDS were measured following standard methods (ASTM, 2005).

General water quality of secondary effluent in the U.S. was determined based on previous studies. The pH values were between 6.5 and 7.3 in all chosen sites. High ammonia concentrations were observed in FTMSA, AVJSA and NHTMA but all of the values were still

within the general range. COD, TOC, and nitrate were slightly higher in FTMSA and this may be due to the high return flow from recycle sludge. Total alkalinity and total dissolved solids of all five sites were within the common range of secondary effluent. It should be noted that the high TSS in AVJSA was from flocculation process and not from the influent.

**Table B.1.** Water characteristics of secondary treated municipal wastewaters from Southwestern Pennsylvania

| Parameters | Unit | General range* | FTMSA | COJMA | AVJSA | MSANK | NHTMA | Detect limit |
|---|---|---|---|---|---|---|---|---|
| pH | | 6-7 | 7.1 | 6.6 | 6.9 | 6.5 | 7.3 | |
| $NH_3$-N | mg/L | 3-73 | 21.0 | 0.3 | 42 | 2 | 30 | 0.01 |
| COD | mg/L | N/A | 102 | 50 | 42 | 41 | 31 | 1 |
| Cl | mg/L | N/A | 199 | 176 | 188 | 352 | 130 | 10 |
| $NO_3$-N | mg/L | N/A | 9.6 | 7.7 | 1.7 | 5.2 | 2.1 | 0.1 |
| Total Alkalinity | mg/L as $CaCO_3$ | 100-250 | 177 | 58.5 | 181 | 62 | 106 | 5 |
| $HCO_3$ Alkalinity | mg/L as $CaCO_3$ | 137-396 | 177 | 58.5 | 181 | 62 | 106 | 5 |
| TOC | mg/L | N/A | 27.0 | 7.7 | 14.6 | 15.8 | 16.0 | 1 |
| TSS | mg/L | N/A | 25 | 113 | 146 | 18 | 6 | 5 |
| TDS | mg/L | 130-1300 | 593 | 415 | 361 | 621 | 350 | 10 |
| Conductivity | µs/cm | N/A | 810 | 695 | 910 | 1022 | 532 | 10 |

Note: **FTMSA**: Secondary treated municipal wastewater; **COJMA**: City of Jeannette Municipal Authority Sewage Treatment Plant; **AVJSA**: Allegheny Valley Joint Sewage Authority; **NHTMA**: Township of North Huntingdon Municipal Authority; **MSANK:** Municipal Sanitary Authority of New Kensington; *: General water quality data collected from Williams, R.B. (1982), Weinberger et al. (1966), Goldstein (1982), Breitstein et al., (1986), Tsai (2006), and Masri et al., (2003).

## B.3 METHODS

Static batch tests were conducted to evaluate the chlorine consumption in these wastewaters following procedures identical to those described in previous chapter. Total chlorine, monochloramine, and free chlorine residuals were measured two to three times for each sampling schedule. It should be noted that pH of wastewater sample was adjusted to 7 in the beginning of the experiment for each sample.

The parallel first order decay model assumes that the overall decay proceeds through two independent first order reactions. After these initial fast reactions, the remaining biocide species, at $C_0$ concentration, can be separated into two fractions from a kinetic point of view: (1) a highly reactive fraction, whose concentration is expressed as $xC_0$, which includes stronger oxidizing agent such as hypochlorite, and (2) a slower reactive fraction with concentration expressed as (l-x) $C_0$, which contains other chlorinated species (e.g. $NH_2Cl$) not included in the previous fraction. Note that x is limited to a range between 0 and 1. The values of $k_1$, $k_2$, and x were calculated using excel solver out of 10,000 iteration to derive the best fit between the model and experimental data.

## B.4 RESULTS AND DISCUSSION

Table B.2 summarizes the model fitting parameters for all five types of secondary effluent when using pre-formed monochloramine as biocide. As described in the previous chapter, $k_1$ and $k_2$ represent the fast and slow reactive components of total chlorine residuals, respectively, and factor x represents the fraction of rapidly decomposing species. The correlation coefficient was calculated by correlating actual values with simulated values, and the standard error indicates the difference between the two values.

Comparing the x values derived from different treatment works at room temperature, it can be seen that TOC concentration significantly affects the portion of faster decaying chloramines. Previous studies have shown the transfer of chlorine from inorganic $NH_2Cl$ to organic amines during wastewater disinfection (Issac and Morris, 1983). Lee and Westerhoff (2009) recently reported a generation rate of 0.16 mg-organic chloramines/mg-dissolved organic

nitrogen, while the chlorine transfer rate from $NH_2Cl$ to nitrogenous compounds was observed to be 200 times faster than reverse reaction (Yoon and Jensen, 1995). That is to say, stability of inorganic chloramines, assuming mainly monochloramine, increased when the major organic nitrogenous component was low in the wastewater. This reflects on the low percentage of fast reacting chlorine in COJMA.

The coefficient $k_1$ represents decomposing rate of fast decaying component, such as organic chloramines. For example, N-Chloroalanine, a common organic chloramine formed during chlorination, has a much faster decomposition rate (0.016 $min^{-1}$, Stanbro and Smith, 1979) than the hydrolysis rate of monochloramine (0.00013 $min^{-1}$, Morris and Issac, 1981). It was observed that high TOC level in the wastewater yielded high consumption rate, $k_1$, regardless of the inorganic ammonia concentration.

The coefficient $k_2$, which reflects the behavior of $NH_2Cl$, has lower value of around 0.002 $min^{-1}$ in COJMA, AVJSA, NHTMA and MSANK, where the secondary effluents had similar TOC concentrations. Similar consumption rate of slow decaying components was observed by Hass and Karra (1984) and our previous studies when using sodium hypochlorite to treat secondary effluent at room temperature. Comparing the $k_1$ and $k_2$ calculated from five different sites, the slower decomposing rate was 100 folds lower than the fast one in most cases.

As the water temperature increased, the slow decomposing rates, $k_2$, increased 2-5 folds in all samples because of sufficient activation energy. On the contrary, the fast decomposing rates, $k_1$, decreased together with the increase of water temperature. Hofstdaler and Bauer (1994) reported that the rate of TOC decomposition increased with temperature from 12 ℃ to 57 ℃ in wastewater. Therefore, it is assumed that a portion of organic matter decomposed due to heating during sample preparation and resulted in lower $k_1$ values.

**Table B.2.** Model parameters for fitting of total chlorine decay when using pre-formed monochloramine in five different secondary treated municipal wastewaters.

| Wastewater type | Temp (℃) | $k_1$ ($Min^{-1}$) | $k_2$ ($Min^{-1}$) | x | Correlation coefficient | Standard error (mg/L) |
|---|---|---|---|---|---|---|
| FTMSA | 23 | 1.884 | 0.006 | 0.239 | 0.988 | 0.240 |
| | 40 | 1.610 | 0.010 | 0.456 | 0.982 | 0.136 |
| COJMA | 23 | 0.100 | 0.002 | 0.102 | 0.999 | 0.075 |
| | 40 | 0.079 | 0.004 | 0.180 | 0.999 | 0.085 |
| AVJSA | 23 | 0.291 | 0.003 | 0.229 | 0.994 | 0.228 |
| | 40 | 0.096 | 0.005 | 0.282 | 0.992 | 0.219 |
| NHTMA | 23 | 0.278 | 0.002 | 0.393 | 0.998 | 0.111 |
| | 40 | 0.158 | 0.004 | 0.279 | 0.995 | 0.155 |
| MSANK | 23 | 0.338 | 0.002 | 0.236 | 0.999 | 0.082 |
| | 40 | 0.114 | 0.003 | 0.353 | 0.993 | 0.158 |

## B.5 SUMMARY AND CONCLUSIONS

The parallel first order model was determined to be useful to simulate the total chlorine decomposition rate when using pre-formed monochloramine in treating secondary effluent. It was shown that the total organic carbon concentration has great impact on both slow and fast decaying component of the biocide. Furthermore, temperature increase reduced the rate of decomposition for fast decaying component and increased the rate of decomposition of slow decaying component.

