A COMPARATIVE STUDY OF NITRIFICATION IN FARGO AND MOORHEAD

WATER DISTRIBUTION NETWORKS

A Thesis Submitted to the Graduate Faculty of the North Dakota State University of Agriculture and Applied Science

By

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In Partial Fulfillment for the Degree of MASTER OF SCIENCE

> Major Department: Civil Engineering

> > October 2012

Fargo, North Dakota

North Dakota State University Graduate School

Title

A Comparative Study of Nitrification in Fargo and Moorhead

Distribution Networks

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ABSTRACT

Nitrification in water distribution networks has become a growing concern for water supplies in the United States. The use of chloramines as a disinfectant in distribution pipe networks has become increasingly popular to reduce the disinfectant byproducts that are formed with free chlorine. In chloraminated systems there is potential for nitrification to occur because it reduces chloramine residuals. As chloramines decompose in the network, ammonia is released. Nitrifiers oxidize ammonia into nitrites, which react with chloramines resulting in its further reduction. As this cycle continues, chloramines will be consumed faster in the network, causing regrowth of heterotrophic bacteria. A study was conducted to compare the Fargo and Moorhead distribution networks for the occurrence of nitrification and their potential to deteriorate water quality. Each distribution network was analyzed independently for variations in operational conditions and water quality parameters that can serve as indications of nitrification in a distribution network.

ACKNOWLEDGMENTS

I would like to thank my advisor Dr. Wei Lin for his guidance and support throughout my graduate research. I would also like to thank my committee members; Dr. B. Sani-Eidukat, Dr. Achintya Bezbaruah, and Cliff McLain for their advice and recommendations.

I would also like to thank the Moorhead Water Treatment Plant for funding this research. Their generosity supported my research which allowed me to utilize their lab, including equipment and chemicals. A special thanks to the water treatment plant staff including; Troy Hall, Cliff Mclain, Gena Dahl, and Kris Knutson for their assistance during the completion of my research.

Finally, I would like to thank my family including my daughter Evelyn Portlock and my wife Cody Portlock for her patience and encouragement. My family has been there for me with love and encouragement; my accomplishments were possible with their support.

DEDICATION

To my daughter Evelyn Portlock, my wife Cody Portlock, and my family.

TABLE OF CONTENTS

ABSTRACTiii
ACKNOWLEDGMENTSiv
DEDICATIONv
LIST OF TABLESix
LIST OF FIGURESx
LIST OF EQUATIONSxiii
LIST OF ACRONYMSxiv
LIST OF APPENDIX TABLESxv
CHAPTER 1. INTRODUCTION1
1.1. Problem Statement
1.2. Objectives
1.3. Scope of Work
CHAPTER 2. BACKGROUND
2.1. Moorhead Treatment Process
2.1.1. Water sources and their uses
2.1.2. Water softening process
2.1.3. Ozonation process
2.1.4. Filtration process
2.1.5. Secondary disinfection
2.2. Fargo Treatment Process
2.2.1. Water sources
2.2.2. Suspended solids and taste/odor removal
2.2.3. Water softening process

2.2.4. Ozonation process	26
2.2.5. Filtration process	28
2.3. Summary of the Fargo and Moorhead Treatment Processes	29
CHAPTER 3. LITERATURE REVIEW	32
3.1. Nitrification	32
3.2. Chloramines	33
3.3. Nitrification in the Distribution Network	35
3.3.1. Impact of pH on nitrification	36
3.3.2. Temperature impact on nitrification in the distribution network	37
3.3.3. Biofilm in the distribution network	38
3.3.4. Impact of nitrite in the distribution network	39
3.4. Nitrification in the Biofilter	40
3.5. Nitrification Control	41
CHAPTER 4. METHODOLOGY	44
4.1. Sample Period and Locations	44
4.2. Distribution Network Sampling Methods	47
4.3. Moorhead Biofilter Sampling	47
4.4. Analytical Methods	47
CHAPTER 5. RESULTS AND DISCUSSION	50
5.1. Water Quality Variations in the Fargo and Moorhead Distribution Network	50
5.1.1. Temperature and pH	50
5.1.2. Chlorine residual	55
5.1.3. Nitrogen (NH_4^+ -N, NO_2^- -N, and NO_3^- -N) concentrations	59
5.1.4. Comparison of chlorine residual, NH ₄ ⁺ -N, and NO ₂ ⁻ -N in the Fargo and Moorhead distribution networks	65

5.1.5. Total organic carbon	71
5.1.5.1. Specific ultraviolet absorbance at 254 nm (SUVA)	74
5.1.5.2. Moorhead biofilter organic removal	77
5.1.6. Bacterial regrowth	78
5.2. Moorhead Biofilter Sampling for Nitrifying Activity	
CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS	84
6.1. Conclusions	
6.2. Recommendations	86
REFERENCES	87
APPENDIX	91

LIST OF TABLES

Table	Page Page
1. Well water quality and capacity (Moorhead WTP 2009)	12
2. Moorhead ozone contact chamber volumes and detention time at 5.0 MGD (Moorhead WTP 2011).	16
3. Fargo contact chamber volume and detention time (Fargo WTP)	
4. Comparison of the Fargo and Moorhead treatment processes.	31
5. Chlorine and ammonia reactions (AWWA M56, 2006).	34
6. Chloramine reactions	35
7. Fargo and Moorhead sample descriptions	44

LIST OF FIGURES

Figure	Page
1. Moorhead WTP process flow diagram (Moorhead WTP 2012).	6
2. Moorhead WTP daily water intakes (2009).	7
3. Red River turbidity measured at the Moorhead WTP (Moorhead WTP 2009)	8
4. Total organic carbon in the Red River and daily precipitation during 2009	9
5. Red River hardness as CaCO ₃	11
6. Red River discharge (USGS gaging station 05054000 Red River of the North at Fargo, ND 2009).	11
7. Moorhead ozone contact chamber (Moorhead WTP 2012).	15
8. Moorhead WTP filter diagram.	20
9. Fargo WTP process flow diagram (Fargo WTP 2011).	22
10. Fargo WTP flow 2010/2011 (Fargo WTP)	23
11. City of Fargo water use between 2006 and 2011.	23
12. Sheyenne and Red River hardness concentrations	24
13. Fargo ozone contact chamber (Fargo WTP 2011 modified from original)	26
14. Sample sites in the Fargo distribution network. (City of Fargo 2010)	45
15. Sample sites in the Moorhead distribution network (City of Moorhead 2009)	46
16. Variation of temperature in the Moorhead distribution network.	52
17. Variation of temperature in the Fargo distribution network	52
18. Variation of pH in the Moorhead distribution network	54
19. Variation of pH in the Fargo distribution network	54
20. Variation of total chlorine in the Moorhead distribution network.	57

21.	Variation of total chlorine in the Fargo distribution network.	57
22.	Variation of ammonia-N, nitrite-N, and nitrate-N at the Moorhead WTP	60
23.	Variation of ammonia-N, nitrite-N, and nitrate-N at Moorhead 1	60
24.	Variation of ammonia-N, nitrite-N, and nitrate-N at Moorhead 2	61
25.	Variation of ammonia-N, nitrite-N, and nitrate-N at Moorhead 3	61
26.	Variation of ammonia-N, nitrite-N, and nitrate-N at the Fargo water treatment plant.	63
27.	Variation of ammonia-N, nitrite-N, and nitrate-N at Fargo 1	63
28.	Variation of ammonia-N, nitrite-N, and nitrate-N at Fargo 2	64
29.	Variation of ammonia-N, nitrite-N, and nitrate-N at Fargo 3	64
30.	Red River nitrate concentrations.	65
31.	Chlorine, nitrite, and ammonia concentrations from the Moorhead water treatment plant sample location	66
32.	Chlorine, nitrite-N, and ammonia-N concentrations from Moorhead 1	67
33.	Chlorine, nitrite-N, and ammonia-N concentrations from Moorhead 2	67
34.	Chlorine, nitrite-N, and ammonia-N concentrations from Moorhead 3	68
35.	Chlorine, nitrite-N, and ammonia-N concentrations from the Fargo WTP	69
36.	Chlorine, nitrite-N, and ammonia-N concentrations from Fargo 1	70
37.	Chlorine, nitrite-N, and ammonia-N concentrations from Fargo 2	70
38.	Chlorine, nitrite-N, and ammonia-N concentrations from Fargo 3	71
39.	Total organic carbon in the Moorhead distribution network	73
40.	Total organic carbon in the Fargo distribution network	73
41.	Variation of SUVA in the Moorhead distribution network	76
42.	Variation of SUVA in the Fargo distribution network	76

43. Moorhead WTP organics.	77
44. Percent TOC removal through the treatment process at the Moorhead WTP	78
45. Percent TOC removal in the Moorhead biofilter and Red River temperature	79
46. Heterotrophic plate counts in the Moorhead distribution network	80
47. Heterotrophic plate counts in the Fargo distribution network	80
48. The four biological filters sampled in the Moorhead water treatment plant	83

LIST OF EQUATIONS

Equation	Page
1. CT	16
2. Required CT	17
3. Moorhead CT	17
4. Giardia log inactivation	27
5. Total virus inactivation	27
6. Nitrosomonas reaction	
7. Nitrobacter reaction	

LIST OF ACRONYMS

AOB.....Ammonia Oxidizing Bacteria

- CFU.....Colony Forming Unit
- DOC.....Dissolved Organic Carbon
- HPC.....Heterotrophic Plate Counts
- MCL.....Maximum Contaminant Level
- MCLG......Maximum Contaminant Level Goal
- MPN.....Most Probable Number
- NOB.....Nitrite Oxidizing Bacteria
- NOM.....Natural Organic Matter
- NTU.....Nephelometric Turbidity Unit
- SUVA.....Specific Ultraviolet Absorbance 254 nm
- THM.....Trihalomethane
- TOC.....Total Organic Carbon
- USEPA.....United States Environmental Protection Agency
- WTP.....Water Treatment Plant

LIST OF APPENDIX TABLES

Table	Page
A1. Fargo WTP sampling data	91
A2. Fargo 1 sampling data	94
A3. Fargo 2 sampling data	97
A4. Fargo 3 sampling data	
A5. Moorhead WTP sampling data	
A6. Moorhead 1 sampling data	
A7. Moorhead 2 sampling data	
A8. Moorhead 3 sampling data	112

CHAPTER 1. INTRODUCTION

Majority of water supplies in the United States utilize free chlorine for disinfection. Reaction of chlorine with natural organic matter (NOM) can produce trihalomethanes (THM's), a known carcinogen, and other disinfection byproducts. The US Environmental Protection Agency amended the Safe Drinking Water Act with the Stage 1 and Stage 2 Disinfection Byproducts Rule (USEPA, 2001). The rule establishes maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for haloacetic acids, total trihalomethanes, chlorite, and bromate. In order to comply with the new regulations, many water suppliers have switched from free chlorine to chloramines as a secondary disinfectant to maintain required chlorine residual in distribution networks.

Chloramine is a weaker disinfectant than free chlorine but is more stable, thus extending disinfectant benefits throughout a water distribution network. Chloramines do not aggressively react with NOM to form chlorinated disinfection byproducts. However, decomposition of chloramines release ammonia that may cause nitrification in distribution networks which leads to further breakdown of chloramines and potential regrowth of bacteria. Nitrification in water distribution networks has become a growing concern for water supplies in the United States as more water systems switch to chloramines as the secondary disinfectant.

Nitrification in distribution networks has been reported in several published articles (Cunliffe, 1991, Lipponen et al., 2002, and Wolfe et al., 1989). It has been shown that nitrification is more likely to occur when chloramine is present and used as a disinfectant in distribution pipelines and reservoirs (Cunliffe 1991, Wolfe 1989;

1

Zhang 2001). Nitrification can cause water quality issues such as loss of chlorine residual, growth of heterotrophic bacteria, and elevated nitrite/nitrate concentrations.

Water supplies utilizing ozonation for primary disinfection and chloramines as secondary disinfectants can be more susceptible to nitrification in their distribution networks. The ozonation process breaks down complex organics into a more biodegradable form. The simple organics provide nutrients to bacteria in water distribution networks. The growth of these bacteria can cause a decrease in chloramines. Additionally, the decrease in chloramines encourages bacteria using these simple organics for growth making these systems more susceptible to nitrification. The EPA requires the removal of these simple organics that can be accomplished through filtration. A secondary disinfectant, typically chloramination, is also required to maintain a chlorine residual to prevent microbial growth.

1.1. Problem Statement

Currently, most research on nitrification in distribution networks is carried out in systems which use chlorination as a primary disinfectant and chloramination in the distribution network. There is a need to study nitrification in ozonationchloramination water distribution systems.

Chloraminated drinking water systems pose a risk for nitrification to occur because ammonia is present. Biodegradable organics formed by ozonation pose an additional risk as simple organics enter the distribution network. The combination of ozonation and chloramination may have a higher probability for nitrification to occur due to these circumstances. The Fargo and Moorhead WTP's have similar treatment processes including similar source waters, softening, ozonation, dual media filtration, and chloramination. There has been limited research comparing two similar treatment plants and their corresponding distribution networks for the occurrence of nitrification. Ozonation-chloramination water distribution systems may be more susceptible to nitrification and a comparative study of similar treatment plants would prove beneficial for future design considerations.

1.2. Objectives

The main goal of this study is to investigate nitrification in the distribution networks and do a comparative study of the Fargo and Moorhead distribution networks. The specific objectives are to

- Identify the design and operational differences at the Fargo and Moorhead WTP that many indicate a potential for nitrification to occur in the distribution network.
- Determine the water quality change through the Fargo and Moorhead distribution network and its potential for nitrification to occur; and
- Combine the analysis of the water treatment plants and distribution networks for future designs and recommendations to minimize the occurrence of nitrification.

Results of this research will provide a better understanding of nitrification in the Fargo and Moorhead distribution networks. The data may be used to enhance operational procedures, to address possible areas of concern in the distribution network, and to gain better understanding of nitrification during a broad variation of temperatures.

1.3. Scope of Work

This study includes reviewing data from the past 2 years (2009 and 2010) from the Moorhead and Fargo water treatment plants. After the data was reviewed, the two water treatment plants reservoirs and their corresponding distribution networks were sampled through 2009-2010. Samples were taken from the finished water reservoirs at each treatment plant and three locations with increasing distance from the treatment plant in each distribution network location. Samples were taken from the Moorhead biofilter to investigate nitrifying activities. All water samples were analyzed in the Moorhead WTP laboratory.

Water quality in the two distribution networks was compared with the data collected in the treatment plants and distribution networks. Certain water quality parameters were compared to indicate nitrifying activity. In addition, the data collected was used to determine if the water quality in their distribution networks deteriorated due to nitrification.

4

CHAPTER 2. BACKGROUND

A description of the Fargo and Moorhead WTP's process design and operation is presented in this chapter. More specifically, this chapter discusses the Fargo and Moorhead treatment plant design, water sources, softening, filter operations, and disinfection strategies. Data presented in this chapter was collected from archived data at the Fargo and Moorhead WTP.

2.1. Moorhead Treatment Process

The Moorhead Water Treatment Plant (WTP) provides potable water to the cities of Moorhead and Dilworth, Minnesota. The cities have a population of 36,804 and 3,711 people, respectively. The Moorhead WTP uses lime softening, ozonation, filtration, and chloramination as its treatment processes shown in Figure 1. The design capacity of the Moorhead WTP is 10.0 million gallons per day (MGD). Currently, the plant produces 5.0 MGD to the users in summer months and the demand gradually reduces to 3.0 MGD in the winter. A daily peak flow of 9.0 MGD has been recorded in the summer months (Knutson, personal communication, 2012).

2.1.1. Water sources and their uses

The Moorhead WTP uses the Red River as its main water source and groundwater as a supplemental source. Supernatant from softening sludge settling pond is also reprocessed. The daily pumping rates of river, well, pond water and total flow for 2009 are shown in Figure 2. On average, 4.42 MGD of water was treated in

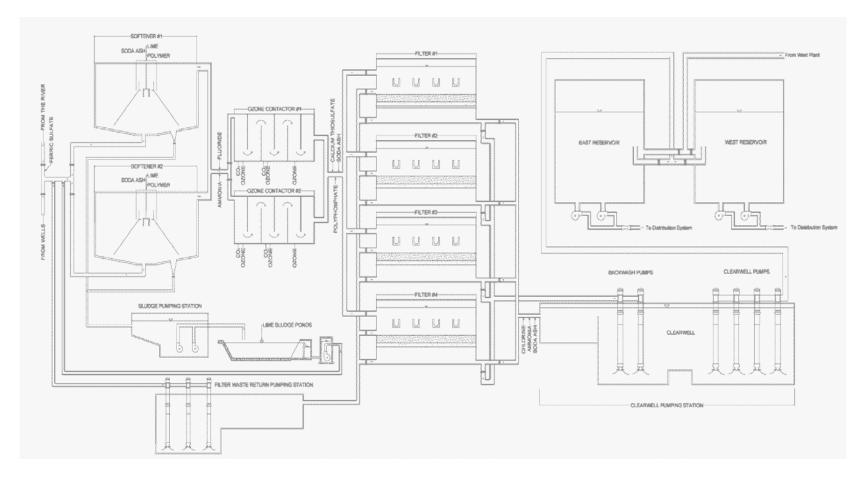


Figure 1. Moorhead WTP process flow diagram (Moorhead WTP 2012).

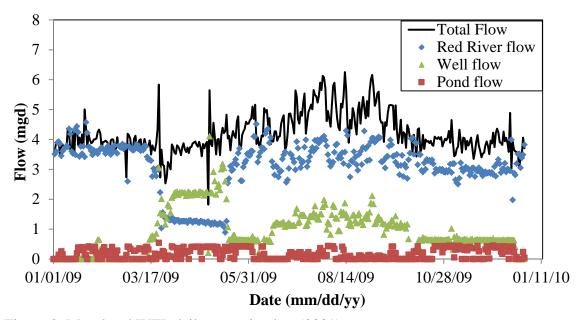


Figure 2. Moorhead WTP daily water intakes (2009).