# APPENDIX C

## ENVIRONMENTAL AND HEALTH IMPACT ASSESSMENT

A preliminary examination of the entire production cycle of each biocide from raw material extraction to final application in a cooling system is required to evaluate fully the benefits and impacts (e.g. energy use, environmental and public health impacts) of the use of these biocides.

An environmental impact analysis consisting of an inventory of raw material and energy required for biocide production and analysis of the relative environmental and public health impact of production, transportation, and treatment use of the biocides was performed in this study. The boundary of the system analyzed is defined in Figure C.1. Relative environmental impacts of specific biocides were evaluated from raw material extraction to final application in the recirculating cooling system. Energy inputs, emissions, and transportation were considered in the analysis. It should be noted that post-usage phase was not considered in this preliminary analysis. In other words, formations of disinfection byproducts (DBPs) were not included in the analysis boundary.

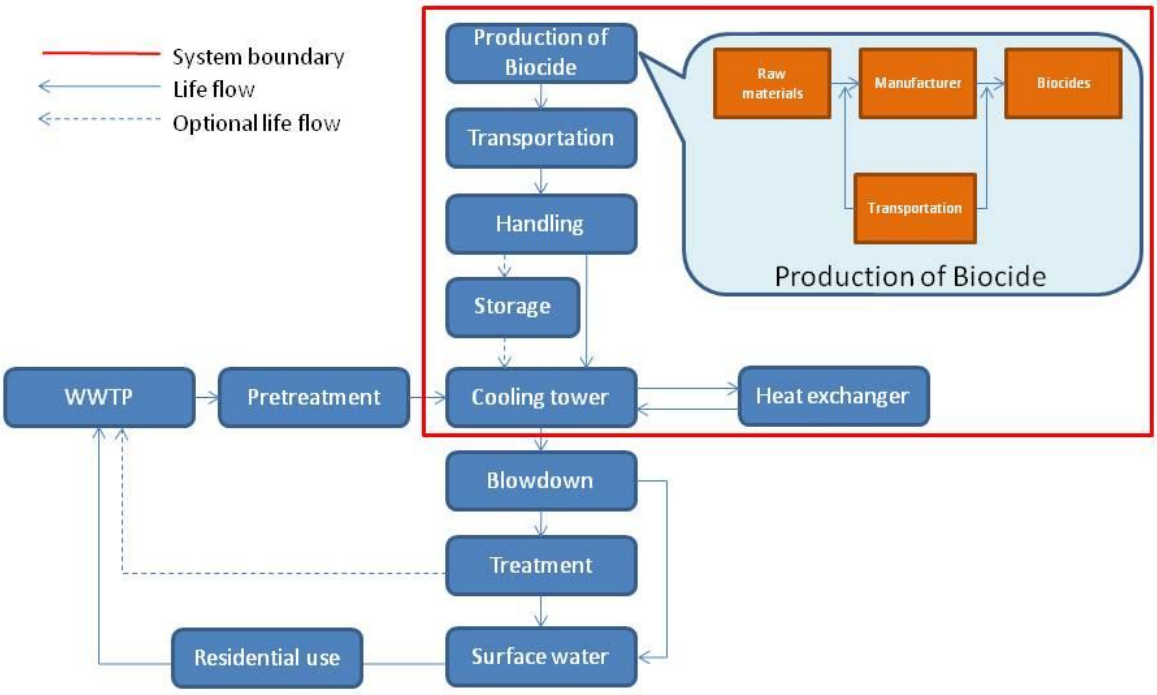


**Figure C.1.** Life cycle of water and biocide chemicals in a recirculating cooling system using treated municipal wastewater.

Each biocide was first identified in four different life cycle database, including GREET (Argonne, 2012), SimaPro (PRé, 2012), National Renewable Energy Laboratory database (NREL, 2012), and Center for Environmental Assessment of Product and Material Systems database (CPM, 2012). Based on the information from these databases, inventory of materials required to produce each biocide was analyzed the following limitations:1) lack of life cycle inventory data for raw chemicals used in biocide generation, 2) limited/dated pricing information about initial equipment setup, raw chemical supply, and construction, and, 3) lack of cost and associated with post-usage treatment.

For environmental impact assessment of the three biocides in a full-scale cooling system, the dosing rate of each biocide obtained from the pilot-scale studies was extrapolated to a full scale 550MW power plant cooling system (NETL, 2008) using 28.8 million liters per day (7.5

MGD) of MWW_NF with consistent quality, A transportation distance between the chemical manufacturer and the power plant of 80 km was assumed. Major environmental and human health impacts, including global warming, carcinogenic, non-carcinogenic, and respiratory effects based on SimaPro impact assessment were included in this study. Human health impacts focused on worker and public safety due to air and dermal exposure to volatile compounds, bacteria and chemicals biological control.

An inventory of total mass of biocide required for proper biological growth control and transportation was assembled for the SimaPro model (Table C.1) and this study focused on a cooling system for a 550MW power plant.

Results of comparative environmental and health impact assessment for three biocides used in this study are shown in Figure C.2. Numerical results derived from SimaPro are normalized to the maximum value observed among the three biocides. Among the three biological growth control strategies, use of $NH_2Cl$ was the most harmful to the environment in terms of global warming potential, while the use of chlorine dioxide resulted in the most adverse impact in human health. According to the SimaPro database, the use of aluminum, zinc, copper, and lead used in the production of $ClO_2$ is at least twice that used for NaOCl and $NH_2Cl$. Use of sodium hypochlorite appears to have the least overall impacts on both environmental and human health impacts. However, the results shown in Figure C.2 would need to be verified when the system boundary includes the post-usage stage and impacts from byproducts formed by different biocides.

**Table C.1.** Inputs to the process-based model of SimaPro for biological growth control using NaOCl, $NH_2Cl$, and $ClO_2$ in CoC 4 MWW_NF

| Chemical | Biocide residual (mg/L) | Precursors | Mass of Pure chemical (kg/day) | Transportation (ton-km) |
|---|---|---|---|---|
| NaOCl | 1 | - | 806 | 432 |
| $NH_2Cl$ | 2-3 | NaOCl<br>$NH_4Cl$<br>NaOH | 1454<br>364<br>4 | 497 |
| $ClO_2$ | 0.5-1 | $NaClO_2$ | 173 | 15 |

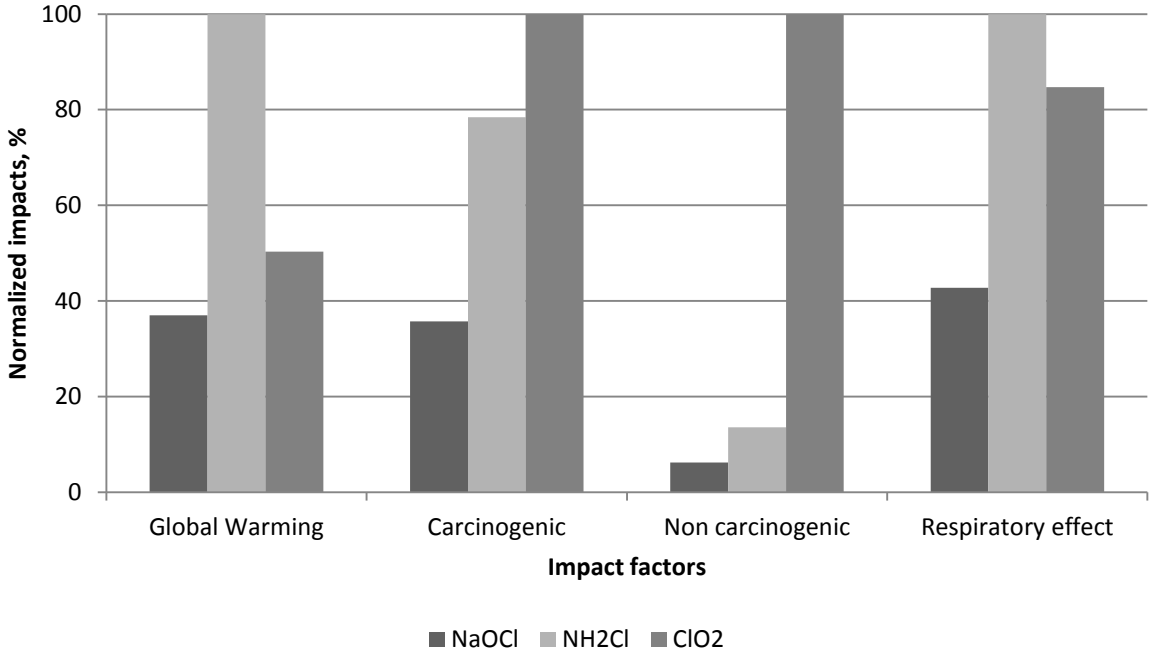


**Figure C.2.** Relative environmental and health impact assessment with SimaPro for the production, transportation, and treatment use of NaOCl, $NH_2Cl$, and $ClO_2$ in a 550 MW power plant recirculating cooling system with MWW_NF as makeup. Note: post-usage phase were not considered in this preliminary analysis.

Among the three biological growth control strategies, chlorination had the least environmentally and health impacts when using tertiary treated effluent as cooling tower makeup within the analyzing boundary. Green house gas emission in the case of $NH_2Cl$ was driven by the high biocide residual requirement. Despite having the lowest dose requirement for appropriate biological growth control, $ClO_2$ still exhibited high public health impact.

# BIBLIOGRAPHY

## Chapter 1


Adams, A.P., Garbett, M., Rees, H. B., abd Lewis, B.G, (1980) Bacterial Aerosols Produced from a Cooling Tower Using Wastewater Effluent as Makeup Water, Water Pollution Control Federation, Vol. 52, No. 3, Part 1, Mar 1980, pp 498-501

Bentham, R.H.; and Broadbent, C.R. (1995) *Current Microbiology*, Vol.30, pp. 167-172

Carducci, A.; Verani, M.;Battistini, R. (2010) Applied Microbiology, Vol. 50, Issue. 1, pp. 24-29

Characklis, W.G., (1990) Microbial fouling. In: Characklis WG, Mashall KC (EDs), *Biofilm*, Wiley, New York, pp 523-584

Chien, S.H.; Hsieh, M.K.; Li, H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2012a) Pilot-scale cooling tower to evaluate corrosion, scaling, and biofouling control strategy for cooling system makeup water, *Rev. Sci. Instrum*. 83, 024101

Chien, S.H.; Chowdhury, I.; Hsieh, M.K.; Li, H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2012b) Control of biological growth in recirculating cooling systems using treated secondary effluent as makeup water with monochloramine, *Water Res.* , Sep, DOI: http://dx.doi.org/10.1016/j.watres.2012.09.027.

Chien, S.H.; Liu, W.; Dzombak, D.A.; Vidic, R.D. (2012c) Impact of tertiary treatment processes on the effectiveness of chloramination for biological growth control in recirculating cooling systems using treated municipal wastewater, *Water Research* (Submitted)

Chien, S.H.; Dzombak, D.A.; Vidic, R.D. (2012d) Comprehensive evaluation of biological growth control by chlorine-based biocides in power plant cooling systems using tertiary effluent, *Environmental Engineering Science* (Submitted)

Costerton, J.W., Lewandowski, Z., Caldwell, D.E., Korber, D.R., and Lappin-Scott, H.M. (1995) Microbial Biofilms, Annual Review of Microbiology, Vol. 49: 711-745.

Costerton, J.W., Stewart, P.S., and Greenberg, E.P. (1999) Bacterial biofilms: a common cause of persistent infections. Science 284:1318–1322

CTI (2008) Guideline: Best Practices for Control of Legionella, Cooling Technology Institute, U.S.A., CTI guidelines WTP-148 (06) http://www.cti.org/downloads/WTP-148.pdf

Dishneau, D. (2007), Frederick County denies cooling water to proposed power plant. The Baltimore Examiner, 17 Sep.

Donlan, R.M. (2002) Biofilms: Microbial Life on Surfeces, Emerg Infect Dis. 2002 September; 8(9): 881–890.

Edelstein, P. H. (1993) Legionnaires' Disease, Clinical Infectious Diseases, Vol. 16, No. 6 (Jun., 1993), pp. 741-747

Feeley, T.J. and Ramezan, M. (2003), Electric Utilities and Water: Emerging Issues and R&D Needs, in Proceedings of 9th Annual Industrial Wastes Technical and Regulatory Conference. Water Environment Federation, San Antonio, TX.

Flemming, H. C. (2002), Biofouling in water systems – cases, causes, and countermeasures, Appl Microbiol Biotechnol, 59: 629-640

Fraser, D. W.; Tsai, T. R.; Orenstein, W.; Parkin, W.E.; Beecham, H.J.; Sharrar, R.G.; Harris, J.; Mallison, G.F.; Martin, S.M.; McDade, J.E.; Shepard, C.C.; and Brachman, P.S. (1977). "Legionnaires' Disease." New England Journal of Medicine 297(22): 1189-1197.

Frayne, C. (1999), "Cooling Water Treatment: Principles and Practice", Chemical Publishing Co., Inc., NY, pp. 122-135, 184-189

Hinrichsen, D.; Robey, B.; and Upadhyay, U.D. (1996). Solutions for a Water-Short World. Baltimore, Johns Hopkins School of Public Health, Population Information Program.

Kenny, J.F.; Barber, N.L.; Hutson, S.S.; Linsey, K.S.; Lovelace, J.K.; and Maupin, M.A (2009) Estimated Use of Water in the United States in 2005. USGS Circular 1344. U.S. Geological Survey, Reston, VA. ISBN 978-1-4113-2600-2

Liu, Y., and Tay, J.H. (2002) The essential role of hydrodynamic shear force in the formation of biofilm and granular sludge, Water Research, Vol 36, Issue 7, pp 1653-1665

Liu, Z., Lin, Y.E., Stout, J.E, Hwang, C.C., Vidic, R.D., and Yu, V.L. (2006) Effect of flow regimes on the presence of Legionella within the biofilm of a model plumbing system, Journal of Applied Microbiology, 101, pp 437-442

Ludensky, M. (2005) Microbiological control in cooling water systems and directory of microbiocides for the protection of materials: A handbook. pp. 121-139. 2005.

Margerum DW, Gray ET Jr, Huffman RT. (1978) Chlorination and the formation of N-chloro compounds in water treatment. In Brinckman FE, Bellama JM, eds, Organometals and Organometaloids: Occurrence and Fate in the Environment. Syposium Series 82. American Chemical Society,Washington, DC, pp 278–291.

Melo, L. F., and Bott, T.R. (1997) Biofouling in water systems. Exp Therm Fluid Sci 14:375–381

Morris, J.C. (1967) Kinetics of reactions between aqueous chlorine and nitrogenous compounds. In: Principles and Applications of Water Chemistry. S.D. Faust and J.V. Hunter, Ed. John Wiley and Sons, Inc., New York. pp. 23-53.

Morris, J. C. and Isaac, R. A. (1983) A critical review of kinetic and thermodynamic constants for the aqueous chlorine-ammonia system, Jolley Water Chlorination Environmental Impact and Health Effects, Vol. 4, Ann Arbor Sci. Publ., Inc., Ann Arbor, Michigan.

Puckorius P. R., and Diehl K. (2003), "Water Reuse Experimencs with Cooling Tower Systems in San Antonio, Texas", Cooling Tower Institute Annual Conference, 2003. Paper No. TP03-03

Rossmoore, H. W. (1995) Handbook of biocide and preservative use, Blackie Academic & Pro Professional, Chapter 3, page 50-77.

Selby, K. A., Puckorius, P. R., and Helm, K. R. (1996) The use of reclaimed water in electric power stations and other industrial facilities, Water, Air, and Soil Pollution, Kluwer Academic Publisher, Netherlands, Vol. 90, pp 183-193.

Stoodley, P., Dodds, I., Boyle, J. D., and Lappin-Scott, H. M. (1999) Influence of hydrodynamics and nutrients on biofilm structure, J Appl Microbiol 85, S19-S28

Sutherland, I. W., (2001) Biofilm exopolysaccharides: a strong and stick framework, Microbiology, 2001, 147, pp 3-9

Vidic, R.D.; Dzombak, D.A.; Hsieh, M.K.; Li, H.; Chien, S.H.; Feng, Y.; Chowdhury, I.; Monnell, J.D. (2009) Reuse of Treated Internal or External Wastewaters in the Cooling Systems of Coal-based Thermoelectric Power Plants, Department of Energy, Grant DE-FC26-06NT42722, National Energy Technology Laboratory, Pittsburgh, PA.