2009 with higher water demand, above 6.5 MGD, observed in summer months. Use of well water varied throughout the year depending on river water quality and other factors. Well water is typically added during the summer months to reduce the plant influent water temperature and improve water quality. During spring floods the Red River has high levels of organics, hardness, and/or turbidity. Well water can be used during this time to improve the influent water quality. Another benefit of groundwater use is that it reduces the chemical cost of treating the surface water because groundwater has less turbidity, hardness, and organics depending on the well. Additionally, as compared with surface water well water has less variation in water quality.

Overall The Red River was used for the majority of 2009 shown in Figure 2. From March 2009 to May 2009 the Red River pumps at the Moorhead WTP were throttled to accommodate additional well water flow which is typically used during flooding. Well flow was used for the majority of the year expect during the winter from January 2009 to March 2009. Well water is not needed during these periods because the Red River has lower turbidly and temperature. The last source of water that the Moorhead WTP utilizes is decant water from the lime sludge ponds which are pumped back into the headworks of the treatment plant. It is a small proportion of daily flow compared to the other water sources but provides water that is already softened reducing the chemical cost of treating the water. Pond water flow rates ranged between 0 to 0.18 MGD and accounts for approximately 4.27% of the total water treated.

Variation of Red River turbidity is shown in Figure 3. There are several times in 2009 when the turbidity spiked in the Red River. Increases in turbidity can be a caused by surface runoff, upstream discharges, and/or flooding. Low turbidity seen from January 2009 to the beginning of March 2009 and November 2009 to December 2009 is during the winter. Typically, there are little to no increase in turbidity because of ice cover. At the end of March there is a turbidity increase which was cause by spring flooding. In the other months, turbidity spikes were caused by runoff attributed to rainfall events.

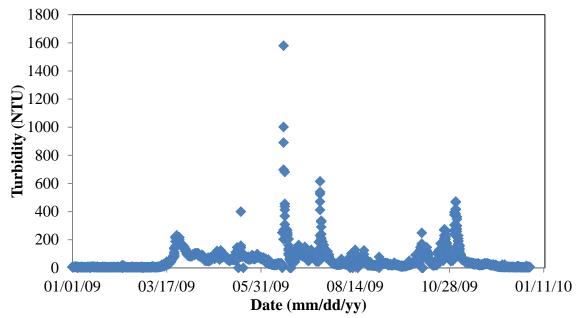


Figure 3. Red River turbidity measured at the Moorhead WTP (Moorhead WTP 2009).

As mentioned earlier there are several benefits when using groundwater in the treatment process, including 1) lowering product water temperature, 2) improving influent water quality, and 3) reducing chemical cost. During the summer months, the Moorhead WTP has to meet certain constraints for industrial users. The well water can assist in lowering its product water temperature near 70°F to meet these requests. It can also be used when the river's hardness increases. Typically, the well's hardness does not change. Depending on which well is pumping, it can be used to minimize surface water variations in hardness. Yearly flooding and precipitation can change the rivers quality resulting in elevated organic levels, as shown in Figure 4.

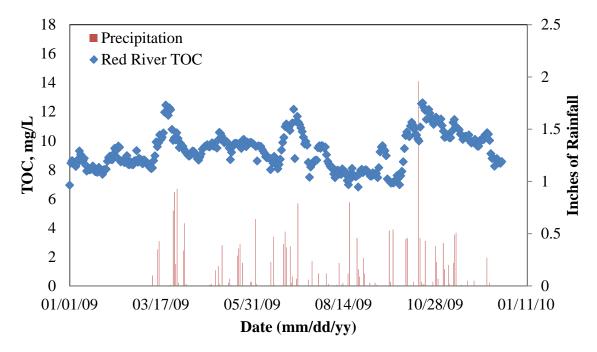


Figure 4. Total organic carbon in the Red River and daily precipitation during 2009.

In the middle of March 2009 there was a flood event that elevated the organics the Red River from 8.5 mg/L to 12.0 mg/L. There are two other instances where the organics in the Red River increased. In June 2009 there were several rain events that occur during a short period which increased the organics in the river. Typical operation at the water

treatment plant includes turning on the well water when the TOC concentrations are up to and above 10.0 mg/L.

The Red River's water hardness varies throughout the year, as shown in Figure 5. The Red Rivers hardness is over 180 mg/L as CaCO₃ which is classified as hard water (Davis and Cornwell 2008). The average concentration of hardness in the Red River is 339 mg/L as CaCO₃. In Figure 5 there are several peaks and depressions in the Red River's hardness concentration. In March 2009 the hardness increased in the Red River during spring runoff. Non-carbonate and carbonate hardness followed a similar pattern. It is important to analyze non-carbonate and carbonate hardness because non-carbonate hardness will cost more money to treat than carbonate hardness. Soda ash is needed for removing non-carbonate hardness in the Red River was comprised of more carbonate hardness. From October 2009 the hardness in the Red River was comprised of more carbonate hardness. From October 2009 to December 2009 the carbonate and non-carbonate hardness were similar indicating that these months increased the cost of treating the surface water.

Figure 6 represents the data that was collected from the USGS Red River gaging station which measures the flow of the Red River in cfs. In March 2009, there is a steep increase in the measured discharge. This event occurred during spring runoff when the river was rising. The Red River water levels rising caused two events to occur. First, surface runoff from snowmelt caused a small increase in flow which was approximately 2,000 cfs. Surface runoff also caused the hardness in the Red River to rise. Secondly, the additional water attributed to flooding which occurred after the surface runoff diluted the Red River reducing the hardness. There are instances where the hardness concentration sharply decreased in Figure 5. Precipitation events occurred in June, July, and November

of 2009 which lowered the hardness for a small period in the Red River. It can also be seen in Figure 6 that there is an increase in the Red River discharge that corresponds directly to the instances when the hardness in the water was lowered.

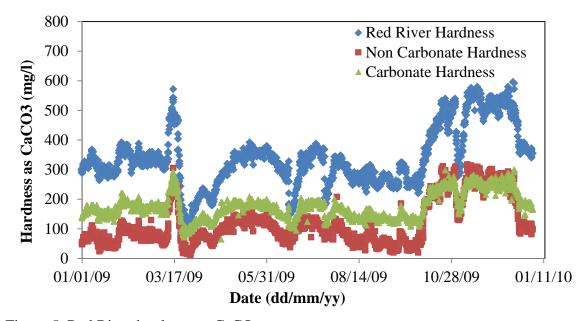


Figure 5. Red River hardness as CaCO₃.

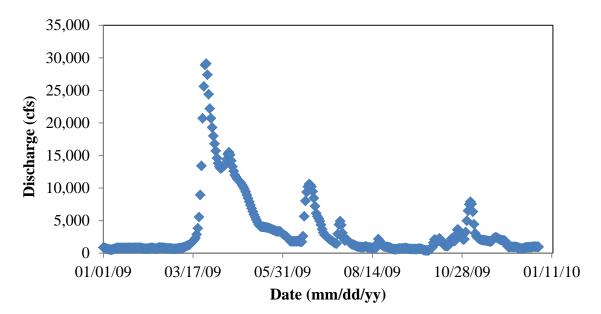


Figure 6. Red River discharge (USGS gaging station 05054000 Red River of the North at Fargo, ND 2009).

There are seven ground water wells that Moorhead WTP can withdraw water from. Water quality characteristics and pumping capacity at these wells are shown in Table 1. The hardness of the wells range from 176 mg/L to 516 mg/L as CaCO₃ indicating hard to very hard water (Davis and Cornwell 2008). Interestingly, the water quality from the Moorhead wells varies because they are located in two aquifers, the Buffalo Aquifer and the Moorhead Aquifer. Wells 6 and 6B have a lower hardness concentration because they are in the Moorhead aquifer which is a deeper aquifer. Wells 1, 2, 8, 9, and 10 are located in the Buffalo aquifer, which is a shallow aquifer. These groundwater wells have low organic concentrations compared to the Red River. Also with an average temperature of 52°F, there is much less variation in temperature compared to the Red River. The majority of the year the water plant operates one ground water well and one river pump. Typically well #6 or well #6B is turned on to decrease the total load of hardness. The remaining wells are used to supplement the main water source (Red River) for the other water quality improvement purposes.

Well	Hardness (mg/L as CaCO ₃)	Calcium hardness (mg/L as CaCO ₃)	Average TOC (mg/L)	рН	Capacity gal/min	Average Temperature (°F)
1	516	316		7.37	1060	
2	460	248		7.47	840	
6	180	120		7.71	450	
6B	176	120	2.96	7.71	550	52
8	464	288		7.47	760	
9	324	204		7.62	995	
10	324	216		7.67	1929	

Table 1. Well water quality and capacity (Moorhead WTP 2009).

2.1.2. Water softening process

The Moorhead WTP has two softening basins that are 50' x 50' with a sidewall depth of 18 ft. The design detention time in the softening basins are 1.7 hours with a surface loading rate of 1.55 gpm/ft^2 . The softening basin was designed with a weir overflow rate of 10.7 gpm/ft. The plant was designed to operate one softening basin with one designed for redundancy.

Lime and soda softening is applied at Moorhead WTP. Soda ash (Na₂CO₃) and lime (Ca(OH)₂) are added to remove hardness in the water. Excess amount of lime is added to cause a series of chemical reactions that has a primary goal of precipitating calcium and magnesium as calcium carbonate and magnesium hydroxide respectively. These compounds are not soluble at a high pH in the softening basin and will settle out of the water. Excess lime softening is used in both of the softening basins which are operated in parallel. Soda ash is added in the softening basin to remove the noncarbonated hardness while lime removes the carbonate hardness. Coagulation polymer is utilized in the softening basin for flocculation and rapid settling.

2.1.3. Ozonation process

Following the lime softening process the water is ozonated for taste and odor control and disinfection. Taste and odor oxidation and disinfection occur in two sequences. The first sequence occurs when high pH water enters the ozone contact chamber where the taste and odor compounds are oxidized. In the first sequence disinfection occurs but there is little residual for disinfection credits. Secondly, the pH is lowered in the following cells where a residual can be maintained and disinfection occurs. Ozone is very reactive and reverts back to oxygen quickly. The instability of ozone makes its application only possible with on site ozone generation. Ozone is generated onsite and starts with a high purity oxygen system that converts atmospheric air to a higher purity, 95% oxygen. The high purity oxygen system feeds oxygen at a capacity of 70 standard cubic feet per second to two ozone generators that are both capable of producing 400 lbs/day of ozone. Ozone is diffused into contact chambers through groups of fine bubble diffusers located at the bottom of the two contact chambers. These contact chambers are operated in parallel and each contact chamber has a hydraulic capacity of 5 MGD. Each contact chamber is divided into 6 cells; A, B, C, D, E, and F, as shown in Figure 7. After softening, the pH is usually elevated above 10.6. The plant was originally designed to feed CO₂ into cell A. This enhanced the capability of the treatment plant to break down taste and odor compounds earlier in the process. After the modification, there are 24 diffusers in cell A, 8 in cell C, and 12 in cell E.

The plant is designed to remove taste and odor compounds at the high pH above 10.6 in cells A and B. Adding CO_2 after lime/soda ash softening, which is referred to as recarbonation, decreases the pH. Carbon dioxide is added through the same ceramic diffusers as ozone and is operated into one of two cells depending on the season. In the summer, CO_2 is diffused into cell A and in the winter the configuration is switched to cell C. In the summer, CO_2 is diffused into Cell A because pH adjustment is needed immediately in the first cell to reduce ozone decomposition due to higher water temperatures. Higher temperatures cause the reaction rates of ozone to increase and an elevated pH decomposes ozone into hydroxyl radicals. Hydroxyl radicals are beneficial for

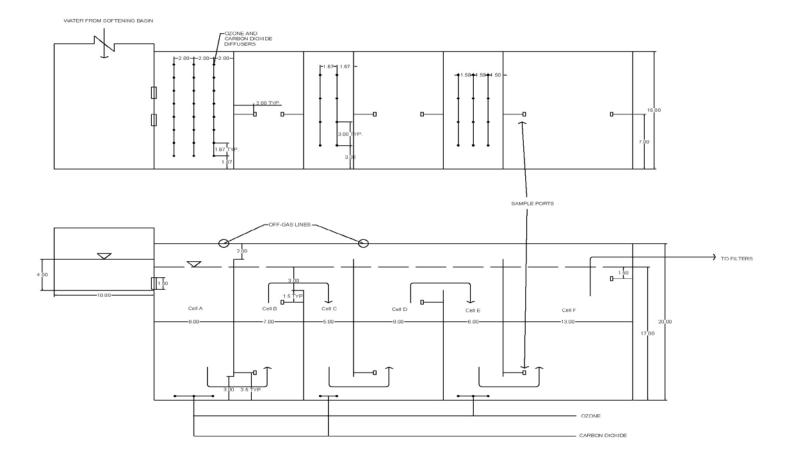


Figure 7. Moorhead ozone contact chamber (Moorhead WTP 2012).

taste and odor removal but have been shown to convert bromide to bromate. There is ongoing research at the water treatment plant regarding bromate formation, which will provide a deeper understanding regarding this subject. Cell C is used in the winter because the lower temperature reduces the reaction rate of ozone, lowering the chance that bromide is converted to bromate. There are pH controllers which monitor and adjust the CO_2 dose rate keeping finished water pH in the range of 9.2-9.5. CO_2 can also be used to control the ozone residual. During rainfall events, runoff will cause a heavy ozone demand. This demand can cause swings in the ozone residual concentration. Adjusting the ozone dose rate can take time to see an effect. When the CO_2 is adjusted the effects are almost immediate. An increase in CO_2 will lower the pH thus increasing the ozone residual.

The ozone contact chambers have a total of 4 monitoring locations which are located in cells D and F at a high and low locations as shown in Figure 7. Ozone concentrations at these locations are used for CT calculations which are measured at the effluent of cell D and cell F.

CT is the concentration of a disinfectant multiplied by the amount of time the disinfectant is in contact with the water (Equation 1). It is a measurement used to demonstrate the level of disinfection treatment in the water.

$$Ct = C (mg/L) \times t (time (min))$$
(1)

Surface water treatment plants are required to remove 3 log Giardia and 4 log viruses in the treatment process (US EPA 1991). Conventional treatment credits all water treatment plants including the Moorhead WTP so the primary disinfectant ozone only has to remove 0.5 log Giardia and 2 log viruses. Conventional treatment must include coagulation, flocculation, sedimentation, and filtration. For ozonation systems, a higher CT value has to

be maintained to achieve 2 log inactivation of viruses compared to achieve 0.5 log inactivation of Giardia. Therefore, CT required for virus inactivation controls. The equation used for the minimum CT requirement at the Moorhead WTP is shown below.

Required
$$CT = -0.03125^{*}(Temp \ ^{\circ}C) + 0.93125$$
 (2)

where,

C is ozone residual concentration,

t is amount of time ozone reacts with water.

The detention time is computed through cells C, D, E, and F. For example C (Cell D) is the concentration of ozone in cell D multiplied by the total volume in cell C and D divided by the influent flow. A baffling factor, which is used to determine the effective contact time of disinfection, of 0.7 is used for all the cells. The primary purpose of cells A and B are for taste and odor removal using a high pH (10.6-11.3). Cells A and B are excluded from CT calculation because the ozone residual is difficult to detect due to rapid ozone decay at high pH (Knutson, personal communication, 2012). The equation the Moorhead WTP uses for Ct calculation is shown in Equation 3. The volume and detention time in each cell are shown in Table 2;

$$Ct = 0.70C_D \times \frac{V_c + V_D}{Q} + 0.70C_F \frac{V_E + V_F}{Q}$$
(3)

where,

0.7 is the baffle factor;

 C_D and C_F are ozone residual concentrations in Cells D and F; V_C, V_D, V_E, V_F are volumes of Cells C, D, E and F; and Q is the water flow rate through the ozonation chamber.

Cell	Volume (gallons)	Detention Time at 5 MGD (min)
А	15260	4.39
В	13352	3.84
С	9537	2.74
D	17167	4.94
E	11445	3.29
F	24797	7.14
Total Contactor	91558	26.36

Table 2. Moorhead ozone contact chamber volumes and detention time at 5.0 MGD (Moorhead WTP 2011).

2.1.4. Filtration process

Primary purpose of media filtration in a water treatment plant is to remove non settleable solids from water. The Moorhead WTP employs dual media filter systems with larger size anthracite grains on top of smaller size sand grains. After a backwash, more dense media (sand) settle more quickly than the less dense media (anthracite). The filters are designed so that the water moves through the media with progressively smaller pores. The largest particles are strained out by anthracite and the remaining particulate matter is trapped through a combination of adhesion and straining.

The Moorhead filters are also operated as biofilters, in which a thin layer of biofilm grows on media surfaces to remove biodegradable organics in treated water. A biofilter is required when ozonation is used in a treatment process. Ozonation oxidizes organics into simple biodegradable forms. The biofilter then can remove these simple organics preventing a food source for bacteria entering the distribution network. Moorhead facility has four dual media filters that follow ozonation shown in Figure 8. Each of the four filters contains 24" of anthracite followed by 12" of sand. There are four troughs located in each filter that are primarily used for backwashing the filters. During normal operation water flows from the ozonation process to an open chamber. It then flows through four troughs and overflows the troughs traveling into the media for filtration.