Wijesinghe, B.; Kaye, R. B.; Fell, C. D. (1996) Reuse of Treated Sewage Effluent for Cooling Water Makeup: A Feasibility Study and a Pilot Plant Study. Water Sci. Technol, 33 (10-11), 363-369.

Zhang, X. Q., Bishop, P. L., and Kupferle, M. J. (1998) Measurement of polysaccharides and proteins in bio® lm extracellular polymers.Water Sci Technol 37, 345-348

**Chapter 2**

Bentham, R.H.; and Broadbent, C.R. (1995) *Current Microbiology*, Vol.30, pp. 167-172

Bernier, M.A. (1994) *ASHRAE Trans*, 100(2):114–21.

Bhopal, R. S.; Barr, G. (1990) *Epidemiology and Infection*, 104 , pp 29-38 doi:10.1017/S0950268800054492

Braun, J.E.; Klein, S.A.; Mitchell, J.W. (1989) *ASHRAE Trans*, 95(2):164–74.

Carducci, A.; Verani, M.;Battistini, R. (2010) Applied Microbiology, Vol. 50, Issue. 1, pp. 24-29

Dexter, A.R.; Richard, G. (2009) Soil Science Society of America Journal, **73** (5), 1641-1651.

Duda, S., Stout, J.E., Vidic, R. (2011) *HVAC&R Research*, 17(5):872–890, ISSN: 1078-9669 print / 1938-5587, DOI: 10.1080/10789669.2011.587588

EPRI (2003) 1005359; California Energy Commisssion, Public Interest Energy Research Program: Sacramento, CA

Green, D.W.; Perry, R.G., Eds. (2007); McGraw-Hill: New York.

Hsieh, M.K.; Li, H.; Chien, S.H.; Monnell, J.; Chowdhury, I.; Dzombak, D.A.; Vidic, R.D. (2010a) *Water Environment Research*, 82 (12), 2346-2356.

Hsieh, M.K.; Dzombak, D.A.; Vidic, R.D. (2010b) *Industrial and Engineering Chemistry Research*, 49 (16): 7313-7322.

Isozumi, R.; Ito,Y.; Ito, I.; Osawa, M.; Hirai, T.; Takakura, S.; Iinuma, Y.; Ichiyama, S.; Tateda, K.; Yamaguchi, K.; Mishima, M. (2005) *Scandinavian Journal of Infectious Diseases, Volume: 37*, Issue: 10, Pages: 709-711

Jack, T.R. (2002) *ASM Handbook*, No. 06072G, Vol. 11, pp. 881- 891

Khan, J-U-R; Yaqub, M.; Zubair, S.M. (2002) *Energy Conversion and Management*, 44 (2003) 2073–2091

Lemouari, M.; Boumaza, M.; Mujtaba, I.M. (2007), *Applied Thermal Engineering*, 27, 902-909.

Li, H; Hsieh, M.K.; Chien, S.H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2011a) *Water Resear*ch, 45 (2), 748-760.

Li, H; Chien, S.H.; Hsieh, M.K.; Dzombak, D.A.; Vidic, R.D. (2011b) *Environmental Science & Technology*, 45(10), pp 4195-4200.

McCabe, W.L.; Smith, J.C.; Harriott, P. (2001) McGraw-Hill, New York.

NCDC (2008a) U.S. Department of Commerce, National Climatic Data Center. (Avaiable at: http://www.ncdc.noaa.gov/oa/climate/online/ccd/maxtemp.html)

NCDC (2008b) U.S. Department of Commerce, National Climatic Data Center. (Avaiable at: http://www.ncdc.noaa.gov/oa/climate/online/ccd/avgrh.html)

Palo, R.E. and Pothier C.A. (2003) *Corrosion 2003*, NACE Symposium: 03-STG-11. Paper No. 03066.

Strigle, R.F., Jr. *Random Packing and Packed Towers*. Houston, TX: Gulf Publication Co., 1987.

Swart, J.S. and Engelbrecht, J.P. (2004) *Water SA*, 30 (5), 145-149.

UNEP (2006) United Nations Environment Programme. (accessible: http://www.energyefficiencyasia.org/energyequipment/ee_es_coolingtowers.html)

USGAO (2003) GAO-03-514, U.S. General Accounting Office, Washington, DC.

Webb, R.L. (1984) *ASHRAE Trans*, 90(2):398–415.

Vidic, R.D.; Dzombak, D.A.; Hsieh, M.K.; Li, H.; Chien, S.H.; Feng, Y.; Chowdhury, I.; Monnell, J.D. (2009) *Department of Energy*, Grant DE-FC26-06NT42722, National Energy Technology Laboratory, Pittsburgh, PA.

**Chapter 3**

Aieta, E. M., Berg, J. D., Roberts, P. V., and Copper, R. C. (1980) Comparision of chlorine dioxide and chlorine in wastewater disinfection, Journal of Water Pollution Control Federation. Vol. 52, No. 4, pp 810-822.

APHA et al. (1998) Standard Methods for the Examination of Water and Wastewater, 20 ed.. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 20005-2605.

ASTM (2000) Standard Guide for Selecting Test Methods to Determine the Effectiveness of Antimicrobial Agents and Other Chemicals for the Prevention, Inactivation and Removal of Biofilm, ASTM E1427-00, American Society for Testing and Materials, West Conshohocken, PA

Bradshaw, D. J., Marsh, P. D., Schilling, K. M. and Cummins, D. (1996) A Modified Chemostat System to Study the Ecology of Oral Biofilms, Journal of Applied Bacteriology, Volume 80, pp. 124-130

Chien, S.H.; Hsieh, M.K.; Li, H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2012) Pilot-scale cooling tower to evaluate corrosion, scaling, and biofouling control strategy for cooling system makeup water, *Rev. Sci. Instrum.* 83, 024101 http://dx.doi.org/10.1063/1.3680563

CTI (2008) Guideline: Best Practices for Control of Legionella, Cooling Technology Institute, U.S.A., CTI guidelines WTP-148 (06) http://www.cti.org/downloads/WTP-148.pdf

Dishneau, D. (2007), Frederick County denies cooling water to proposed power plant. The Baltimore Examiner, 17 Sep.

Dondero, T.J., Rendtorff, R.C., Mallison, G.F., Weeks, R.M., Levy, J.S., Wong, E.W., and Schaffner, W. (1980) An outbreak of Legionnaires' disease associated with a contaminated air-conditioning cooling tower. New England Journal of Medicine. 302:365–370

Duda, S., Stout, J. E., Vidic, R. (2011) Biological control in cooling water systems using nonchemical treatment devices, HVAC&R Res. 17(5), 872.

EPA (1999) Alternative Disinfectants and Oxidants Guidance Manual, *United States Environmental Protection Agency*, EPA 815-R-99-014, April 1999.

Feeley, T.J. and Ramezan, M. (2003), Electric Utilities and Water: Emerging Issues and R&D Needs, in Proceedings of 9th Annual Industrial Wastes Technical and Regulatory Conference. Water Environment Federation, San Antonio, TX.

Frayne, C. (1999) Cooling Water Treatment: Principles and Practice, *Chemical Publishing Co., Inc*., NY, pp. 122-130.

Gould,J. P., Richards, J. T., and Miles, M. G. (1984) The formation of organic chloramines during the aqueous chlorination of cytosine and 5-methylcytosine, Water Research, Vol 18, No. 8, pp. 991-999.

Havelaar, A.H., and Nieuwstad, Th.J. (1985) Bacteriophages and Fecal Bacteria as Indicators of Chlorination Efficiency of Biologically Treated Wastewater. Journal (Water Pollution Control Federation), Vol. 57, No. 11 (Nov., 1985), pp. 1084-1088

Hsieh, M. K., Li, H., Chien, S. H., Monnell, J. D., Chowdhury, I., Dzombak, D. A., Vidic, R. D. (2010) Corrosion control when using secondary treated municipal wastewater as alternative makeup for cooling tower systems. Water Environment research, Vol. 82, No. 12, pp. 2346-2356.

Hsieh, M.K., Walker, M.E., Safari, I., Chien, S.C., Abbasian, J., Vidic, R.V., and Dzombak, D.A. (2012), "Ammonia Stripping in Open-Recirculating Cooling Water Systems," accepted for publication, Environmental Progress & Sustainable Energy, DOI 10.1002/ep.11648

Kenny, J.F., Barber, N.L., Hutson, S.S., Linsey, K.S., Lovelace, J.K., and Maupin, M.A (2009) Estimated Use of Water in the United States in 2005. USGS Circular 1344. U.S. Geological Survey, Reston, VA. ISBN 978-1-4113-2600-2

Kirmeyer, G., Martel K., Thompson G., and Radder L. (1993) Optimizing Chloramine Treatment. American Water Works Research Foundation; 2nd edition (December 7, 2003) pp. 20~23. ISBN-10: 1583213317.

Lee, W. and Westerhoff, P. (2009) Formation of organic chloramines during water disinfection - chlorination and chloramination. Water Research, Vol. 43, pp 2233-2239.

Li, H.; Chien, S.H.; Hsieh, M.K.; Dzombak, D.A.; Vidic, R.D. (2011a) Escalating water demands for energy production and the potential for use of treated municipal wastewater, Environmental Science & Technology, 45(10), pp 4195-4200.

Li, H., Hsieh, M. K. , Chien, S.H., Monnell, J. D., Dzombak, D. A., and Vidic, R. D. (2011b) Control of mineral scale deposition in cooling systems using secondary-treated municipal wastewater. Water Research, Vol. 45, No. 2, pp. 748-760.

Ludensky, M. (2005) Microbiological Control in Cooling Water Systems. *Directory of Microbiocides for the Protection of Materials: a Handbook*, pp. 121-139

Margerum DW, Gray ET Jr, Huffman RT. (1978) Chlorination and the formation of N-chloro compounds in water treatment. In Brinckman FE, Bellama JM, eds, Organometals and Organometaloids: Occurrence and Fate in the Environment. Syposium Series 82. American Chemical Society,Washington, DC, pp 278–291.

Morris, J.C. (1967) Kinetics of reactions between aqueous chlorine and nitrogenous compounds. In: Principles and Applications of Water Chemistry. S.D. Faust and J.V. Hunter, Ed. John Wiley and Sons, Inc., New York. pp. 23-53.

Morris, J. C. and Isaac, R. A. (1983) A critical review of kinetic and thermodynamic constants for the aqueous chlorine-ammonia system, Jolley Water Chlorination Environmental Impact and Health Effects, Vol. 4, Ann Arbor Sci. Publ., Inc., Ann Arbor, Michigan.

Morton, S., Bartlett, C.L., Bibby, L.F., Hutchinson, D.N., Dyer, J.V., and Dennis, P.J. (1986) Outbreak of *Legionnaires*' disease from a cooling water system in a power station. Br J Ind Med. Sep;43(9):630–635.

Ndiongue, S., Huck, P. M., and Slawson, R. M. (2004) Effects of temperature and biodegradable organic matter on control of biofilms by free chlorine in a model drinking water distribution system. Water Research, 39(2005), 953-964

Nieuwenhuijsen, M.J., Toledano, M.B., Eaton, N.E., Fawell, J., and Elliott, P. (2000) Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. Occup Environ Med, vol. 57, pp 73-85.

Obuekwe C. O., Westlake D. W. S., Cook F. D., and Costerton J. W. (1981) Surface Changes in Mild Steel Coupons from the Action of Corrosion-Causing Bacteria. Applied and Environmental Microbiology, Volume 41, NO.3, pp. 766-774

Osborn, D. W. (1969) Factors affecting the use of purified sewage effluents for cooling purposes. Jour. 1. W.P.C. 69, 456.

Palin, A. (1950) A Study of the Chloro Derivatives of Ammonia. Water and Water Engineering. 54:248-258.

Rao, T. S., Nanacharaiah, Y. V. and Nair, K. V. K. (1998) Biocidal Efficacy of Monochloramine against Biofilm Bacteria. *Biofouling*, 1998, Volume 12 (4), pp. 321-332.

Prosser, B. L. T., Taylor, D., Dix, B. A. and Cleeland, R. (1987) Method of Evaluating Effects of Antibiotics on Bacterial Biofilm, Antimicrobial Agents and Chemotherapy, Oct. 1987, pp. 1502-1506

Rebhun, M. and E. Gideon (1988). "Reuse of Wastewater for Industrial Cooling Systems." Journal (Water Pollution Control Federation) 60(2): 237-241.

Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., Gunten, U., and Wehrli, B. (2006) The challenge of micropollutants in aquatic systems. Science, Vol. 313, no. 5790, pp 1072-1077.

Turetgen, I. (2004) Comparison of Efficacy of Free Residual Chlorine and Monochloramine against Biofilms in Model and Full Scale Cooling Towers. *Biofouling*, April 2004, Volume 20 (2), pp. 81-85

Vidic, R.D.; Dzombak, D.A.; Hsieh, M.K.; Li, H.; Chien, S.H.; Feng, Y.; Chowdhury, I.; Monnell, J.D. (2009) Reuse of Treated Internal or External Wastewaters in the Cooling Systems of Coal-based Thermoelectric Power Plants, Department of Energy, Grant DE-FC26-06NT42722, National Energy Technology Laboratory, Pittsburgh, PA.

Vikesland, P.J., Ozekin, K. and Valentine, R.L., (2001) Monochloramine decay in model and distribution system waters. *Wat. Res*. 35 7, pp. 1766–1776.

Wijesinghe, B.; Kaye, R. B.; Fell, C. D. (1996) Reuse of Treated Sewage Effluent for Cooling Water Makeup: A Feasibility Study and a Pilot Plant Study. Water Sci. Technol, 33 (10-11), 363-369.

White, G. C. (1999) Handbook of Chlorination and Alternative Disinfectants, 4th ed., A Whiley-Interscience Publication, John Wiley & Sons, Inc., New York. pp. 542-545

Wolfe, R. L., Ward, N. R., and Olson, B. H. (1984) Inorganic Chloramines as Drinking Water Disinfectants: A Review, Journal of American Water Works Association, 1984, Volume 75, pp. 74-88

Wolfe, R. L., Ward, R. N., and Olson, B. H. (1985) Interference in the Bacterial Properties of Inorganic Chloramines by Organic Nitrogen Compounds, Environmental Science & Technology, 1985, Volume 19, No. 12, pp. 1192-1195

Yu, V.L. (2008) Cooling towers and legionellosis: A conundrum with proposed solutions, Int. J. Hyg. Environ. Health, 211, pp. 229-234

**Chapter 4**

APHA (2012) *Standard Methods for the Examination of Water and Wastewater*, 22 ed.. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 20005-2605.

Asano, T., and Levine, A.D. (1998) *Wastewater Reclamation, Recycling, and Reuse: An Introduction, Wastewater Reclamation and Reuse*, Water Quality Management Library – Vol. 10, Technomic Publishing Co., Inc., Lancaster, Pennsylvania.

AWT (2003) Legionella 2003: An Update and Statement by the Association of Water Technologies, *Association of Water Technologies*, Rockville, MD, 20850. http://awt.org/IndustryResources/Legionella03.pdf

Bentham, R. H. (1993) Environmental factors affecting the colonization of cooling towers by Legionella spp. in South Australia., *International Biodeterioration & Biodegradation*, 31(1): 55-63.

Borsheim, KY (2000) Bacterial production rates and concentrations of organic carbon at the end of the growing season in the Greenland Sea, *Aquatic microbial ecology: international journal* (0948-3055), 21 (2), p. 115

Bott, T.R. (2011) *Industrial Biofouling: Occurrence and Control*, Elsevier, ISBN: 0444532242, 9780444532244, pp. 197-202

Butterfield, P.W.; Camper, A.K.; Ellis, B.D.; and Jones, W.L. (2002) Chlorination of model drinking water biofilm: Implications for growth and organic carbon removal, *Water Research*, 36: 4391.