During a backwash the filters go through an air scour where air is pumped underneath the media to break up and dislodge attached particles. After the air scour backwash water is pumped up through the media wasting any water that was used for backwashing. The water flows out of the troughs and into a waste basin. This process removes the dirty water after the air scour has cleaned the media. After the backwash is finished, the filters start filtering but the water is wasted until a minimum turbidity of 0.1 NTU is satisfied. Once the minimum turbidity is satisfied the filter backwash is complete and they are able to filter water. The filters are operated for 72 hrs in the summer and 82 hrs in the winter before a backwash is needed

2.1.5. Secondary disinfection

Chloramination follows biofiltration and is also referred to as secondary disinfection. Chlorine and ammonia are injected before the clearwell, forming chloramines. At the Moorhead WTP, chlorine gas is diffused into the water and then ammonia is added at a weight ratio of 5:1 Cl₂:NH₃. Chloramines are effective at preventing regrowth of bacteria and other microorganisms. The long residual time in the pipe network makes it beneficial when compared to other disinfectants.

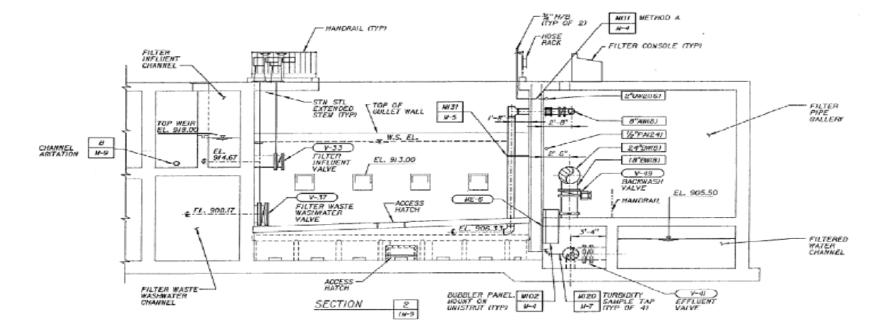


Figure 8. Moorhead WTP filter diagram.

The water is pumped from the clearwell to one of two reservoirs with a total capacity of 5.5 million gallon. The two reservoirs are interconnected so the water quality in both reservoirs is similar. From these reservoirs, the finished water is pumped into the distribution network. Fluoride is added to the finished water before being pumped into the distribution network

2.2. Fargo Treatment Process

The Fargo WTP services a population of close to 100,000 in the city of Fargo, ND. Water treatment processes in Fargo WTP includes pre sedimentation, lime softening, ozonation, filtration, and chloramination, as shown in Figure 9. The plant has a design capacity of 30 MGD. The plant typically pumps 13 MGD in the summer months and then reduces to 9 MGD in the winter. A daily peak flow of 23 MGD has been recorded during the summer months (Fargo WTP).

2.2.1. Water sources

Water sources for the Fargo WTP include the Red River and the Sheyenne River. In 2010, 60% of the treated water was from the Red River while 40% was from the Sheyenne River as shown in Figure 10 (Fargo WTP 2011). The past five years of water use data follow the similar trend (Figure 11). There are several factors that the operators take into account when deciding which water source to use. The decision to choose either river was indicated to be primarily based on the hardness concentrations, more specifically the non-carbonate hardness. The river with lower non carbonate hardness would reduce the use

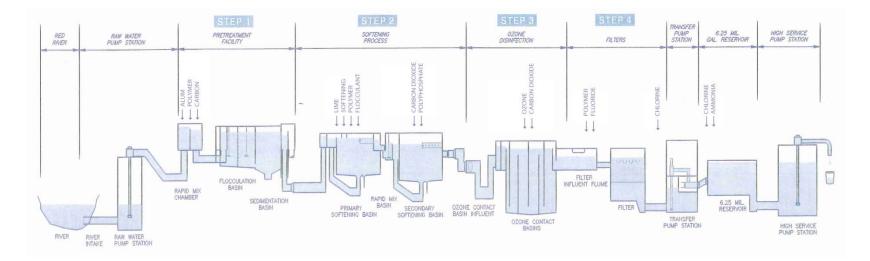


Figure 9. Fargo WTP process flow diagram (Fargo WTP 2011).

of soda ash, a more expensive chemical. The data that was collected does not clearly indicate that the chosen water source is based on hardness concentrations, there may be other factors.

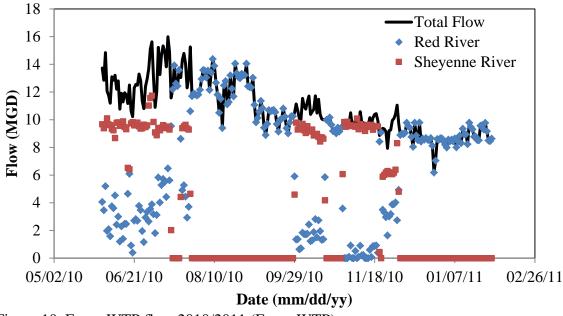


Figure 10. Fargo WTP flow 2010/2011 (Fargo WTP).

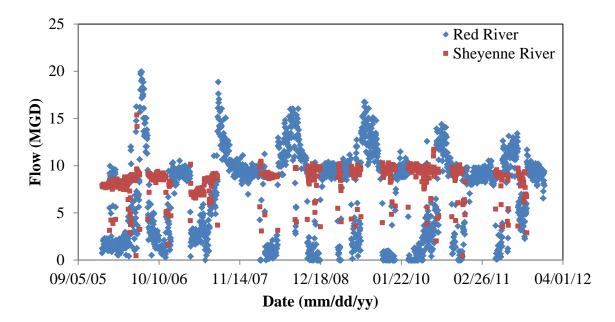


Figure 11. City of Fargo water use between 2006 and 2011.

The Red River is the primary water source for the Fargo WTP. The Sheyenne River is used in addition to the Red River and also used when the hardness in the Red River increases above the Sheyenne. The Sheyenne River has a higher hardness concentration than the Red River (Figure 12) which would lead to an overall increase in chemical cost if the Sheyenne River was the primary water source year round.

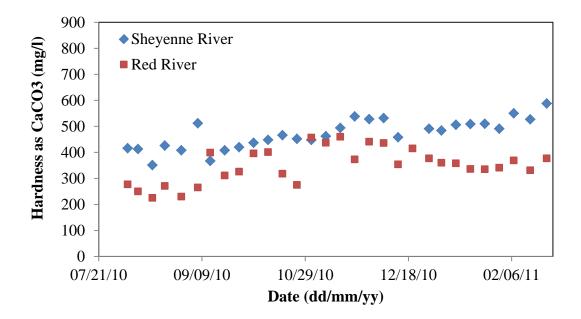


Figure 12. Sheyenne and Red River hardness concentrations.

2.2.2. Suspended solids and taste/odor removal

The Fargo WTP treatment process begins with two rapid mixing basins that have a design capacity of 15 MGD each with a total capacity of 30 MGD. The detention time at the design capacity is 30 seconds. The original design of the rapid mix chamber provided the capability of feeding aluminum sulfate ($Al_2(SO_4)_3$), a coagulant polymer, PAC (Powdered Activated Carbon), potassium permanganate, and chlorine. Currently, aluminum sulfate ($Al_2(SO_4)_3$) and a coagulant polymer are being fed. Taste and odor

compounds are present in the source water at the Fargo WTP during spring runoff. During spring runoff powder activated carbon can be added to control taste and odor.

Following the rapid mix chamber water flows into a flocculation basin. There are two flocculation basins with a design capacity of 15 MGD per basin. The detention time at the design capacity is 20 minutes. The flocculation basin is designed to agitate the chemically treated water by mixing to enhance coagulation. Following the flocculation basin is two sedimentation basins with a design capacity of 15 MGD. The flocculation basins contain plate settlers with 4 rows and 152 plates per row. The effective loading rate of the basin is 0.75 gpm/ft². This process allows small particles to colloid and agglomerate into heavier floc, which settle out by gravity into the sedimentation basin.

2.2.3. Water softening process

Following pre-sedimentation there are three softening basins that have a design capacity of 10 MGD per basin. The basins were designed to operate with a 1.88 gpm/ft² surface loading rate and a weir overflow rate of 7 gpm/ft². The softening basins were originally designed to operate in series which is referred to as primary and secondary softening. The original design was to add lime in one basin and soda ash in the second basin. The purpose was to split the treatment process and precipitate carbonate hardness in the primary basin and non carbonate hardness in the secondary softening basin.

The original design was modified to integrate lime/soda ash softening in the primary basin and pH adjustment in the second basin. The primary softening chemicals added are lime, soda ash, an anionic polymer, and a coagulant polymer. Prior to the secondary softening basins CO_2 diffusers were installed to lower the pH before ozonation.

 CO_2 diffusers were installed after the primary softening basin and prior to the secondary softening basin to maintain a pH of 9.2 during the winter and 8.2 in the summer. The chemicals added to the secondary softening basins are CO_2 and a polyphosphate.

2.2.4. Ozonation process

The Fargo WTP has two 9,000 gallon liquid oxygen storage tanks for the two ozone generators with a maximum design production of 835 lb/day. The system has two operational ozone contact basins with a total of three. The design capacity of each contact basin is 15 MGD with a total operational capacity of 30 MGD. The Fargo WTP contact chambers are shown in Figure 13.

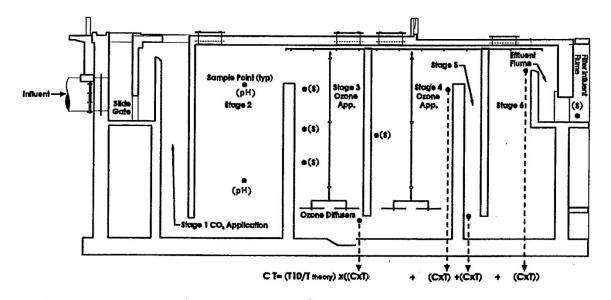


Figure 13. Fargo ozone contact chamber (Fargo WTP 2011 modified from original).

The Fargo WTP has the same requirement as the Moorhead WTP to remove 3 log Giardia and 4 log viruses. Credit is given for conventional treatment so ozone only needs to remove 0.5 log Giardia and 2 log viruses. Conventional treatment includes coagulation, flocculation, sedimentation, and filtration. Each of the ozone chambers contains six stages which vary in size as shown in Table 3. The water flows through a slide gate entering Stage 1. CO₂ can be diffused in this stage but typically occurs in the secondary softening basin. Stage 2 is used to ensure there is enough detention time for the pH to stabilize if it is added in Stage 1. The contact chamber is controlled to maintain a pH of approximately 9.0. Stages 3 and 4 are where ozone is diffused into the water. There are a total of 30 diffusers in each stage. Stage 5 has an ozone residual monitor but typically, there is little ozone providing minimal CT credit. Stage 6 is monitored for ozone residual but there is little to no ozone. CT is calculated through an equation which incorporates the residuals measured at the end of stage 3, 4, 5, and 6. The detention times are calculated through stage 3, 4, 5, and 6 that are based on the plant flow. The equations that the Fargo WTP uses to calculate total Giardia log inactivation and total virus log inactivation are shown below.

Giardia log inactivation.

Giardia Inactivation = $(0.62 \times \sum \text{CT Values}) \times 1.038 \times e^{(0.0714 \times \text{Temperature} (^{\circ}\text{C}))}$ (4) <u>Total virus inactivation.</u>

Virus Inactivation = $(0.62 \times \sum \text{CT Values}) \times 2.1744 \times e^{(0.0714 \times \text{Temperature} (^{\circ}\text{C}))}$ (5)

Once the virus and Giardia log inactivation is calculated, the value is divided by the disinfection requirement that is 2.0 for viruses and 0.5 for Giardia. A ratio above 1 is in compliance. The limiting factor for ozone is virus removal. The virus inactivation equation will control.

Stage	Volume (gallons)	Detention Time at 15 MGD (min)
1	10,417	1
2	42,318	4.06
3	31,693	3.04
4	38,411	3.69
5	7812	0.75
6	30,389	2.92
Total Contactor	161,040	15.46

Table 3. Fargo contact chamber volume and detention time (Fargo WTP).

2.2.5. Filtration process

Following ozonation, hydroflourosilic acid and a filter aid (when needed) are added prior to the six dual media sand filters. Hydrofluorosilic acid is added in the water so to protect teeth and prevent tooth decay. The Safe Drinking Water Act sets the maximum contaminant level of fluoride at 4.0 mg/L. The recommended level of fluoride is 1.2 mg/L. The filter aid is a proprietary polymer blend to aid when filter effluent turbidities are > 0.1NTU. The six dual media sand filters contain 24" of anthracite and 12" of sand. The filters were designed to operate as biofilters but have not been operating that way. The Fargo WTP backwash their filters with free chlorine killing any bacteria that was able to grow. In the summer the filters are run for 60 hrs and in the winter 72 hrs.

It was only recently discovered that the media filters do not behave like biofilters (Fargo WTP 2010). The filters were backwashed with chlorinated water instead of chloraminated water. Chlorine killed most bacteria attached to the media. The 60 to 72 hour filter runs did not give the bacteria enough time to proliferate and utilize the partially oxidized organics. Upon this discovery, operators continued operation using chorine backwashes and have been extending the backwash time with success. The primary purpose of extending the backwashes was not to grow more bacteria but since there were little to no signs of head loss filtration can be extended. Operators have been able to double the filter run times with little to no head loss or turbidity increases.

The filters have under drain tanks that gravity feed into the clearwell. In the under drain tanks 0.30 mg/L of chlorine is added. A transfer pump forces water from the clearwell into the 6.25 MG finished water reservoir. In transition to the reservoir chlorine and ammonia is added. Once in the finished water reservoir it is pumped into the distribution network.

2.3. Summary of the Fargo and Moorhead Treatment Processes

There are similarities and differences of the Fargo and Moorhead treatment plant and distribution networks. Key items were highlighted to emphasize important information pertaining to this research.

The primary water source between the two treatment plants is the Red River but Moorhead's ability to use well water can reduce organics, hardness, and the temperature of the product water. The Sheyenne River is a surface water source which has more organics, hardness, and temperature fluctuations similar to the Red River.

The Fargo WTP has a flocculation basin which removes colloidal particles before softening. The Moorhead WTP does not have a flocculation basin but uses the softening basins and filters to remove colloidal particles. Interestingly, even though the Fargo WTP has a flocculation basin, the Moorhead WTP accomplishes softening without a flocculation basin.

Primary disinfection is ozonation for the two water treatment plants. Two different processes accomplish taste and odor removal between the Moorhead and Fargo WTP. The Moorhead WTP removes taste and odor in the first ozone cell utilizing high pH ozonated water. The Fargo WTP removes taste and odor by the addition of activated carbon. Primary disinfection between the two treatment plants is accomplished by ozonation. Bromate has been a concern for the water treatment plants and the way they minimize bromated formation is different. Moorhead adds ammonia prior to ozonation to inhibit the formation of bromate. Fargo has a lower pH before ozonation reducing the chance bromated is formed.

The Fargo and Moorhead WTP have sand/anthracite media filters to remove particles and simple organics. The Moorhead WTP operates their filter as a biofilter where the Fargo WTP operates their filter with minimal bacterial growth. Fargo backwashes their media filters with chlorinated which kill the majority of attached bacterial growth. Moorhead uses chloraminated water for backwashing the media filters which is a weaker oxidizing agent promoting more bacterial regrowth.

Secondary disinfection is similar between the two treatments plants using a chloramine residual in the distribution network. The Moorhead WTP operated at an average 2.5 mg/L total chlorine residual while Fargo operated at a much higher 4.0 mg/L total chlorine residual in 2009/2010. The higher chloramines residual that Fargo maintains is due to a larger distribution network. Table 4 below summarizes these similarities and differences between the Fargo and Moorhead WTP.

	Fargo	Moorhead
Primary Water Source	Red River (60% Annually)	Red River (80% Annually)
Auxiliary Water Source	Sheyenne River (40% Annually)	Well Water (20% Annually) -Lower temperature, organics, and hardness.
Removal of Colloidal Particles	Flocculation Basin	None
Softening	Lime/Soda Ash	Lime/Soda Ash
Taste and Odor Removal	Activated Carbon -Spring application	High pH and Ozonation -Year round
Disinfection	Ozone	Ozone
Minimize Bromate Formation	Low pH and Ozonation	Ammonia
Biofilter	Sand/Anthracite Filter -Not operated as a biofilter	Sand/Anthracite Biofilter -Operated as a biofilter
Secondary Disinfection	Chloramine -High chloramines 4.0 mg/L	Chloramine -Lower chloramines 2.5 mg/L
Capacity	30 MGD	10 MGD
	Similarities	Differences

Table 4. Comparison of the Fargo and Moorhead treatment processes.

CHAPTER 3. LITERATURE REVIEW

In this chapter the process of nitrification is discussed. Literature regarding chloramine disinfection and reactions that could potentially promote nitrification are reviewed. There is an overview of parameters including temperature, pH, and biofilms that affect nitrification in water distribution networks. In addition, nitrification control strategies are presented.

3.1. Nitrification

Nitrification is a two-step microbial process that oxidizes ammonia (NH₃) to nitrite (NO_2^-) and then nitrate (NO_3^-) . The first step is achieved when ammonia oxidizing bacteria (AOB) metabolize free ammonia to nitrite. *Nitrosomonas* is the common bacteria identified for oxidizing free ammonia. It has been shown that *Nitrosolobus, Nitrosococcus,* and *Nitrosovibrio* can also oxidize free ammonia to nitrite (AWWA M56, 2006).

Nitrosomonas reaction:

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$$
 (6)

The second step is when nitrite oxidizing bacteria (NOB) metabolize nitrite into nitrate. *Nitrobacter* is the common bacteria identified as contributing to the oxidization of nitrite to nitrate. *Nitrocystis, Nitrospira, and Nitrospina* can also complete the reaction (AWWA M56, 2006).

Nitrobacter reaction:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$
 (7)

Nitrifying bacteria are mostly obligate chemolithotrophs which are microorganisms that oxidize inorganic substrates such as ammonia and nitrite to obtain energy and use CO₂

as carbon source. Some *Nitrobacter* species are different from most of the nitrifying bacteria. They are facultative chemolithotroph microorganisms which mean that they can use carbon dioxide or organic substrates as a carbon source (Holt 2000).