Chandy, J.P. and Angles, M.L. (2001) Determination of nutrients limiting biofilm formation and the subsequent impact on disinfectant decay, *Water Res.*, 35 (11), pp. 2677–2682

Chien, S.H.; Hsieh, M.K.; Li, H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2012a) Pilot-scale cooling tower to evaluate corrosion, scaling, and biofouling control strategy for cooling system makeup water, *Rev. Sci. Instrum.* 83, 024101

Chien, S.H.; Chowdhury, I.; Hsieh, M.K.; Li, H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2012b) Control of biological growth in recirculating cooling systems using treated secondary effluent as makeup water with monochloramine, *Water Res.* , Sep, DOI: http://dx.doi.org/10.1016/j.watres.2012.09.027.

Choudhury, M.R.; Hsieh, M.K.; Vidic, R.D.; Dzombak, D.A. (2012) Corrosion Management in Power Plant Cooling Water Systems Using Tertiary Treated Municipal Wastewater as Makeup Water, *Corrosion Science*, Vol. 61, doi:10.1016/j.corsci.2012.04.042

Cloete, T.E.; Jacobs, L.; and Brozel, V.S. (1998) The chemical control of biofouling in industrial water systems, *Biodegradation*, Vol. 9 , pp. 23–37

CTI (2008) Guideline: Best Practices for Control of Legionella, Cooling Technology Institute, U.S.A., *CTI guidelines*, WTP-148 (06) http://www.cti.org/downloads/WTP-148.pdf

Diehl, A.C.; Speitel, G.E.; Jr, Symons, J.M.; Krasner, S.W.; Hwang, C.J.; and Barrett, S.E. (2000) DBP formation during chloramination, *J. Am. Water Works Assoc.*, 92, 76–90

Dishneau, D. (2007) Frederick County denies cooling water to proposed power plant. The Baltimore Examiner, 17 Sep.

Dondero, T.J.; Rendtorff, R.C.; Mallison, G.F.; Weeks, R.M.; Levy, J.S.; Wong, E.W.; and Schaffner, W. (1980) An outbreak of Legionnaires' disease associated with a contaminated air-conditioning cooling tower, *New England Journal of Medicine*, 302:365–370

Escobar, I.C.; Randall, A.A.; and Taylor, J.S. (2001) Bacterial Growth in Distribution Systems: Effect of Assimilable Organic Carbon and Biodegradable Dissolved Organic Carbon, *Environ. Sci. Technol.,* 35 (17), pp 3442–3447

Farmer, R.W.; Dussert, B.W.; Kovacic, S.L. (1996) Improved granular activated carbon for the stabilization of wastewater pH, American Chemical Society, Division of Fuel Chemistry, 41 (1), pp. 456–460

Feeley, T.J. and Ramezan, M. (2003) Electric Utilities and Water: Emerging Issues and R&D Needs, Proceedings of 9th Annual Industrial Wastes Technical and Regulatory Conference, Water Environment Federation, San Antonio, TX.

Frayne, C. (1999) *Cooling Water Treatment: Principles and Practice*, Chemical Publishing Co., Inc., NY, pp. 122-130.

Hsieh, M.K.; Li, H., Chien; S.H., Monnell, J.D.; Chowdhury, I.; Dzombak, D.A; and Vidic, R.D. (2010) Corrosion control when using secondary treated municipal wastewater as alternative makeup water for cooling tower systems, *Water Environment Research*, 82, 2346–2356.

Hsieh, M.K.; Walker, M. E.; Safari, I.; Chien,S-H; Abbasian, J.; Vidic, R.D.; and Dzombak1, D.A. (2012) Ammonia stripping in open-recirculating cooling water systems, *Environmental Progress & Sustainable Energy*: NA/NA, DOI: 10.1002/ep.11648.

Humphris, T.H. (1977) The Use of Sewage Effluent as Power Station Cooling Water, *Water Res.* Vol. 11, No. 2, pp. 217-223

Huitric, S.J.; Kuo, J; Creel, M.; Tang, C.C.; Snyder, D.; Horvath, R.; and Stahl, J. (2006) Reclaimed Water Disinfection Alternatives to Avoid NDMA and THM Formation, *Proceedings of the Water Environment Federation 2006*, (8): 4397-4412.

Jenner, H.A.; Whitehouse, J.W.; Taylor, C.J.L.; and Khalanski, M. (1998) Cooling water management in European power stations: biology and control, *Hydroécologie Appliquée* 1-2., Electricité de France, Paris

Kainulainen, T.K.; Tuhknen, T.A.; Vartiainen, T.K.; and Kalliokoski, P.J. (1995) Removal Of Residual Organics From Drinking Water By Ozonation and Activated Carbon Filtration: A Pilot Plant Study, *Ozone: Science & Engineering*, **17**(4): 449-462.

Kirchman, D.L.; Meon, B.; Cottrell, M.T.; Hutchins, D.A.; Weeks, D.; and Bruland, K.W. (2000) Carbon versus Iron Limitation of Bacterial Growth in the California Upwelling Regime, *Limnology and Oceanography* , Vol. 45, No. 8, pp. 1681-1688

Kirmeyer, G., Martel K., Thompson G., and Radder L. (1993) Optimizing Chloramine Treatment. American Water Works Research Foundation; 2nd edition (December 7, 2003) pp. 20~23. ISBN-10: 1583213317.

Lee, W. and Westerhoff, P. (2009) Formation of organic chloramines during water disinfection – chlorination versus chloramination, *Water Research*, 43(8): 2233-2239.

Lee, W.H.; Wahman, D.G.; Bishop, P.L.; and Pressman, J.G. (2011) Free chlorine and monochloramine application to nitrifying biofilm: comparison of biofilm penetration, activity, and viability, *Environ. Sci. Technol.*, 2011, 45 (4), pp 1412–1419

Li, H.; Hsieh, M.K.; Chien, S.H.; Monnell, J.D.; Dzombak, D.A.; Vidic, R.D. (2011) Control of mineral scale deposition in cooling systems using secondary-treated municipal wastewater, *Water Research*, 45 (2): 748-760.

Liu, W.; Chien, S.H; Dzombak, D.A.; and Vidic. R, D. (2012) Mineral scaling mitigation in cooling systems using treated municipal wastewater: bench-scale and pilot-scale studies, *Water Res.*, Sep, 15;46(14):4488-98

Liu, Z.; Lin, Y.E.; Stout, J.E.; Hwang, C.C.; Vidic, R.D.; and Yu, V.L. (2006) Effect of flow regimes on the presence of *Legionella* within the biofilm of a model plumbing system, *Journal of Applied Microbiology*, 101(2):437-42.

Ludensky, M. (2005) Microbiological Control in Cooling Water Systems. *Directory of Microbiocides for the Protection of Materials: a Handbook*, pp. 121-139

Meesters, K.P.H.; Groenestijn, J.W.V.; and Gerritse, J. (2003) Biofouling reduction in recirculating cooling systems through biofiltration of process water, *Water Research*, 37:525-532

Morris, J. C. and Isaac, R. A. (1983) A critical review of kinetic and thermodynamic constants for the aqueous chlorine-ammonia system, *Jolley Water Chlorination Environmental Impact and Health Effects*, Vol. 4, Ann Arbor Sci. Publ., Inc., Ann Arbor, Michigan.

Musikavong, C.; Wattanachira, S.; Marhaba, T.F.; and Pavasant, P. (2005) Reduction of organic matter and trihalomethane formation potential in reclaimed water from treated industrial estate wastewater by coagulation, *Journal of Hazardous Materials*, 127(1–3): 48-57.

Osborn, D. W. (1969) Factors affecting the use of purified sewage effluents for cooling purposes, *Jour. Institute of Water Pollution Control*, 69: 456.

Palin, A. (1950) A Study of the Chloro Derivatives of Ammonia. Water and Water Engineering. 54:248-258.

Rajagopal, S.; Jenner, H.A.; and Venugopalan, V.P. (2012) *Operational and Environmental Consequences of Large Industrial Cooling Water Systems*, Springer, ISBN: 1461416973 and 978-1461416975.

Reay, D.S.; Nedwell, D.B.; Priddle, J.; and Ellis-Evans, J.C. (1999) Temperature dependence of inorganic nitrogen uptake: reduced affinity for nitrate at suboptimal temperatures in both algae and bacteria, *Appl. Environ. Microbiol.*, 65(6):2577

Rebhun, M. and Engel, G. (1988) Reuse of Wastewater for Industrial Cooling Systems, *Journal of Water Pollution Control Federation*, 60(2): 237-241.