The theoretical oxygen demand of *nitrosomonas* is 3.43 mg of oxygen to oxidize 1.0 mg of ammonia-N to nitrite-N. The theoretical amount of oxygen that *nitrobacter* needs to oxidize 1.0 mg of nitrite-N to nitrate-N is 1.14 mg.

Wezernak (1967) studied nitrogenous oxygen demand using BOD bottles. He carried out 10 experiments for *nitrosomonas sp.* and 5 experiments for *nitrobacter agilis*. For each test 12 BOD bottles were used, 6 for initial determinations and 6 for final determinations. The results were then averaged. His data was similar to the estimated stochiometeric values. Wezernak found that 3.22 mg of oxygen was needed to oxidize 1.0 mg of ammonia-N and 1.11 mg of oxygen was needed to oxidize 1.0 mg of nitrite confirming the stoichiometric relationships.

3.2. Chloramines

Chloramines are produced through the reaction of ammonia with free chlorine. Chloramination is typically applied as a secondary treatment process that controls microbial growth in finished water. Choloramines exist in three forms, monochloramine, dichloramine, and trichloramine, depending on water pH (Table 5). Monochloramine is the dominate species when pH is greater than 7.

Chloramine can have two competing effects on ammonia oxidizing bacteria. It will inactivate the bacteria when chloramine is present and the nitrifying bacteria will grow from the presence of ammonia through chloramine decomposition (AWWA M56, 2006).

Ammonia oxidizing bacteria is resistant to monochloramine when compared to free chlorine (Wolfe 1989). At a concentration of 1.0 mg/L monochloramine, 99% inactivation occurred after 33 minutes and at a concentration of 1.0 mg/L as free chlorine 99% inactivation occurred after 2 to 3 minutes (Wolfe 1989). Wolfe reported AOB was 13 times more resistant to monochloramine than free chlorine.

Reaction #	Chlorine and Ammonia Reactions	
1	$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$ Monochloramine pH >7	
2	$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$ Dichloramine pH 4-7	
3	$NH_2Cl + HOCl \rightarrow NCl_3 + H_2O$ Trichloramine pH 1-3	

Table 5. Chlorine and ammonia reactions (AWWA M56, 2006).

Ammonia can be released from chloramine through several reactions as shown in Table 6. Reaction 1 releases ammonia through chloramine decay and reaction 2 releases ammonia when chloramine reacts with organic matter. In addition, reaction 3 releases ammonia through a reaction with reduced iron that has been released by corrosion processes. Reaction 4 is similar to reaction 1 but the mechanism differs. Reaction 4 releases ammonia through an auto catalytic reaction that is accelerated on concrete surfaces from reinforced concrete and also concrete lined pipes through reactions with pipe surfaces (Woolschlager et al., 2001). In the last reaction, nitrite exhibits a chloramine demand releasing ammonia. Ammonia released from these reactions may support growth of nitrifying bacteria.

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Table 6	Chloramine	reactions
1 aoic 0.	Cinorannie	reactions.

Reactions	Description of Reaction	Overall Reaction
1	Release of ammonia through chloramine decay	$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+$
2	Release of ammonia through oxidation of organic matter by chloramine	$1/10 C_5H_7O_2N + NH_2Cl + 9/10H_2O \rightarrow 4/10CO_2 + 1/10HCO3^2 + 11/10NH^+ + Cl^-$
3	Release of ammonia through reaction of chloramine with corrosive pipe surfaces	$1/2NH_2Cl + H^+ + Fe^{2+} \rightarrow Fe^{3+} + 1/2NH_4^+ + 1/2Cl^-$
4	Release of ammonia through catalysis reactions of chloramine with pipe surfaces	$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+$
5	Release of ammonia through oxidation of nitrite by chloramine	$NH_2Cl + NO_2^- + H_2O \rightarrow NH_3 + NO_3^- + HCl$

(Woolschlager et al., 2001)

3.3. Nitrification in the Distribution Network

The maximum contaminant level for nitrate and nitrite in drinking water are 10 ppm and 1 ppm, respectively. High levels of nitrate and nitrite can reduce the oxygen carrying capacity in a toddler's blood, also known as blue baby syndrome (Knobeloch et al., 2000). Nitrification in water distribution networks can occur to some extent in all chloraminated water supplies. Nitrification will cause reduction of total chlorine residuals and lead to elevated nitrite and nitrate concentrations. Nitrite and nitrate concentrations have been reported above 1.5 mg/L and 2.0 mg/L respectively (Cunliffe, 1991). Depletion of chloramines by nitrification may also lead to regrowth of heterotrophic bacteria. There are currently recommendations to keep heterotrophic bacteria < 500 CFU/mL (EPA 2012).

3.3.1. Impact of pH on nitrification

Nitrification occurs in chloraminated water systems over a wide pH range. Nitrifying bacteria have been observed at a pH of 6.5 to 9.4 in water distribution networks (Harrington 2002; Skadsen, 2002; Wilczak et al., 1996). Even though the nitrifiers were observed at this range, nitrifiying bacteria are sensitive to changes in pH as are most bacteria. The optimum pH for *Nitrosomonas* is between 7.0 and 8.0 while *Nitrobacter* is between 7.5 to 8.0 (Keen and Prosser, 1987). The growth of NOB is inhibited at a pH <5.5 (Keen and Prosser, 1987).

Many utilities have used pH to control nitrification (AWWA M56, 2006). Reducing the pH to <5.5 is not practical due to the corrosivity of low pH water. Skadsen et al. (2002) studied the effectiveness of maintaining a high pH (above 9.3) in the distribution network to control nitrification. Two sets of experiments were conducted to determine if pH would affect nitrification. The first set was a six week experiment where the finished water pH was ≤ 8.5 and then raised to a pH of ≥ 9.4 for an additional six weeks in the winter. The other experiment set was the same principal but carried out in late summer. The winter experiments showed little nitrification. During the summer months nitrification was observed in the distribution network. Distribution networks samples at the lower pH had an average concentration of 27.7 μ g/L NO₂⁻-N, and at the higher pH an average concentration of $18.7 \,\mu g/L \,\text{NO}_2$ -N (Skadsen et al., 2002). A long term study raising the pH above 9.3 at the water treatment plant was conducted. Skadsen et al. (2002) found that it was effective at controlling nitrification 6 out of the 8 years. In one year nitrification occurred but quickly diminished. The other year it was deemed necessary to free-chlorinate the distribution network to stop the nitrification process.

3.3.2. Temperature impact on nitrification in the distribution network

It is widely accepted that temperature in the distribution network can affect the growth of nitrifying bacteria. Temperature can affect the biological reactions in two ways: by influencing the rates of enzymatically catalyzed reactions and by affecting the rate of substrate diffusion to the cells (Grady et al., 1999). Both enzymatic reaction and substrate diffusion rates increase with temperature.

Nitrifying bacteria have been seen to grow in temperatures ranging from 5°C to 34°C in the distribution network (Cunliffe 1991, Lipponen et al., 2002; and Wolf et al., 1990). The temperature ranges are where nitrifying bacteria have been observed and does not imply nitrification can occur in the upper and lower temperature limits. There is a narrow temperature range for optimal nitrifying bacteria growth for AOB and NOB. The optimal temperature for Nitrosomonas bacteria (AOB) is between 25-30°C and the optimal temperature for Nitrobacter bacteria is between 5-37°C (Holt et al., 2000 and Watson et al., 1989:). In a Finnish study by Lipponen et al. (2002) samples were taken from 15 drinking water distribution networks with varying treatment processes. Lipponen et al. found no correlation between the presence of nitrifying bacteria and temperature. A total of 1-5 samples were taken from each distribution network which may under represent the correlation between nitrifying bacteria and temperature. In addition to testing for temperature impact, samples from the water distribution systems were tested for ammonia oxidizing bacteria and nitrite oxidizing bacteria. The fifteen drinking water systems had either groundwater or surface water as water sources. Disinfection methods included no chlorination, chlorination, and choramination. The majority of AOB bacteria were found in systems with surface water as sources and using chloramines as disinfectants. In this study

sediment samples were taken from the various distribution networks using a cleaning swab that is pushed through the pipe and out of a hydrant. The sediment samples taken from groundwater non chlorinated distribution networks contained the majority of nitrite oxidizing bacteria. Despite low temperatures of 5°C, nitrifying bacteria were present. Although nitrification occurring may have been difficult to determine from the few samples taken, there is a potential for nitrification with an average total chlorine concentration of 0.17 mg/L and high numbers of nitrifiers observed in sediment samples.

3.3.3. Biofilm in the distribution network

A mechanism that may contribute to the abundance of nitrifying bacteria is their persistent survival in biofilms. In drinking water systems the majority of microbes are attached to pipe surfaces in a thin film or slime layer within the pipe. Nitrifying bacteria can grow in aggregates and attach to these surfaces. The slime layer offers protection from disinfection (Stewart et al., 1997).

Cunliffe (1991) sampled five chloraminated water distribution systems in South Australia and nitrifying bacteria were detected in 64% of the samples. Surprisingly 20% of those samples contained more than 5.0 mg/L of monochloramine. The distance from the chloramine dosing station and the frequency of nitrifying bacteria being detected were correlated. It was suggested that the resistance to monochloramine was not the only contributing factor. A second factor that could have contributed to the high number of nitrifiers is the biofilm. The bacteria in the biofilm of the highly chloraminated waters (> 5.0 mg/L total chlorine) could have been disrupted during sampling. The frequent detection of nitrifying bacteria at the ends of distribution systems could be due to a combination of increased water age, which would favor the formation of biofilms, and lower chloramines residuals.

Biofilms can develop in pipes regardless of the material, PVC, plastic, ductile iron, or cast iron. Some materials provide more favorable conditions for nitrification to occur. For example, unlined cast iron pipes or older pipes with heavy tuberculation may provide favorable conditions for bacterial growth (AWWA M56, 2006). Lipponen et al. (2004) surveyed two full scale drinking water networks supplying chloraminated water. Town 1 had a treatment process which includes chemical coagulation, rapid sand filtration, slow sand filtration, and chloramination. The second study area referred to as Town 7 had a treatment process which includes chemical coagulation, rapid sand filtration, ozonation, and chloramination. In both networks the pipings were constructed of cast iron and polyethylene. Nitrifying bacteria in the biofilm were recorded in both materials but the highest numbers were found at the distal sites of both networks up to 1,000,000 MPN/cm². Also the highest numbers of heterotrophic bacteria were observed at the distal sites up to 8,900,000 MPN/cm².

3.3.4. Impact of nitrite in the distribution network

The presence of nitrite can affect the water quality in a water distribution network. Research has focused on ammonia oxidizing bacteria that increase nitrite concentrations in the distribution system. Nitrite has been shown to exert a demand causing monochloramine loss (Valentine, 1985). Typically, nitrite is not found in raw waters except in water treatment plants where incomplete nitrification occurs (Lieu et al., 1993). The systems where incomplete nitrification occurs are more susceptible to nitrification episodes. Vikesland et al. (2001) conducted an experiment to examine the effect that nitrite had on monochloramine demand. The experiment was conducted with a monochloramine concentration of 3.55 mg/L and a nitrite concentration of 0.5 mg/L. At a concentration of 0.5 mg/L nitrite exerted a significant demand on monochloramine. The result is a decrease in monochloramine concentration by 50% over a period of 160 hours. The author indicated that the 50% decrease in monochloramine concentration underestimated the demand and nitrite exerts a long term demand that is not fully realized within the 200 hour experiment (Vikesland et al., 2001).

3.4. Nitrification in the Biofilter

Gravity filtration through granular media, such as sand or anthracite, is commonly used to polish drinking water. Granular activated carbon is also used in conjunction with advanced oxidation (Kasuga et al., 2010). Ozonation oxidizes organic material promoting bacterial growth in the filter. The process of bacteria removing simple organics through the filter is also referred to as a biofiltration. A biofilter can remove simple organics reducing the risk of bacterial regrowth in the distribution network. The removal of simple organics and suspended solids (turbidity) are the primary uses of a dual media sand filter biofilter in ozonation water plants. Nitrification takes place in biofilters when ammonia is present in the water.

Kihn et al. (2000) performed a study that measured the potential activity of fixed nitrifying bacteria in drinking water treatment biological filters. The authors developed a technique to estimate the fixed nitrifying biomass by determining the potential nitrifying activity. The potential nitrifying activity was calculated by obtaining the optimal temperature, incubation time, and ammonia concentration. Once attained these parameters were used in the study to measure the production of oxidized nitrogen $(NO_2^--N \text{ and } NO_3^--N)$. The method was applied to a full scale facility in Quebec, Canada operating activated carbon filters. The potential nitrifying activity and ammonia concentrations were measured at different depths in the filter. The nitrifying biomass decreased with an increasing depth of the filter. The ammonia was completely oxidized within the first 25 cm of the filter however the nitrifying biomass persisted in the lower part of the filter.

3.5. Nitrification Control

The chlorite ion was added into a distribution network as a way to mitigate nitrification. Chlorite has been added to a distribution network and shown to be control nitrification even at low doses of 0.10 mg/L (McGuire et al., 2006). The chlorite ion inhibits ammonia oxidizing bacteria production in several ways. It can alter the cell membrane permeability, impair the cells enzyme production, and damage the nucleic acids (Stewart and Olson, 1996).

McGuire et al. (2006) conducted research to demonstrate the effect that chlorite had on nitrification. McGuire used a setup of 12 parallel plug flow pilot treatment trains that had varying parameters. The influences include high chloramine dosage, free chlorine, a continuous feed of chlorite ion, and intermittent feeds of chlorite ion. Several treatment trains varied the chlorite ion concentrations to demonstrate if a low chlorite ion feed can control nitrification. The results showed that a continuous feed of the chlorite ion prevented nitrification. The nitrite concentrations in the control group were 0.5 mg/L over a period of 25 weeks. A constant feed of 0.1 mg/L chlorite eliminated nitrite production. A single large feed of chlorite ion (0.8 mg/L) was shown to eliminate nitrite production for 6 weeks. After 6 weeks nitrite production resumed to the concentrations before the single large feed of chlorite.

One other experiment that was conducted in the treatment trains was the effect of a single large feed of free chlorine to the system. The purpose of this experiment is to demonstrate that utilities can switch to free chlorine for a period of time to eliminate nitrification in their distribution network. A reactor that was receiving a 5:1 chlorine to ammonia ratio (2.5 mg/L Cl₂ and 0.5 mg/L NH₃-N was dosed with 3.0 mg/L of free chlorine. The reactor had nitrification occurring with nitrite concentrations of 0.40 mg/L. Within one week of the free chlorine dose, nitrite concentrations decreased to near 0.0 mg/L. This created an immediate drop in nitrite levels for 7 weeks. Full scale use of sodium chlorite has been demonstrated by McGuire in Glendale, California in 2009. The water utility in Glendale was experiencing nitrification. Three distribution network reservoirs. Three phases were set up to examine nitrification. Three distribution network reservoirs were monitored and water was pumped in a series which were labeled as 968 (9.1 MG), 1290 (6.0 MG), and 1666 (1.2 MG). Labeling is in reference to their corresponding elevations. Chlorite addition was dosed at 968.

The first phase was dosing chlorite at 0.6 mg/L for 6 months. The first reservoir, 968, experienced little nitrification compared to previous years with nitrite concentrations < 0.010 mg/L. Reservoir 1290 and 1666 did not have similar results. Concentrations of nitrite in reservoir 1290 and 1666 were 0.100 mg/L in both reservoirs before introducing chlorite, indicating nitrification was already present (McGuire 2009). After several months of chlorite dosing nitrite concentrations levels reached 0.2 mg/L to 0.3 mg/L NO₂⁻-N,

42

which indicates chlorite was not successful reducing nitrification when nitrification was already present in a reservoir. After several months the reservoirs were drained and cleaned with phosphoric acid and put back in service where the chlorite feed resumed. Even after the reservoir was cleaned with an acid solution and chlorite was being fed continuously nitrification control was not consistent compared to reservoir 968. It was believed that AOB from the biofilms in the pipeline between the reservoirs needed to be cleaned also in addition to cleaning the reservoirs.

In the second phase, no chlorite was added and breakpoint chlorination was used in the distribution network for 6 months to inactivate any nitrifying bacteria. In the beginning of phase 2 it was difficult to achieve breakpoint chlorination after adding sodium hypochlorite to the reservoirs. There seemed to be a significant oxidant demand. It was only until break point chlorination was achieved that microbial control in reservoirs 1290 and 1666 was achieved. The third phase was to reintroduce 0.6 mg/L of chlorite into the system. During the three months, phase 3 nitrification was not observed. Nitrite concentrations in all reservoirs did not increase above 0.03 mg/L and generally below 0.012 mg/L.

This study indicated that the use of chlorite at a dose of 0.6 mg/L can prevent nitrification. It was observed that if there are large quantities of ammonia oxidizing bacteria present chlorite will be controlled for a period of time but develop a resistance to chlorite (McGuire 2009). In addition, once nitrification was present in reservoirs 1290 and 1666 the addition of chlorite did little to minimize nitrification.

43

CHAPTER 4. METHODOLOGY

4.1. Sample Period and Locations

The Fargo and Moorhead distribution network samples were taken from June 2010 the end of March 2011. Four sample locations in each distribution system were chosen to represent the network. It was important that the sample locations covered the origin of treated water to the furthest point in their distribution network. To accomplish this, the locations were selected in a straight pattern from the WTP to the end of the distribution network. The distances between the sampling locations were equally spaced. The Fargo sample sites can be seen in Figure 14. The Moorhead sample sites are shown in Figure 15. The sample sites in the Moorhead distribution network are approximately 1 mile apart and approximately 2 miles apart in the Fargo distribution network. Lastly the sites were selected based upon accessibility. The sampling locations and their corresponding distance from the water treatment plant are shown below in Table 7.