Simoes, M.; Perieira, M.O.; and Vieira, M.J. (2003) Monitoring the effects of biocide treatment of pseudomonas fluorescens biofilms formed under different flow regimes, *Water science & technology*. ISSN 0273-1223 47:5 (2003) 217-223.

Stackelberg, P.E.; Gibs, J.; Furlong, E.T.; Meyer, M.T.; Zaugg, S.D.; and Lippincott, R.L (2007) Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds, *Science of the Total Environment*, 377 (2007) 255-272, ISSN: 0048-9697

Valentine, R.L. (1998) Chloramine Decomposition in Distribution System and Model, Waters, AWWA, Denver, CO. 49

Vidic, R.D.; Dzombak, D.A.; Hsieh, M.K.; Li, H.; Chien, S.H.; Feng, Y.; Chowdhury, I.; Monnell, J.D. (2009) Reuse of Treated Internal or External Wastewaters in the Cooling Systems of Coal-based Thermoelectric Power Plants, Department of Energy, Grant DE-FC26-06NT42722, National Energy Technology Laboratory, Pittsburgh, PA.

Westerhoff, P.; Chao P.; and Mash, H. (2004) Reactivity of natural organic matter with aqueous chlorine and bromine, *Water Res.*, 38(6): 1502-1513.

**Chapter 5**

Abou-Rass, M. and S. W. Oglesby (1981) The effects of temperature, concentration, and tissue type on the solvent ability of sodium hypochlorite, Journal of Endodontics 7(8): 376-377

Adams, A.P., Garbett, M., Rees, H. B., abd Lewis, B.G, (1980) Bacterial Aerosols Produced from a Cooling Tower Using Wastewater Effluent as Makeup Water, Water Pollution Control Federation, Vol. 52, No. 3, Part 1, Mar 1980, pp 498-501

APHA (2012) *Standard Methods for the Examination of Water and Wastewater*, 22 ed.. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 20005-2605.

Asano, T., and Levine, A.D. (1998) Wastewater Reclamation, Recycling, and Reuse: An Introduction, Wastewater Reclamation and Reuse, Water Quality Management Library – Vol. 10, Technomic Publishing Co., Inc., Lancaster, Pennsylvania.

ASTM (2000) Standard Guide for Selecting Test Methods to Determine the Effectiveness of Antimicrobial Agents and Other Chemicals for the Prevention, Inactivation and Removal of Biofilm, ASTM E1427-00, American Society for Testing and Materials, West Conshohocken, PA

Chien, S.H.; Hsieh, M.K.; Li, H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2012a) Pilot-scale cooling tower to evaluate corrosion, scaling, and biofouling control strategy for cooling system makeup water, *Rev. Sci. Instrum*. 83, 024101

Chien, S.H.; Chowdhury, I.; Hsieh, M.K.; Li, H.; Monnell, J.; Dzombak, D.A.; Vidic, R.D. (2012b) Control of biological growth in recirculating cooling systems using treated secondary effluent as makeup water with monochloramine, *Water Res.* , Sep, DOI: http://dx.doi.org/10.1016/j.watres.2012.09.027.

Chien, S.H.; Liu, W.; Dzombak, D.A.; and Vidic, R.D. (2012c) Impact of tertiary treatment processes on the effectiveness of chloramination for biofouling control in recirculattting cooling systems using treated municipal wastewater, Water Research, Submitted.

Characklis, W.G., (1990) Microbial fouling. In: Characklis WG, Mashall KC (EDs), Biofilm, Wiley, New York, pp 523-584

Choudhury, M.R.; Hsieh, M.K.; Vidic, R.D.; Dzombak, D.A. (2012) Corrosion Management in Power Plant Cooling Water Systems Using Tertiary Treated Municipal Wastewater as Makeup Water, Corrosion Science, Vol. 61, doi:10.1016/j.corsci.2012.04.042

Costerton, J.W., Stewart, P.S., and Greenberg, E.P. (1999) Bacterial biofilms: a common cause of persistent infections. Science 284:1318–1322

CTI (2008) Guideline: Best Practices for Control of Legionella, Cooling Technology Institute, U.S.A., CTI guidelines WTP-148 (06) http://www.cti.org/downloads/WTP-148.pdf

Dishneau, D. (2007) Frederick County denies cooling water to proposed power plant. The Baltimore Examiner, 17 Sep.

Edelstein, P. H. (1993) Legionnaires' Disease, Clinical Infectious Diseases, Vol. 16, No. 6 (Jun., 1993), pp. 741-747

Flemming, H. C. (2002), Biofouling in water systems – cases, causes, and countermeasures, Appl Microbiol Biotechnol, 59: 629-640

Feeley, T.J. and Ramezan, M. (2003) Electric Utilities and Water: Emerging Issues and R&D Needs, Proceedings of 9th Annual Industrial Wastes Technical and Regulatory Conference, Water Environment Federation, San Antonio, TX.

Fraser, D. W.; Tsai, T. R.; Orenstein, W.; Parkin, W.E.; Beecham, H.J.; Sharrar, R.G.; Harris, J.; Mallison, G.F.; Martin, S.M.; McDade, J.E.; Shepard, C.C.; and Brachman, P.S. (1977). "Legionnaires' Disease." New England Journal of Medicine 297(22): 1189-1197.

Frayne, C. (1999), "Cooling Water Treatment: Principles and Practice", Chemical Publishing Co., Inc., NY, pp. 122-135, 184-189

Grant, D.M., and Bott, T.R. (2005) Biocide Dosing Strategies for Biofilm Control, Heat Transfer Engineering, 26(1): 44-50

Hsieh, M.K.; Li, H., Chien; S.H., Monnell, J.D.; Chowdhury, I.; Dzombak, D.A; and Vidic, R.D. (2010) Corrosion control when using secondary treated municipal wastewater as alternative makeup water for cooling tower systems, Water Environment Research, 82, 2346–2356.

Hsieh, M.K.; Walker, M. E.; Safari, I.; Chien,S-H; Abbasian, J.; Vidic, R.D.; and Dzombak1, D.A. (2012) Ammonia stripping in open-recirculating cooling water systems, Environmental Progress & Sustainable Energy: NA/NA, DOI: 10.1002/ep.11648.

Kim B.R., Anderson, J. E., Mueller, S. A., Gaines, W. A., and Kendall, A. M. (2002) Literature review – Efficacy of various disinfectants against Legionella in water systems, Water Research, Vol. 36, pp 4433- 4444

Li, H.; Chien, S.H.; Hsieh, M.K.; Dzombak, D.A.; Vidic, R.D. (2011a) Escalating water demands for energy production and the potential for use of treated municipal wastewater, Environmental Science & Technology, 45(10), pp 4195-4200.

Li, H., Hsieh, M. K. , Chien, S.H., Monnell, J. D., Dzombak, D. A., and Vidic, R. D. (2011b) Control of mineral scale deposition in cooling systems using secondary-treated municipal wastewater. Water Research, Vol. 45, No. 2, pp. 748-760.

Liu, W.; Chien, S.H; Dzombak, D.A.; and Vidic. R, D. (2012) Mineral scaling mitigation in cooling systems using treated municipal wastewater: bench-scale and pilot-scale studies, Water Res., Sep, 15;46(14):4488-98

LeChevalier, M. W.; Cawthorn, C. D.; and Lee, R. G. (1988) Inactivation of biofilm bacteria, Applied and Environmental Microbiology, 54:2492–2499

LeChevalier, M.W.; Olson, B.H.; and McFeters, G.A. (1990) Assessing and controlling bacterial regrowth in distribution systems, Denver, CO: American Water Works Association

Ludensky, M. (2005) Microbiological control in cooling water systems and directory of microbiocides for the protection of materials: A handbook. pp. 121-139. 2005.

Melo, L. F., and Bott, T.R. (1997) Biofouling in water systems. Exp Therm Fluid Sci 14:375–381

NETL (2008) Water Requirements for Existing and Emerging Thermoelectric Plant Technologies, DOE/NETL-402/080108 http://www.netl.doe.gov/energy-analyses/pubs/WaterRequirements.pdf

Palin, A. (1950) A Study of the Chloro Derivatives of Ammonia. Water and Water Engineering. 54:248-258.Rao, T. S., Nanacharaiah, Y. V. and Nair, K. V. K. (1998) Biocidal Efficacy of Monochloramine against Biofilm Bacteria. Biofouling, 1998, Volume 12 (4), pp. 321-332.