Site	Description	Distance from WTP (Miles)
MWTP	Moorhead Water Treatment Plant	0
M1	Moorhead State University	1
M2	Minnesota State Technical College	2
M3	Residential Location	3.5
FWTP	Fargo Water Treatment Plant	0
F1	NDSU's Diversity Center	2.5
F2	M and H Gas Station	4.0
F3	Fargo Jet Center	5.0

Table 7. Fargo and M	Ioorhead samp	le descriptions.
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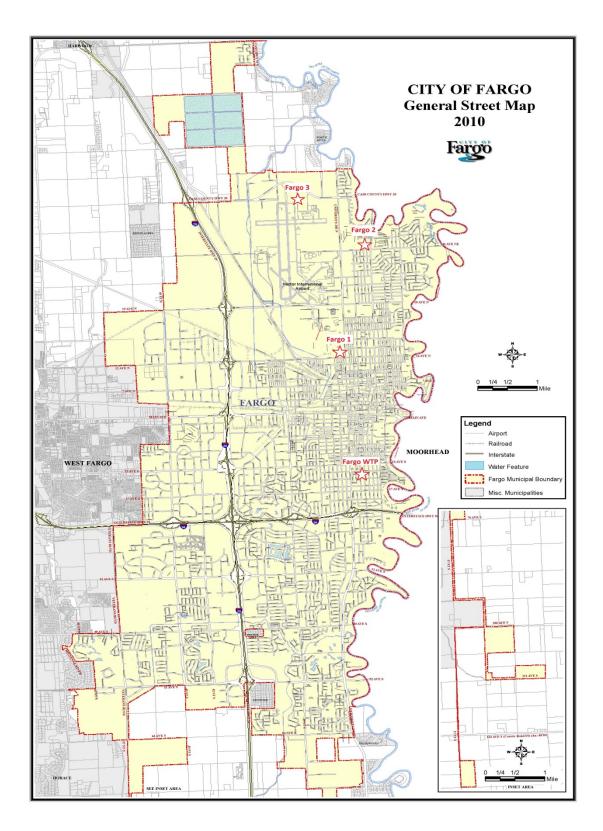


Figure 14. Sample sites in the Fargo distribution network. (City of Fargo 2010).

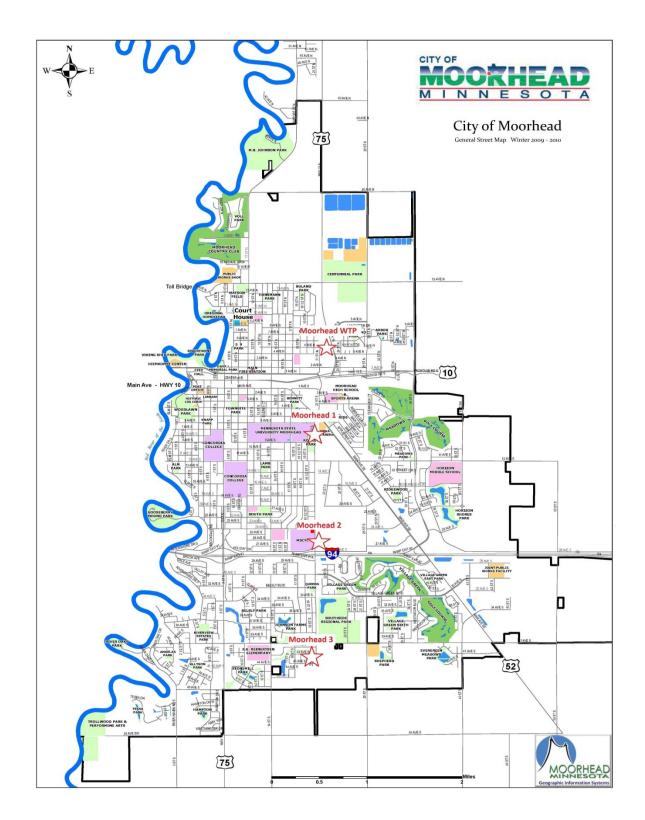


Figure 15. Sample sites in the Moorhead distribution network (City of Moorhead 2009).

4.2. Distribution Network Sampling Methods

The samples were collected in the same order through 2010 and 2011. First, sampling would take place at the Fargo WTP and then collect the distribution network samples in the order of site 1, site 2, and site 3. Following the Fargo sampling, the Moorhead WTP was sampled. The distribution network sites were sampled in the order of site 1, site 2, and site 3. All samples were collected in 1 liter amber bottle to prevent exposure to sunlight. Water was allowed to run for 5 minutes at each location before samples were taken. The sample bottles were filled to the top to minimize any aeration. Samples were analyzed immediately at the Moorhead WTP following collection.

4.3. Moorhead Biofilter Sampling

The Moorhead biofilter samples were taken from August 2009 to November 2009. The biofilter was sampled for NH_3 -N, NO_2^- -N, and NO_3^- -N. Each filter was sampled independently during the period. All samples were collected in 1 liter amber bottles and analyzed immediately at the Moorhead WTP after the samples were taken.

4.4. Analytical Methods

NH₃-N was analyzed using an Orion 9512HPBNWP ammonia sensing electrode with an Orion 720A meter in accordance with standard methods (APHA et al., 2005). The ammonia probe was calibrated before each use and proper membrane maintenance was followed.

NO₂⁻-N was analyzed using NitriVer® 3 Nitrite Reagent Powder Pillows 10 ml in accordance with standard methods (APHA et al., 2005). A Hach DR 4000

spectrophotometer was used to colorimetrically determine concentrations at the 507 nm wavelength. This method is capable of detecting nitrite up to concentrations of 0.30 mg/L $NO_2^{-}N$. Concentrations exceeding the upper limit were diluted with deionized water and measured.

NO₃⁻-N was analyzed using a Thermo Orion 250A+ in conjunction with a VWR SympHony Nitrate Ion Selective Electrode and VWR SympHony Double Junction Reference Half-Cell in accordance with standard methods (APHA et al., 2005).

Total organic carbon was analyzed using an O-I Analytical Model 1010 TIC-TOC analyzer in accordance with standard methods (APHA et al., 2005). The TOC analyzer was calibrated using linear least squares regression. The solution used was a 1000 mg/mL KHP Analytical TOC standard stock solution purchased from Ultra Scientific. Calibration was performed using four TOC concentrations; 0.2 mg/L, 0.5 mg/L, 2.5mg/L, and 15 mg/L for the calibration curve. The calibration of the TOC analyzer was performed monthly.

Dissolved organic carbon was also analyzed using the O-I Analytical Model 1010 TIC-TOC machine in accordance with standard methods (APHA et al., 2005). The samples were filtered through a Whatman 0.45 μ m glass fiber filter and then analyzed with the TIC-TOC machine.

Heterotrophic bacteria cultures were analyzed and performed in accordance with standard methods (APHA et al., 2005). The pour plate method was performed using 1 mL sample volume. The media used was R2A agar. Samples were thoroughly mixed before media incubation. The samples were incubated for 5 days before counting the bacteria. The samples analyzed for heterotrophic bacteria always were accompanied by QC checks. A blank media disk was incubated with samples to minimize error and detect contamination.

48

Total chlorine residual was analyzed using the Hach DR 4000 in accordance with standard methods (APHA et al., 2005). Hach DPD Total Chlorine Reagent Powder Pillows 25 mL was used.

Specific ultraviolet absorbance (SUVA) is the DOC/UVA 254 nm. DOC concentrations were measured by the DOC analyzer and the UVA 254 nm was measured by the Hach DR 4000. Ultraviolet absorbance at 254 nm was analyzed using the Hach DR 4000 in accordance with standard methods (APHA et al., 2005). A TOC standard with a concentration of 1000 mg/L as TOC from VWR labs was used to calibrate the Hach DR 4000 for UVA 254 nm measurement.

The pH and temperature was measured in the lab using an Orion 815600 Ross combination electrode in accordance with standard methods (APHA et al., 2005). The Orion 720A+ was also used. The pH meter was calibrated before use utilizing a 3 point buffer calibration curve and calibrated before each use.

CHAPTER 5. RESULTS AND DISCUSSION

To gain a better understanding of the Fargo and Moorhead water distribution networks a sampling plan was developed. Water quality tests including temperature, pH, Cl₂, NH₄⁺-N, NO₂⁻-N, NO₃⁻-N, HPC, SUVA, TOC, and DOC were analyzed for every sample. These parameters indicate the water quality in a distribution network and assist at identifying nitrification in a distribution network. To better understand the potential impact of nitrification in biofilters on nitrification in distribution network, effluents samples from Moorhead Water Treatment Plant biofilters were taken. Sampling results and discussion are presented in this chapter.

5.1. Water Quality Variations in the Fargo and Moorhead Distribution Network

Moorhead Water Treatment Plant treats water from the Red River which is often blended with ground water. Ground water is added to improve influent water quality and to lower the temperature. The Fargo water treatment plant uses Red River as its primary water source and Sheyenne River as a secondary source. Fargo does not have the benefit of using ground water.

5.1.1. Temperature and pH

Samples were taken from four sites in the Moorhead distribution network, Moorhead WTP, Moorhead 1, Moorhead 2, and Moorhead 3, with increasing distance from the WTP. Water temperature at the four sample locations varied throughout the year (Figure 16). Higher temperature was observed above 23.0°C and dropped to below 6.0°C. Groundwater can affect the temperature of the finished water in a treatment plant typically lowering summer temperatures and increasing winter temperatures. From the sampling data, the Moorhead WTP had 1-4 °C lower temperature in the summer and 2-5°C higher temperature in the winter. Moorhead blends ground water with surface water which acts as a buffer lowering the temperature swing typically seen by only using surface water.

All four sample locations show a decreasing temperature from summer to winter. Interestingly Moorhead 1 had the lowest temperature in the winter. The temperature at Moorhead 1 and 2 is less than the WTP temperature in the winter indicating that the surrounding soil must be cooling the water. At Moorhead 1 and Moorhead 2, the pipe depth could be shallow compared to the other sample location. Typically, water mains are buried to maintain a minimum cover to prevent freezing. A shallow pipe would be closer to the ground surface and subject to air temperature influences. In addition, Moorhead 1 and Moorhead 2 are close to the I94 water tower. During the winter, air temperature will cool the water in the tower affecting the temperature in locations near the water tower. Moorhead 3 changes from being the lowest temperature in the summer to being the highest in the winter and had the least variation. The longer the water travels in a distribution network, the more time the water has to equalize in the soil. This indicates that the surrounding soil impacts the water temperature.

Samples were taken from four sites in the Fargo distribution network; the Fargo WTP, Fargo 1, Fargo 2, and Fargo 3. The sample locations numbered F1-F3 with increasing distance from the Fargo WTP. The temperature in the Fargo distribution network ranged from 25.4°-5.5°C (Figure 17). The highest and lowest temperatures were recorded at the Fargo WTP. The Fargo WTP's temperature varied because the Red or Sheyenne River is more susceptible to seasonal change. In the distribution network, the

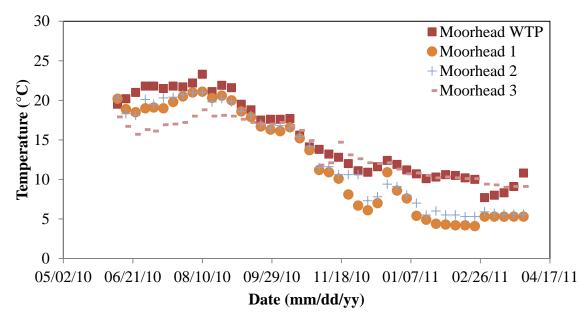


Figure 16. Variation of temperature in the Moorhead distribution network.

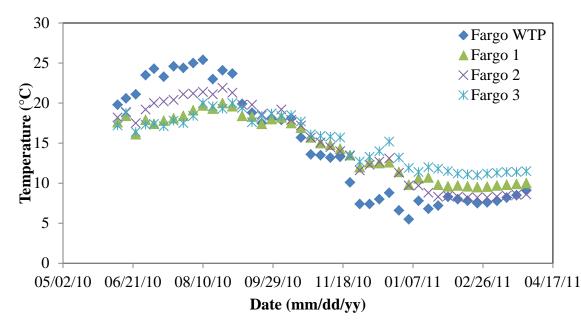


Figure 17. Variation of temperature in the Fargo distribution network.

temperature gradually decreased from the summer to winter. The average temperature difference from the water treatment plant to Fargo 1, 2, and 3 were 0.09 °C, 0.19 °C, and 0.67 °C respectively. This indicates that the distance water travels and air temperature affect the water temperature more as water travels further from the water treatment plant.

The Fargo distribution network had a higher temperature in the summer and cooler temperature in the winter when compared to the Moorhead distribution network. The Fargo WTP uses only surface water which is subject to greater temperature fluctuations than the Moorhead facility which uses groundwater. In Fargo, the lowest temperature recorded in the distribution network was the WTP and in Moorhead it was location #1 and #2. Interestingly, comparing the temperature at the Fargo WTP with the Moorhead WTP during summer was 2°C higher and 2-3°C lower in the winter. In both distribution networks the furthest location had the least fluctuation from winter to summer months.

The distribution network pH in Moorhead varied from 9.07 to 9.36 (Figure 18). The WTP controls the pH of the finished water with a goal of 9.20. The water treatment plant had an average finished water pH of 9.23 and a standard deviation of 0.055. Moorhead 3 had an average pH of 9.21 with a SD of 0.071. Moorhead 1 and Moorhead 2 showed similar results. In the distribution network there was not a significant change in pH.

The distribution network pH in Fargo varied from 8.74 to 9.17 shown in Figure 19. The pH is controlled by the water treatment plant with a goal of 9.00. In the distribution network there is no significant degradation of pH spatially or through the summer and winter seasons. The pH values in the three sample locations were similar to the water treatment plant's effluent pH.

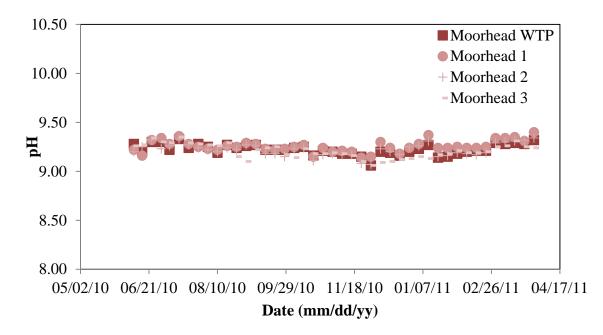


Figure 18. Variation of pH in the Moorhead distribution network.

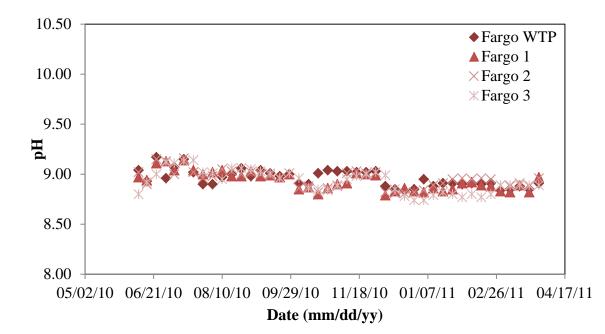


Figure 19. Variation of pH in the Fargo distribution network.

The Fargo and Moorhead distribution network showed no signs of the pH decreasing through the summer and winter months. In addition, there were no signs of degradation spatially in the network samples. The Fargo distribution network maintained a pH around 9.00 while Moorhead's pH was elevated near 9.23. The difference in pH is in the operation of the facilities. Both facilities followed a decreasing pH trend from summer to winter months which are controlled by the amount of CO_2 applied. Ozone decay is directly related to temperature and pH. At higher temperatures, ozone is less stable therefore increasing ozone decay. Also, when the pH of the water is higher, more hydroxyl radicals are formed which convert bromide to bromated (Song et al., 1997). This is a factor for the Moorhead WTP because it operates at a higher pH of 10.6 in the first cell of the ozone contact chamber for the removal of taste and odors. The Fargo WTP operates at a lower pH because ozonation is primarily used for disinfection and not taste and odor removal. Both facilities were able to use a higher pH in the winter to disinfect the water because the lower water temperature does not decay ozone as fast in the summer months. Also, both facilities maintain a higher pH with the finished water pH above 9.0 to ensure that the calcium carbonate coatings in the distribution system remain intact.

5.1.2. Chlorine residual

The Moorhead water treatment plant controls the chlorine residual in clearwell. The goal is to have a combined chlorine residual in the reservoirs at 2.40-2.80 mg/L. There are residual monitoring locations in the clearwell and reservoir. Chlorine residual in the four sample locations ranged from 2.75 mg/L to 1.25 mg/L combine chlorine as shown below in Figure 20. At the Moorhead WTP, Moorhead 1, and Moorhead 2 stable combined

chlorine concentrations was maintained with an average of 2.39 mg/L, SD=0.192 mg/L. A slight decrease in chlorine residual was observed between the WTP, Moorhead 1, and Moorhead 2, while Moorhead 3 had more than a 45% reduction in chlorine residuals in several periods. Moorhead 3 sustained concentrations near 2.25 mg/L until the beginning of September. The total chorine concentration decreased to 1.4 mg/L from 2.25 mg/L. In the middle of August there was a decline in total chlorine concentration which is attributed to nitrification and is discussed further in section 5.1.4. From November to March 2011, Moorhead 3 showed a lower chlorine residual concentration which can be a combination of several factors. The residence time in the pipe is elevated in the winter due to decreased flow. The water temperature in the residential location was 10°C higher than sample locations 1 and 2 during the winter months, which accelerated chloramine decomposition. The other two locations in the distribution network were fairly stable when compared with the WTP at the lower temperature.