Puckorius P. R., and Diehl K. (2003), "Water Reuse Experimencs with Cooling Tower Systems in San Antonio, Texas", Cooling Tower Institute Annual Conference, 2003. Paper No. TP03-03

Rossmoore, H. W. (1995) Handbook of biocide and preservative use, Blackie Academic & Pro Professional, Chapter 3, page 50-77.

Selby, K. A., Puckorius, P. R., and Helm, K. R. (1996) The use of reclaimed water in electric power stations and other industrial facilities, Water, Air, and Soil Pollution, Kluwer Academic Publisher, Netherlands, Vol. 90, pp 183-193.

Sirtes, G.; Waltimo, T.; Schaetzle, M.; and Zehnder, M. (2005) The Effects of Temperature on Sodium Hypochlorite Short-Term Stability, Pulp Dissolution Capacity, and Antimicrobial Efficacy, Journal of Endodontics 31(9): 669-671

Stampi, S.; Luca, G.D.; Onorato, M.; Ambro giani, E.; and Zanetti, F. (2002) Peracetic acid as an alternative wastewater disinfectant to chlorine dioxide, Journal of Applied Microbiology, 93(5): 725-731

USEPA (1991) Guidance manual for compliance with the filtration and disinfection requirements for public water systems using surface water sources, U.S. Environmental Protection Agency, Washington, D.C., Contact# 68-01-6989 http://water.epa.gov/lawsregs/rulesregs/sdwa/swtr/upload/guidsws.pdf

USEPA (1999) Alternative Disinfectants and Oxidants Guidance Manual, United States Environmental Protection Agency, EPA 815-R-99-014, April 1999.

Yu, V.L. (2008) Cooling towers and legionellosis: A conundrum with proposed solutions, Int. J. Hyg. Environ. Health, 211, pp. 229-234

Vidic, R.D. and Dzombak, D.A. (2009) Reuse of Treated Internal or External Wastewaters in the Cooling Systems of Coal-based Thermoelectric Power Plants, Department of Energy, Grant DE-FC26-06NT42722, National Energy Technology Laboratory, Pittsburgh, PA.

Zaidi M. K., (2006), "Wastewater Reuse – Risk Assessment, Decition-Making and Environmental Security", Proceeding of the NATO Advanced Research Workshop, Istanbul, Turkey, pp. 81-90.

Zhang, Z.; Mccann, C.; Hanrahan, J.; Jencson, A.; Joyce, D.; Fyffe, S.; Piesczynski, S.; Hawks, R.; Stout, E.S.; Yu, V.L.; and Vidic, R.D. (2009) Legionella control by chlorine dioxide in hospital water systems, Journal AWWA, 101:5 117-127.

**Appendix A**

Haas, C.N. and Karra, S.B. (1984) Kinetics of wastewater chlorine demand exertion, *Journal WPCF*, 56(2): 170-173.

March, J.G., Gual, M., and Ramonell, J. (2005) A kinetic model for chlorine consumption in grey water, *Desalination*, 181: 267-273.

Powell, J.C., Hallam, N.B., West, J.R., Forster, C.F, and Simms, J. (2000) Factors which control bulk chlorine decay rates, *Water Research*, 34(1): 117-126.

**Appendix B**

ASTM (2005). American Society for Testing and Materials, in *Annual Book of ASTM Standards*, Philadelphia, PA.

Bone C.C., Harringtom G.W., Oldenburg P.S., Noguera D.R. (1999) "Ammonia Release from Chloramine Decay: Implications for the Prevention of Nitrification Episodes", *Proceedings of AWWA Annual Conference*, Chicago, IL.

Breitstein, L.; Tucker, R.C. (1986), "Water Reuse and Recycle in the U.S. Steam Electric Generating Industry – An Assessment of Current Practice and Potential for Future Applications," National Technical Information Service. 1986.

Goldstein, D.J.; Casana, J.G., (1982) "Municipal Wastewater Reuse in Power Plant Cooling Systems," Water Reuse, Chapter 19, 1982, Ann Arbor, Michigan.

Haas, C.N. and Karra, S.B. (1984) Kinetics of wastewater chlorine demand exertion, *Journal WPCF*, 56(2): 170-173.

Hofstadler, K., R. Bauer, et al. (1994) "New Reactor Design for Photocatalytic Wastewater Treatment with TiO2 Immobilized on Fused-Silica Glass Fibers: Photomineralization of 4-Chlorophenol." Environmental Science & Technology 28(4): 670-674.

Issac, R.A., and Morris, J.C. (1983) Transfer of Active Chlorine from Chloramine to Nitrogenous Organic Compounds. Environ. Sci. Technol., 17, 738.

Lee, W. and Westerhoff, P. (2009) Formation of organic chloramines during water disinfection – chlorination versus chloramination, *Water Research*, 43(8): 2233-2239.

March, J.G., Gual, M., and Ramonell, J. (2005) A kinetic model for chlorine consumption in grey water, Desalination, 181: 267-273.

Masri, M.; Therkelsen, R., (2003), Electric Power Research Institute. "Use of Degraded Water Sources as Cooling Water in Power Plants," October 2003. Prepared for California Energy Commission

Morris J. C. and Isaac R. A. (1981) “A critical review of kinetic and thermodynamic constants for the aqueous chlorine-ammonia system.” In Water Chlorination: Environmental Impact and Health Effects, Vol. 4, pp. 49–62. Ann Arbor Science, Ann Arbor, MI.

Powell, J.C., Hallam, N.B., West, J.R., Forster, C.F, and Simms, J. (2000) Factors which control bulk chlorine decay rates, *Water Research*, 34(1): 117-126.

Stanbro, W. D. and Smith, W. D. (1979) “Kinetics and Mechanism of the Decomposition of N–Chloroalanine in Aqueous Solution.” Environmental Science and Technology, Vol. 13: 466–451.

Tsai, S.P., Nalco Company., (2006), "A Synergistic Combination of Advanced Separation and Chemical Scale Inhibitor Technologies for Efficient Use of Impaired Water as Cooling Water in Coal-based Power Plant," Quarterly reports, Mar 31-Jun 30 and Jul 1-Sep 30, 2006. Prepared for Department of Energy (DOE Award Number: DE-FC26-06NT42721)

Valentine R. L. and Jafvert C. T. (1988) General acid catalysis of monochloramine disproportionation. Environ. Sci. Tech. 22(6), 691–696.

Valentine R.L., Ozekin K., Vikesland P.J. (1998) “Chloramine Decomposition in Distribution System and Model Waters”, AWWA Research Foundation, Denver, CO.

Williams, R.B., (1982), "Wastewater Reuse-An Assessment of The Potential and Technology," Water Reuse, Chapter 5,, Ann Arbor, Michigan.

Weinberger, L.W.; Stephan, D.G.; Middleton, F.M. (1966), "Solving Our Water Problems-Water Renovation and Reuse." Ann. N. Y. Acad. Sci. 136, pp. 131-154.

Yoon, J., and Jensen, J.N. (1995) Chlorine Transfer from Inorganic Monochloramine in Chlorinated Wastewater. Water Environmental Research, 67, 163.

**Appendix C**

Argonne (2012) GREET model, Transportation Technology R&D Center, United States Department of Energy. http://greet.es.anl.gov/

CPM (2012) Life Cycle Inventory Data”, Center for Environmental Assessment of Product and Material Systems, Göteborg, Sweden. http://www.cpm.chalmers.se/CPMDatabase/Start.asp

NETL (2008) Water Requirements for Existing and Emerging Thermoelectric Plant Technologies, DOE/NETL-402/080108 http://www.netl.doe.gov/energy-analyses/pubs/WaterRequirements.pdf

NREL (2012) U.S. Life-Cycle Inventory Database, National Renewable Energy Laboratory, U.S. Department of Energy, Golden, CO 80401-3305 http://www.nrel.gov/lci/

PRé (2012) SimaPro Database, Pre Consultants, Printerweg 18, 3821 AD Amersfoort, The Netherlands http://www.pre-sustainability.com/databases