The Fargo water treatment plant controls the combined chlorine residual in the clearwell. The goal is to have a combined chlorine residual of 3.75 mg/L. The Fargo WTP, Fargo 1, Fargo 2, and Fargo 3 chlorine concentrations varied from 4.0 mg/L to below 2.0 mg/L as shown in Figure 21. The average concentration at the Fargo WTP was 3.64 mg/L, Fargo 1 was 2.86 mg/L, Fargo 2 was 3.15 mg/L, and Fargo 3 was 2.26 mg/L. The residual in the three samples locations decreased spatially. Fargo 1 and Fargo 2 had similar residual concentrations. Fargo 3 showed the highest reduction in chlorine levels which was over 50%. The organics in the Fargo distribution network were moderately high which can cause chlorine reduction. The distance to the last sample location is approximately 6 miles and can also cause chlorine loss.

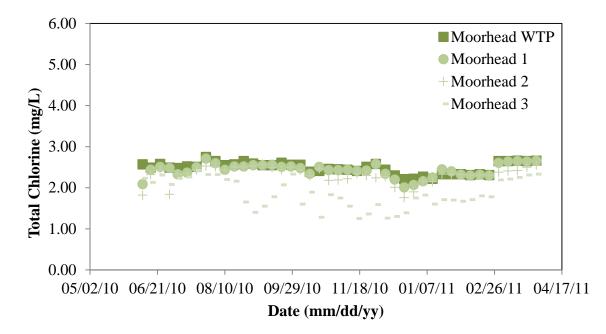


Figure 20. Variation of total chlorine in the Moorhead distribution network.

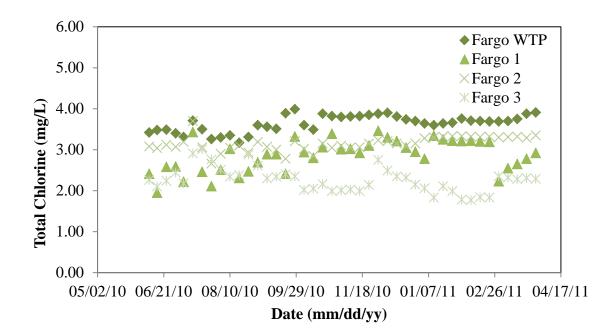


Figure 21. Variation of total chlorine in the Fargo distribution network.

There are several factors that can affect chlorine residual in the distribution network including; detention time, seasonal changes in temperature, and organic concentrations. Therefore, the Fargo and Moorhead WTP have different operating set points for chloramination. Fargo maintains a chloramine concentration of 3.17 mg/L to 3.99 mg/L in their reservoir while Moorhead maintains a residual of 2.21-2.75 mg/L according to sampling data. Both treatment plants operate under the maximum residual disinfectant level (MRDL) which is 4.0 mg/L as Cl₂. Also the treatment plants maintain the recommended minimum 0.5 mg/L as Cl₂ in their distribution network. Fargo must maintain a higher chloramine concentration because of a larger distribution network and higher organic concentrations which cause a larger demand than Moorhead. From the Fargo WTP to Fargo 3 there was an average decrease in chloramine concentration of 1.29 mg/L. Between the Fargo WTP, Fargo 1, and Fargo 2 the average chloramine reduction was 1.09 mg/L. The majority of chloramine loss occurred in the closest sample locations to the treatment plant. The Fargo WTP maintained a minimum residual of 1.77 mg/L at the end of the sampling locations while the Moorhead WTP maintained a minimum residual of 1.25 mg/L. The Moorhead distribution network showed differing trends of chloramine residuals. In Moorhead, the WTP to location Moorhead 3 had an average decrease in chloramine concentration of 0.61 mg/L. Between the Moorhead WTP, Moorhead 1 and Moorhead 2 there was an average decrease in chloramine concentration of 0.22 mg/L, thus the majority of chloramine reduction occurred from Moorhead 2 and Moorhead 3 sample location.

5.1.3. Nitrogen $(NH_4^+-N, NO_2^--N, and NO_3^--N)$ concentrations

Ammonia, nitrite, and nitrate concentrations at the Moorhead WTP, Moorhead 1, Moorhead 2, and Moorhead 3 are shown in Figure 22, 23, 24, and 25. NH₄⁺-N and NO₂⁻-N at the Moorhead WTP remained low and stable throughout the sampling period with NH₄⁺-N less than 0.2 mg/L and NO₂⁻N less than 0.1 mg/L, except a period in later Jun and July in 2010 when NO₂⁻-N was slightly higher, near 0.2 mg/L. NH₄⁺-N and NO₂⁻-N concentrations at Moorhead 2 and 3 are close to the values measured at Moorhead WTP, indicating that there was not significant ammonia release from chloramine decomposition and no nitrification occurred. Concentration of NH₄⁺-N at Moorhead 3 was consistently higher than NH_4^+ -N levels at other sites from November 2010 until April 2011. An increase of NO₂⁻-N and decrease of NH₄⁺-N at the same time was observed at Moorhead 3 in later August and early September of 2010, indicating a nitrification episode. Although the magnitudes of nitrification and NH_4^+ -N increase at Moorhead 3 are fairly small, they do raise some water quality concerns at this farthest site in the Moorhead water distribution network. A comparison of total chlorine residual data with NH₄⁺-N levels shows that increase of NH_4^+ -N at Moorhead 3 was closely related to the chloramine decay. Under proper conditions nitrification may occur with elevated NH₄⁺-N in water. More explanation and discussion of the nitrification episode is presented in Section 5.1.4. A dramatic increase of NO₃⁻-N, from 0.5 mg/L to 1.70 mg/L, was observed at all sampling sites in the winter months. The elevated levels of NO_3 -N was caused by the water quality change in the Red River and will be discussed further later.

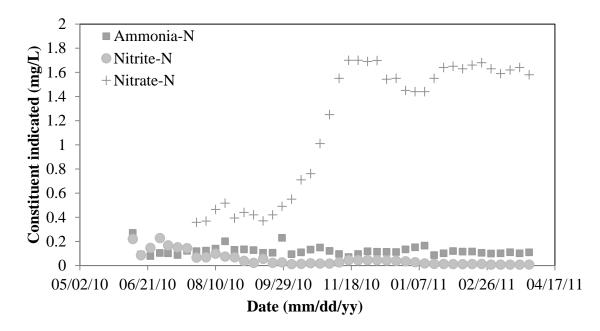


Figure 22. Variation of ammonia-N, nitrite-N, and nitrate-N at the Moorhead WTP.

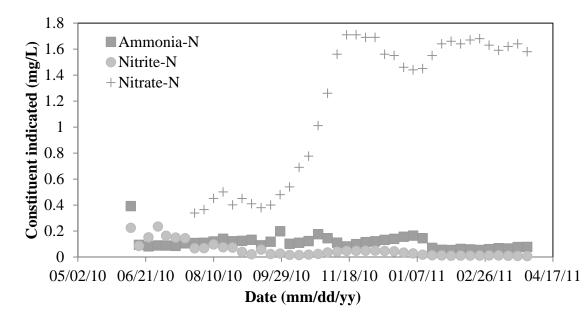


Figure 23. Variation of ammonia-N, nitrite-N, and nitrate-N at Moorhead 1.

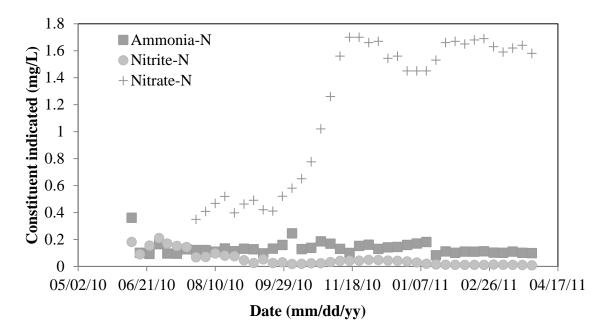


Figure 24. Variation of ammonia-N, nitrite-N, and nitrate-N at Moorhead 2.

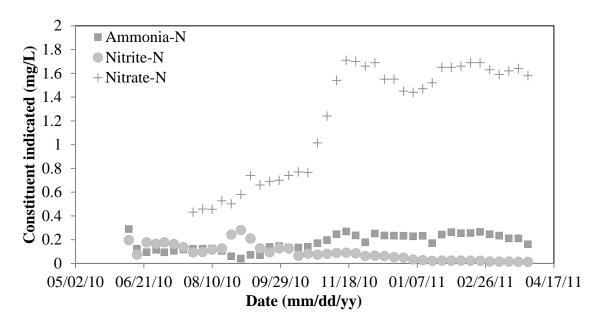


Figure 25. Variation of ammonia-N, nitrite-N, and nitrate-N at Moorhead 3.

Ammonia, nitrite, and nitrate concentrations at the Fargo WTP, Fargo 1, Fargo 2, and Fargo 3 are shown in Figure 26, 27, 28, and 29. NH_4^+ -N concentrations increased from the Fargo WTP to the further locations with the WTP below 0.2 mg/l and the furthest location Fargo 3 as high as 0.49 mg/L indicating chloramine decomposition. Fargo 1 was typically below 0.36 mg/L, although one instance in June the concentration of NH_4^+ -N was 0.50 mg/L. NH_4^+ -N in Fargo 2 was below 0.255 mg/L, there was one instance in June where the concentration increased to 0.364 mg/L. NO_2^- -N concentrations at the Fargo WTP and the sampling locations remained low and relatively stable with the concentration below 0.05 mg/L in all locations. Interestingly, with the higher concentration of NH_4^+ -N, nitrification was not observed in any sample location in Fargo.

Fargo maintains a higher chloramine residual above 1.50 mg/L as Cl_2 even at the furthest location indicating that maintain a higher residual above 1.50 mg/L as Cl_2 could prevent nitrification. Although nitrification was not observed during this study in Fargo, the higher concentrations of NH_4^+ -N available for nitrifying bacteria do raise some water quality concerns if an area in the Fargo distribution network had lower chloramine residuals. This study only covered three sampling locations in the distribution network and there could be areas of concern. The dramatic increase of NO_3^- -N in the winter months from 0.5 mg/L to 1.7 mg/L was observed in the Fargo distribution network as well. The elevated level of NO_3^- -N was caused by the water quality change in the Red River and will be discussed further later.

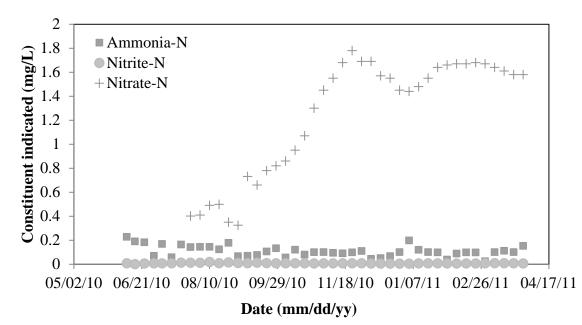


Figure 26. Variation of ammonia-N, nitrite-N, and nitrate-N at the Fargo water treatment plant.

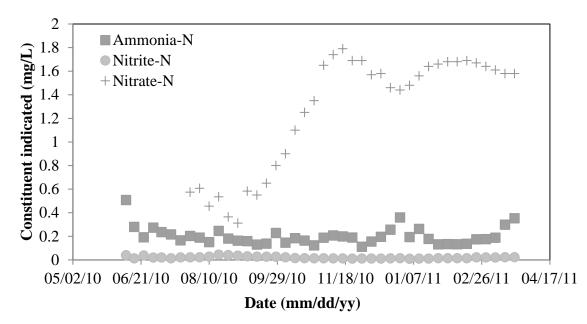


Figure 27. Variation of ammonia-N, nitrite-N, and nitrate-N at Fargo 1.

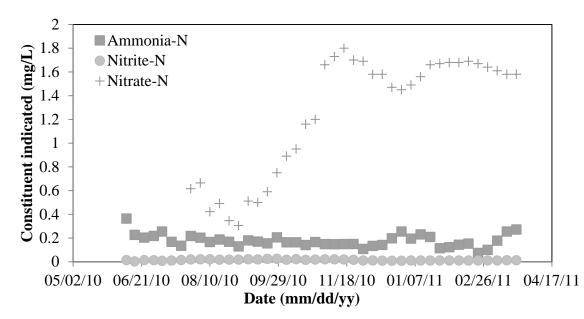


Figure 28. Variation of ammonia-N, nitrite-N, and nitrate-N at Fargo 2.

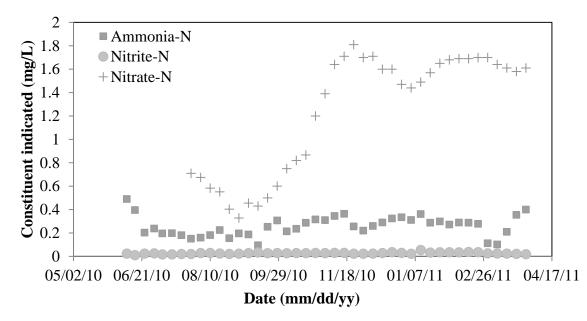


Figure 29. Variation of ammonia-N, nitrite-N, and nitrate-N at Fargo 3.

A similar trend was observed in the Fargo and Moorhead WTP reservoir related to nitrate concentrations. The nitrate concentrations started to significantly increase at the beginning of September 2009 so further testing was required. The influent water was tested at the Moorhead WTP and indicated that the elevated nitrate concentrations can be attributed to the background nitrate in the river that can be seen in Figure 30. This was a small sampling period because the nitrate concentrations in the Red River were not tested regularly during this study.

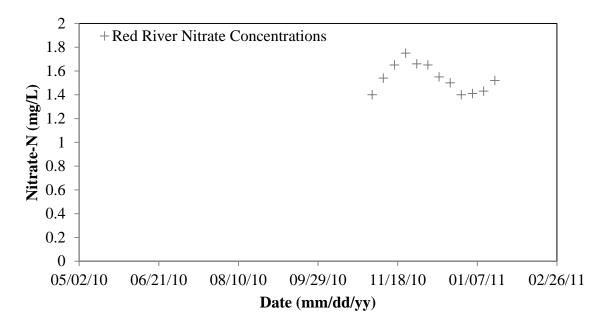


Figure 30. Red River nitrate concentrations.

5.1.4. Comparison of chlorine residual, NH₄⁺-N, and NO₂⁻-N in the Fargo and

Moorhead distribution networks

Figure 31 shows the concentrations of total chlorine residual, NH_4^+ -N, and NO_2^- -N for the Moorhead WTP. The Moorhead WTP maintains total chlorine levels with a concentration of 2.5 mg/L. Ammonia and nitrite in the source water are relatively low when compared to the concentrations in the effluent of the plant. In the Moorhead WTP,

 NH_4^+ -N is added after softening which contributes to the available ammonia in the reservoirs. NO_2^- -N concentrations at the WTP were typically below 0.10 mg/L except in June where the concentration reached 0.23 mg/L. The NH_4^+ -N that is added in the treatment process feeds the biofilter and essentially the nitrifying bacteria. The nitrifying bacteria are able to utilize the NH_4^+ -N converting it to NO_2^- -N. During the summer nitrifying bacteria are able to convert more NH_4^+ -N to NO_2^- -N than in the winter because of higher temperatures.

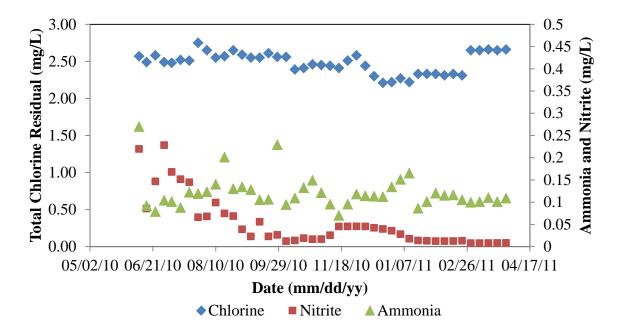


Figure 31. Chlorine, nitrite, and ammonia concentrations from the Moorhead water treatment plant sample location.

In Figures 32 and 33 the chloramine residual is still stable with a concentration near 2.5 mg/L except in December when the residual decreased to 1.70 mg/L. Nitrification was not observed as the concentration of NO_2^- -N change and the chloramine residual went up to 2.5 mg/L several weeks later. Ammonia is not being consumed in either location because the concentration of NO_2^- -N does not change between the sampling sites. The nitrite present in the water is from the WTP effluent.

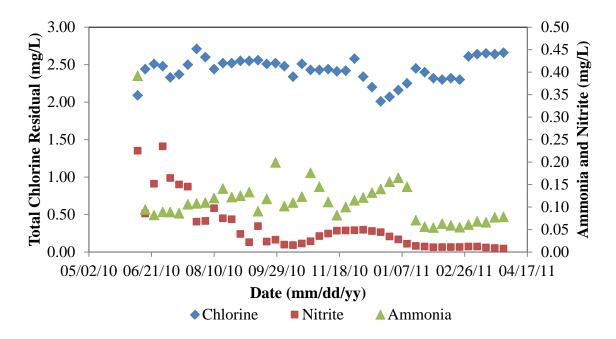


Figure 32. Chlorine, nitrite-N, and ammonia-N concentrations from Moorhead 1.

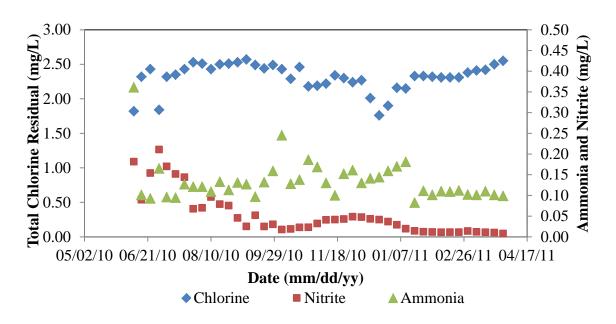


Figure 33. Chlorine, nitrite-N, and ammonia-N concentrations from Moorhead 2.

Figure 34 is the residential location and furthest from the water treatment plant. At this location chloramines residuals were not stable. At the end of August 2010 the residual

is consumed to a concentration of 1.4 mg/L. The concentration is above the standard of 0.5 mg/L chloramine residual at the end of the distribution network but this is significant due to the nitrite production. Once the chloramine residuals deplete to a lower concentration ammonia oxidizing bacteria are able to consume ammonia and produce nitrite. Previous research has indicated that AOB are capable of growth in the presence of 1.2 - 1.5 mg/L chloramine residuals (Wolfe et al., 1988). The distance the water travels to this location and increasing temperature could account for chloramine reduction. Interestingly this does not account for the residual increasing right after it was depleted. One block from the residential location is a public school that could account for the residual activity. The water in the residential location was likely relatively stagnant in the summer months due to the school's summer vacation. The school started close to the time that the chloramine residual increased.

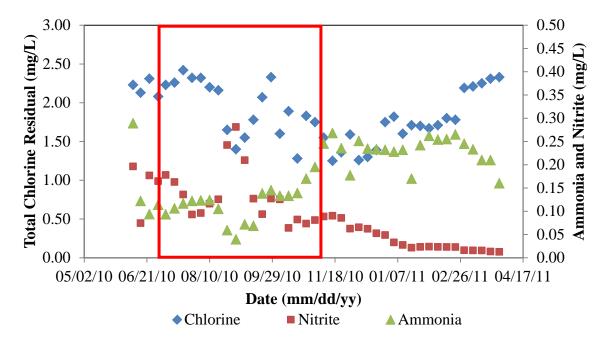


Figure 34. Chlorine, nitrite-N, and ammonia-N concentrations from Moorhead 3.

Figure 35 is the Fargo WTP and the concentrations of Cl_2 , NH_4^+ -N, and NO_2^- -N. The Fargo WTP maintains chloramine levels with a concentration of 3.8 mg/L with an average ammonia concentration of 0.109 mg/L. The nitrite levels were an average concentration of 0.0084 mg/L indicating little to no nitrification in the biofilter.

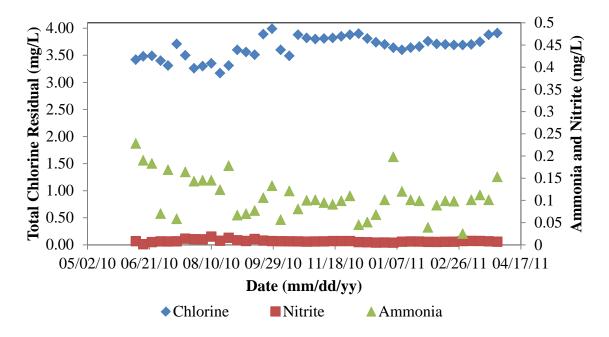
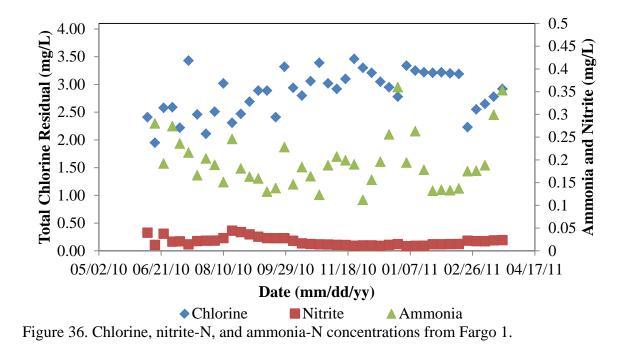


Figure 35. Chlorine, nitrite-N, and ammonia-N concentrations from the Fargo WTP.

Figures 36 and 37 represent Fargo 1 and Fargo 2. Chloramine concentrations from Fargo 1 and Fargo 2 were on average 2.86 mg/L and 3.15 respectively. Interestingly the average ammonia concentrations in the water were 0.200 mg/L and 0.177 mg/L respectively indicating chloramine decomposition, which releases more free ammonia in the water as the concentration of chloramines decreases.



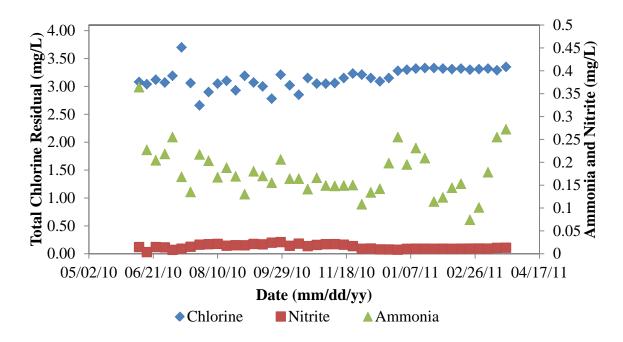


Figure 37. Chlorine, nitrite-N, and ammonia-N concentrations from Fargo 2.

Figure 38 represent Fargo 3 and the concentrations of chloramine, nitrite-N, and ammonia-N. Chloramine levels were the lowest at this location with an average of 2.26

mg/L and an average ammonia concentration of 0.258 mg/L. This also agrees with the statement above regarding chloramine decomposition. The nitrite concentrations were still relatively low with an average concentration of 0.027 mg/L. Nitrification was not observed in the Fargo distribution network because they maintained a minimum chloramine concentration above 1.78 mg/L. The higher concentration of chloramines could prevent nitrification from occurring. There is a potential for nitrification to occur in the Fargo distribution network if chloramine concentrations were lowered because there are high levels of free ammonia.

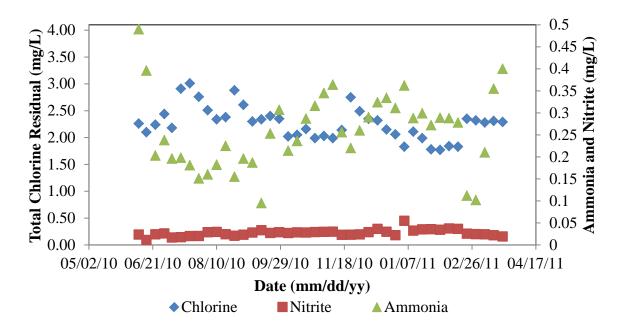


Figure 38. Chlorine, nitrite-N, and ammonia-N concentrations from Fargo 3.

5.1.5. Total organic carbon

Organic carbon is generally considered to have a positive effect on nitrification (Zhang 2010). There is a chloramine demand when high levels of organics are present which promotes the release of free ammonia. In addition, high levels of organics will decrease the total chlorine residual promoting bacterial growth. The Red River has a high amount of organic matter occurring from natural sources. The average total organic carbon (TOC) in the Red River for 2010 was 9.31 mg/L with a standard deviation of 0.989 mg/L. Well water that the Moorhead water treatment plant incorporates has a far less TOC concentration in 2010 averaging 2.81 mg/L with a standard deviation of 0.875 mg/L. Figure 39 shows the TOC in the Moorhead distribution network. The TOC ranged from 2.41 mg/L to 4.55 mg/L. The organic content gradually increases from the summer to winter season which can be a caused by lower river flows in the winter. In the summer, the WTP uses well water in addition to the river flow. Well water is low in organics, which decrease the organic load in the summer. In addition, softening, ozonation, and biofiltration remove organics from the influent water. During the period of sampling from June 2010 to March 2011 the average TOC removal for the Moorhead WTP was 63%.

The organics in the Fargo distribution network originate from the Red or Sheyenne River. The water treatment plant has the ability to use either water source depending on their needs. Total organic carbon concentrations in the Fargo distribution network are shown in Figure 40. The TOC ranged from 3.86 mg/L to 6.56 mg/L. The organics gradually increased from the summer to winter months.

The Moorhead distribution network had less total organic carbon than the Fargo distribution network. The average TOC in Fargo was 5.13 mg/L while Moorhead's TOC was 3.52 mg/L. This is due to a combination of factors. Moorhead uses well water which decreases the total organics into the plant. Also, the biofilter in Moorhead can remove up to 10% of the organics in the summer. One of the most significant contributors to the lower TOC in Moorhead is that plant's design removes more organics because in the winter there is less well flow and the biofilter does not function as in the summer. The Fargo WTP's

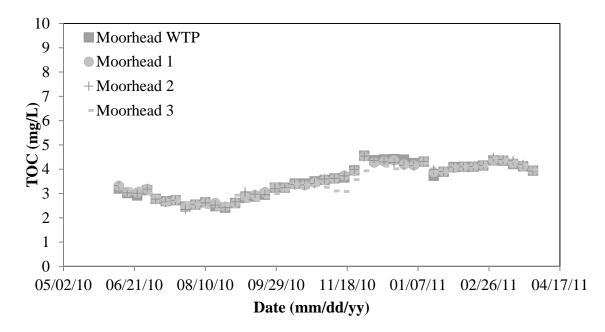


Figure 39. Total organic carbon in the Moorhead distribution network.

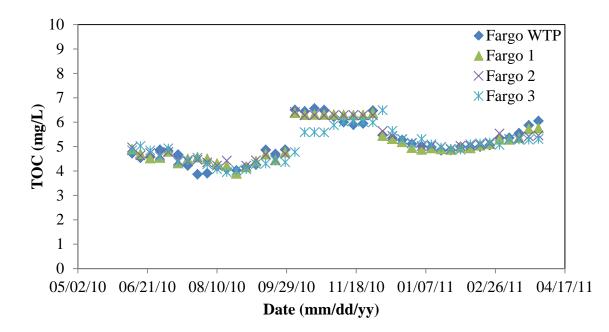


Figure 40. Total organic carbon in the Fargo distribution network.

filter does not operate as a biofilter consequently reducing the capacity of total organics removed in the WTP. Both distribution networks did not show a significant change in total organic carbon concentration spatially throughout the sampling sites.

The distribution systems did follow a similar trend from summer to winter months as the organic concentrations increased from the summer to winter but there are differences to be noted. The highest organic concentrations in the Fargo WTP occurred in early October and in the Moorhead WTP it occurred at the end of November. In the summer both treatment plants must maintained a higher ozone dose because temperature affects ozone degradation. In warm temperatures, ozone is less stable therefore the treatment plants need a higher ozone dose to maintain disinfection. This is also true in the winter as there are more organics in both systems. The treatment systems do not need as much ozone because in the cooler water ozone is more stable. Also as mentioned earlier, Fargo is able to use a lower pH which also affects the ozone dose. At a lower pH the Fargo WTP can use less ozone because it is more stable. The combination of a lower pH, influence of only surface water, and a biofilter that is not operated in that manner, explains why the organic concentrations are higher compared to Moorhead.

5.1.5.1. Specific ultraviolet absorbance at 254 nm (SUVA)

Natural waters contain organic material that derive from the decomposition of soil and plant materials which is the main source contributing to the DOC in surface waters (Thurman 1985). Natural organic matter can be broadly divided into two groups: humic substances and non-humic substances (Drewes et al., 2006). Humic substances are complex aromatic organics that are resistant to biodegradation and non-humic substances are biodegradable and referred to as biodegradable organic matter. Aromatic organic carbon can absorb ultraviolet light at 254 nm and is used to indicate the aromaticity of the dissolved organic carbon. Specific Ultraviolet Absorbance (SUVA) is the $\frac{UVA_{254nm}}{DOC}$ and is used to determine the ratio of aromatics relative to the total dissolved organic carbon.

SUVA concentrations change in the water treatment process. The Red River will typically have a high SUVA concentration. After the softening process the SUVA concentration will decrease because of coagulation/flocculation. Furthermore, ozonation breaks down the carbon aromatic bonds, which decreases the SUVA concentration. Interestingly, after filtration the SUVA values will increase because the simple organics that were broken down are consumed if there is an active biofilter.

SUVA was measured at the four locations in the Moorhead distribution network (Figure 41). The values ranged from 0.6627 L/mg-m to 1.267 L/mg-m. Ultraviolet absorbance at 254 nm in the distribution network stayed constant with an average of 0.030 1/cm and standard deviation of 0.00392 1/cm.

SUVA samples were taken at the four locations in the Fargo area (Figure 42). The SUVA values ranged from 0.749 to 1.11 L/mg-m. There was no significant change in SUVA through the summer and winter seasons. There was also no significant change between the sample locations in the distribution network.

SUVA in the Fargo and Moorhead distribution network were below 3.0 L/mg-m indicating that the organics were easily biodegradable and not of humic-like character (Edzwald 1993). Fargo and Moorhead SUVA values were near 1.0 L/mg-m and did not increase near 3.0 L/mg-m throughout the summer and winter months. A low SUVA value in the distribution network is preferable to minimize bacterial regrowth. Interestingly to

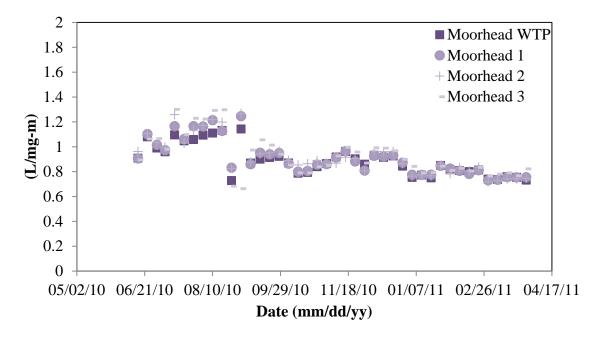


Figure 41. Variation of SUVA in the Moorhead distribution network.

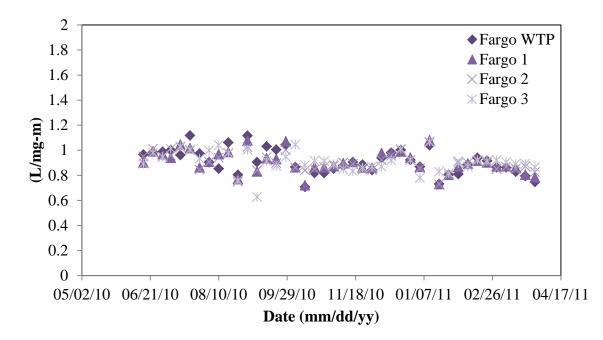


Figure 42. Variation of SUVA in the Fargo distribution network.

note, during the summer months the Moorhead treatment plant and distribution network had 0.2 L/mg-m higher SUVA concentrations. During the summer the Moorhead biofilter was more active than the Fargo filter thus removing more dissolved organic carbon.

5.1.5.2. Moorhead biofilter organic removal

The Moorhead WTP organic concentrations from the influent, softening basin, filter influent, and clearwell are shown in Figure 43. The majority of the organics in the water treatment plant are removed through the accelator. During the winter there is little removal through the biofilter and the summer shows more removal. This is a temperature dependent relationship and is shown in Figure 45.

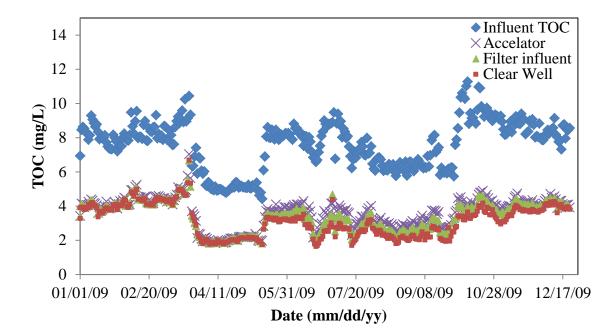


Figure 43. Moorhead WTP organics.

The percent removal of organics in each treatment stage is shown in Figure 44. The TOC removed in the softener ranged from 30% to 70%. The biofilter and ozone account for a percentage of less than 20%. The total TOC removal ranged from 50% to 75%.

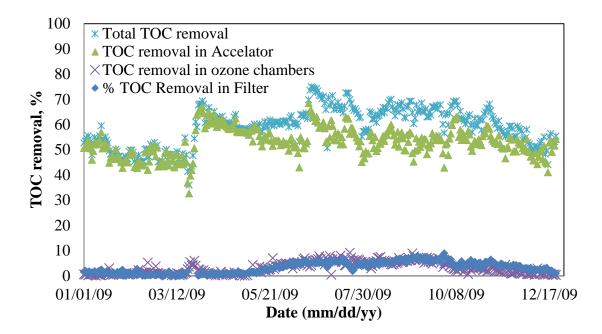


Figure 44. Percent TOC removal through the treatment process at the Moorhead WTP.

The percent of TOC removed through the Moorhead biofilter and ozone contact chambers are shown in Figure 45. The river temperature is also shown because it is a function of the biofilter efficiency. In the winter, colder temperatures reduce ozone effectiveness and also hinder bacteria that are able to utilize the simple organics. In the winter ozone is only removing 1% to 6% of the organics. In the summer the range is from 3% to 10%. The biofilter follows the same tread.

5.1.6. Bacterial regrowth

Bacterial regrowth in a distribution network can cause water quality problems. In a distribution network heterotrophic bacteria are almost always found when nitrification occurs (Zhang et al., 2009). Heterotrophic plate counts in Moorhead distribution network samples are shown in Figure 46. Heterotrophic plate counts ranged

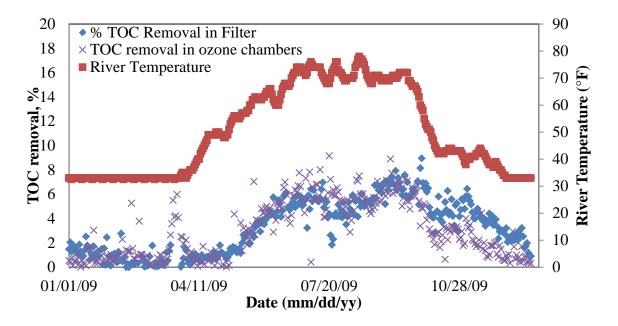


Figure 45. Percent TOC removal in the Moorhead biofilter and Red River temperature. from 0 to 556 CFU/mL. The Moorhead WTP showed no signs of growth. Moorhead 1 had the highest plate counts for all the four locations. It also had a chloramine residual concentration that was 2.43 mg/L and the Moorhead WTP was 2.48 mg/L. There was little loss of chloramine residual even though bacteria was able to grow higher than the other locations. This could be due to older pipe near the sampling location. Older cast iron pipe can harbor bacteria in a biofilm and protect them from disinfection.

Heterotrophic bacteria can serve as indications of bacterial regrowth. Figure 47 is the heterotrophic plate counts in the Fargo distribution network. Heterotrophic plate counts ranged from 0 to 812 CFU/ml. The Fargo WTP showed no signs of growth. Fargo 1 and Fargo 2 had similar plate counts of heterotrophic bacteria with Fargo 2 being slightly higher. Fargo 3 had the highest plate counts for all the locations. Fargo 3 had the highest plate counts due to the higher water age in the pipe network at that location. Also, even though the temperature was lower in the winter months at the furthest location

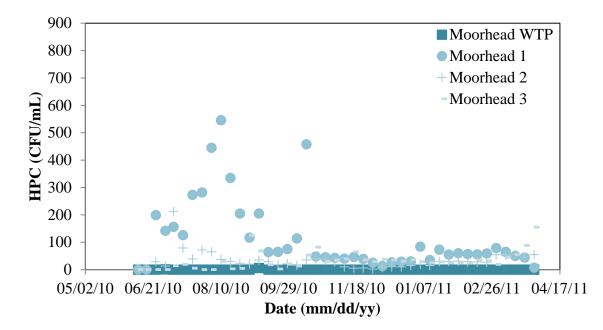


Figure 46. Heterotrophic plate counts in the Moorhead distribution network.

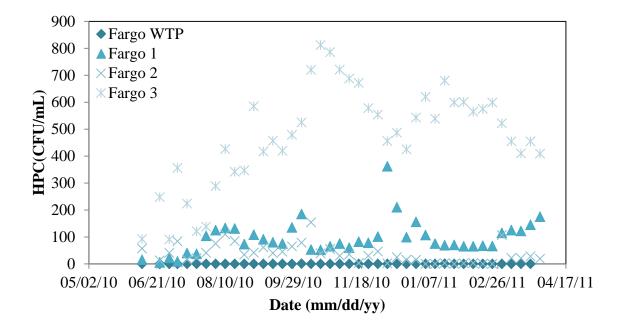


Figure 47. Heterotrophic plate counts in the Fargo distribution network.

heterotrophic bacteria proliferated. Since there was a longer residence time in the pipe during the winter months heterotrophic bacteria were able grow in the distribution network. The large plate count numbers were recorded in October and gradually decreased in the cooler months.

The Moorhead distribution network had less bacteria regrowth than the Fargo distribution network. Both water treatment plant sampling points showed little to no growth. In Moorhead, the site with the largest heterotrophic plate counts was sample location 1. As mentioned earlier this could be due to an older section of pipe. The other locations did not indicate high heterotrophic bacterial counts. During the winter months the heterotrophic plate counts did not exceed 200 CFU/mL and in the summer they did not exceed 250 CFU/mL. In Fargo, the highest heterotrophic bacteria counts were at the furthest location, Fargo 3 that had plate counts above 800 CFU/mL. Fargo 3 is the furthest from the WTP and has more potential for bacterial growth. Overall the Fargo distribution network had more regrowth of heterotrophic bacteria.

The most heterotrophic growth was seen at Fargo 3 during the winter as mentioned earlier. The chlorine residual during the winter months was approximately 0.33 mg/L lower at Fargo 3 than the other sample locations. Compared to the Moorhead 3, Fargo 3 did have a higher chloramines concentration. The lower chlorine residual and longer detention time during the winter gave heterotrophic bacteria a more favorable environment for growth.

81

5.2. Moorhead Biofilter Sampling for Nitrifying Activity

The biofilter in the Moorhead WTP has caused some operational issues in the past including maintaining chloramine residuals in the clearwell. The purpose of studying the biofilter is to better understand the nitrifying activity present and the effect it may have in their distribution network.

The four biological filters in the Moorhead water treatment plant were sampled in September 2010 and results are shown in Figure 48. Influent and effluent samples were taken from biological filters for analysis of concentrations of NO_2^- -N and ammonia nitrogen (NH₃-N). The influent and effluent concentrations are represented in respect to hours of service. Each filter has a different service time associated with its backwashing schedule. To maintain at least three filters in operation all the time and an operation cycle of 80 hours between backwashes, the filters are operated at schedules approximately 20 hours apart from each other.

The influent concentration of ammonia was 0.13 mg/L in all four filters. The effluent concentration of ammonia was near 0.01 mg/L in the filters. The filters removed 92% of the influent ammonia. The influent NO₂⁻-N was less than 0.01 mg/L. The concentration of NO₂⁻-N in the effluent varied between each filter. The two filters with the least hours in service had the highest NO₂⁻-N concentrations. The filters with 45.8 and 67.5 hours had lower NO₂⁻-N concentrations. After a filter backwash the AOB and NOB slough off. This decreases the amount of bacteria on the filter media. Once the filter media settle and are in service ammonia oxidizing bacteria are able to utilize the free ammonia in the water thus NO₂⁻-N concentrations are relatively high. After the filter has been in service for several days nitrite oxidizing bacteria are able to utilize the nitrite being produced and

convert it to nitrate. The lower nitrite concentrations in filters that have been in service for several days corroborate the observation.

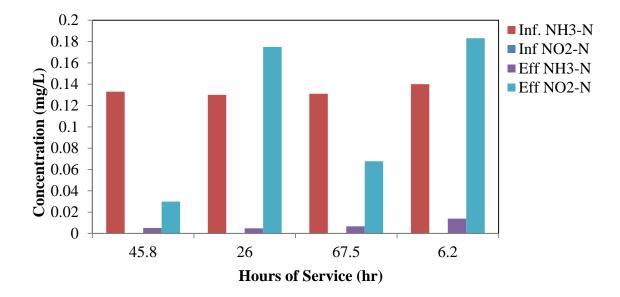


Figure 48. The four biological filters sampled in the Moorhead water treatment plant.

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The research presented in this thesis was undertaken to compare two similar water treatment plants and their corresponding distribution networks for the occurrence of nitrification and do a comparative study between both systems for operational and design variances. This was the first time two similar ozonation facilities and distribution networks that have similar designs and operational conditions have been studied for nitrification.

The major findings of this research are as follows: The major findings of this research are as follows:

• There was more chloramine decay observed in the Fargo distribution network compared to the Moorhead distribution network in more than one sampling location. The Fargo WTP and Fargo 3 had an average total chlorine residual of 3.64 mg/L and 2.26 mg/L respectively. The Moorhead WTP and Moorhead 3 had an average total chlorine residual of 2.48 mg/L and 1.87 mg/L respectively. The majority of chloramine decay occurred in the summer months. The Moorhead distribution network had less chloramine decay when compared to Fargo which is due to a combination of factors including; a higher removal of organics in the softening basins, the use of high pH during ozonation, and an effective active biofilter. In addition to lower influent organic content, the use of well water also lowers the water temperature that may reduce reaction rates in the distribution network in the summer months. In addition, Moorhead has a smaller system and shorter water age resulting in less chloramine degradation. The chlorine residual in the distribution network prevents water quality from deterioration. Excess chloramine decay may result in loss of disinfection power and release ammonia providing a climate for nitrification.

- Although there was a higher chloramine residual maintained throughout the Fargo distribution network it was because there was a higher dose at the treatment plant. The Fargo WTP maintained a chloramine residual of 4.0 mg/L and the Moorhead WTP maintained a residual of 2.5 mg/L.
- Except one situation, no nitrification was observed in both distribution networks. The one nitrification event was observed at Moorhead 3 during the summer at an area of low water use and low total chlorine residual. Based on this study a concentration above 1.5 mg/L may prevent nitrification from occurring in a distribution network.
- The organics in the Moorhead distribution network were lower than Fargo due to a combination of well water, an active biofilter, and less organics removed in the softening process.
- Nitrification occurred in the biofilter, it effectively oxidized NH₃-N that was added prior in the treatment process to NO₂⁻-N and NO₃⁻-N. Although it is possible for nitrifying bacteria to be carried to the distribution network, there is no evidence that the biofilter seeded the distribution network.
- Regrowth of heterotrophic bacteria was observed in both distribution networks from heterotrophic plate counts. It appears more heterotrophic bacterial growth was observed in aged and pipes located near the end of the networks. Although Fargo had higher chlorine residuals, more heterotrophic growth was observed in

Fargo indicating heterotrophic growth has a higher tolerance to chlorine than nitrifying bacteria. The Fargo system may support more heterotrophic growth because it has more total organic carbon.

 Based on network sampling nitrification in the Fargo and Moorhead distribution network is minimal. There was one instance of nitrification occurring in the Moorhead distribution network at the furthest location. Nitrification was not observed in the Fargo distribution network.

6.2. Recommendations

Based on the information obtained from this research, the following recommendations are suggested for future studies:

- Enumerating ammonia oxidizing and nitrite oxidizing bacteria in both distribution networks. By enumerating nitrifying bacteria one could establish if large populations exist in either distribution network.
- Sampling the biofilm in the distribution network would provide a better understanding where or if nitrifying communities develop in a distribution network.
- Develop a water quality model based on the parameters sampled to predict the potential nitrifying activity which would be beneficial for utilities.
- Until only recently, the Fargo water treatment plant is looking into the operation of their filter as a biofilter. If they were to continue operation of their facility with a biofilter a more in depth comparison of the Fargo and Moorhead biofilter should be established.

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APPENDIX

Table A1. Fargo WTP sampling data.

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-m	HPC CFU/ml	NO ₃ ⁻ -N ppm
6/10/2010	9.04	19.80	3.42	0.008	0.23	4.72	4.80			0	
6/16/2010	8.93	20.60	3.48	0.002	0.19	4.54	4.45	0.043	0.966	0	
6/23/2010	9.17	21.10	3.49	0.006	0.18	4.57	4.58	0.045	0.983	0	
6/30/2010	8.96	23.50	3.40	0.008	0.07	4.87	4.45	0.044	0.989	0	
7/6/2010	9.07	24.30	3.31	0.008	0.17	4.82	4.29	0.043	1.001	0	
7/13/2010	9.15	23.30	3.71	0.008	0.06	4.68	4.58	0.044	0.961	0	
7/20/2010	9.02	24.60	3.50	0.014	0.16	4.22	3.67	0.041	1.118	0	
7/27/2010	8.90	24.40	3.26	0.013	0.14	3.86	3.49	0.034	0.974	0	0.40
8/3/2010	8.90	25.00	3.30	0.013	0.15	3.91	3.87	0.035	0.905	0	0.41
8/10/2010	8.97	25.40	3.35	0.019	0.15	4.19	3.98	0.034	0.853	0	0.49
8/17/2010	9.00	23.00	3.17	0.009	0.12	4.08	3.67	0.039	1.062	0	0.50
8/24/2010	9.06	24.10	3.31	0.016	0.18	4.02	3.73	0.030	0.804	0	0.35
8/31/2010	8.98	23.70	3.60	0.010	0.07	4.17	3.67	0.041	1.117	0	0.32

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-m	HPC CFU/ml	NO ₃ ⁻ -N ppm
9/7/2010	9.04	19.90	3.56	0.009	0.07	4.26	3.76	0.034	0.905	0	0.73
9/14/2010	9.01	18.80	3.51	0.013	0.08	4.87	4.27	0.044	1.031	0	0.66
9/21/2010	8.98	17.50	3.89	0.010	0.11	4.70	4.18	0.042	1.005	0	0.78
9/28/2010	9.00	18.00	3.99	0.008	0.13	4.87	4.49	0.047	1.046	0	0.82
10/5/2010	8.91	17.90	3.60	0.008	0.06	6.50	5.77	0.050	0.866	1	0.86
10/12/2010	8.90	18.10	3.49	0.008	0.12	6.44	7.35	0.052	0.707	0	0.95
10/19/2010	9.01	15.70	3.88	0.008	0.08	6.56	6.35	0.052	0.819	0	1.07
10/26/2010	9.04	13.60	3.82	0.007	0.10	6.50	6.36	0.052	0.818	0	1.30
11/2/2010	9.03	13.50	3.80	0.008	0.10	6.21	6.22	0.053	0.853	0	1.45
11/9/2010	9.03	13.20	3.81	0.008	0.10	6.00	6.16	0.054	0.877	0	1.55
11/16/2010	9.02	13.30	3.82	0.008	0.09	5.89	6.07	0.055	0.906	0	1.68
11/23/2010	9.02	10.10	3.85	0.009	0.10	5.95	6.10	0.054	0.886	0	1.78
11/30/2010	9.03	7.40	3.88	0.009	0.11	6.48	6.18	0.052	0.841	0	1.69
12/7/2010	8.88	7.40	3.90	0.006	0.05	5.47	5.11	0.048	0.939	0	1.69
12/14/2010	8.85	8.00	3.81	0.006	0.05	5.35	5.00	0.049	0.981	0	1.57

Table A1. Fargo WTP sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-m	HPC CFU/ml	NO ₃ ⁻ -N ppm
12/21/2010	8.83	8.80	3.74	0.005	0.07	5.27	4.89	0.049	1.003	0	1.55
12/28/2010	8.85	6.60	3.70	0.005	0.10	5.11	4.88	0.045	0.923	0	1.45
1/4/2011	8.95	5.50	3.64	0.005	0.20	5.02	4.72	0.041	0.869	0	1.44
1/11/2011	8.88	7.80	3.60	0.007	0.12	4.98	4.90	0.051	1.040	0	1.48
1/18/2011	8.91	6.80	3.64	0.008	0.10	4.84	4.79	0.035	0.731	1	1.55
1/25/2011	8.91	7.20	3.66	0.007	0.10	4.85	4.84	0.039	0.805	0	1.64
2/1/2011	8.90	8.30	3.76	0.007	0.04	4.99	5.43	0.044	0.810	0	1.66
2/8/2011	8.91	8.00	3.71	0.007	0.09	4.98	4.97	0.044	0.886	0	1.67
2/15/2011	8.90	7.80	3.70	0.007	0.10	5.00	4.90	0.046	0.939	0	1.67
2/22/2011	8.91	7.50	3.69	0.007	0.10	5.06	5.02	0.046	0.917	0	1.68
3/1/2011	8.84	7.60	3.69	0.009	0.03	5.35	5.32	0.046	0.864	0	1.67
3/8/2011	8.85	7.80	3.70	0.009	0.10	5.36	5.33	0.046	0.864	0	1.64
3/15/2011	8.88	8.20	3.75	0.009	0.11	5.55	5.55	0.046	0.830	0	1.61
3/22/2011	8.85	8.50	3.88	0.008	0.10	5.88	5.79	0.046	0.795	0	1.58
3/29/2011	8.91	9.10	3.91	0.007	0.15	6.05	6.02	0.045	0.747	0	1.58

Table A1. Fargo WTP sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
6/10/2010	8.97	17.60	2.41	0.040	0.51	4.89	5.10			15	
6/16/2010	8.94	18.40	1.95	0.013	0.28	4.70	4.77	0.043	0.901	0	
6/23/2010	9.11	16.10	2.58	0.038	0.19	4.53	4.54	0.045	0.991	5	
6/30/2010	9.13	17.90	2.59	0.020	0.27	4.55	4.55	0.044	0.967	22	
7/6/2010	9.04	17.40	2.22	0.021	0.24	4.80	4.68	0.044	0.940	9	
7/13/2010	9.14	17.80	3.43	0.014	0.22	4.32	4.31	0.045	1.045	40	
7/20/2010	9.04	18.10	2.46	0.022	0.17	4.49	4.23	0.043	1.017	37	
7/27/2010	9.00	18.40	2.11	0.022	0.20	4.57	4.64	0.040	0.863	104	0.57
8/3/2010	9.02	19.10	2.51	0.022	0.19	4.50	4.41	0.040	0.907	125	0.61
8/10/2010	9.04	19.70	3.02	0.028	0.15	4.31	4.13	0.040	0.969	133	0.46
8/17/2010	8.98	19.70	2.31	0.028	0.15	4.21	4.15	0.040	0.985	133	0.40
								0.041			
8/24/2010 8/31/2010	8.98 9.03	20.00	2.47 2.69	0.041	0.18	3.90 4.16	3.90 3.81	0.030	0.770	73 108	0.36

Table A2. Fargo 1 sampling data.

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
	•										
9/7/2010	8.98	18.40	2.89	0.031	0.16	4.40	4.34	0.036	0.830	91	0.58
9/14/2010	8.99	18.30	2.89	0.028	0.13	4.69	4.60	0.043	0.936	80	0.55
9/21/2010	8.97	17.40	2.41	0.028	0.14	4.45	4.20	0.039	0.929	75	0.65
9/28/2010	9.00	18.00	3.32	0.028	0.23	4.77	4.39	0.047	1.070	135	0.80
10/5/2010	8.85	18.20	2.94	0.022	0.15	6.39	6.02	0.052	0.863	185	0.90
10/12/2010	8.87	17.50	2.80	0.016	0.18	6.30	7.36	0.053	0.720	53	1.10
10/19/2010	8.80	16.90	3.06	0.015	0.16	6.31	6.13	0.053	0.865	52	1.25
10/26/2010	8.86	15.70	3.39	0.014	0.12	6.31	6.15	0.053	0.861	65	1.35
11/2/2010	8.90	15.00	3.01	0.014	0.14	6.31	6.19	0.054	0.873	75	1.40
11/9/2010	8.91	14.80	3.02	0.014	0.19	6.30	6.25	0.056	0.896	60	1.65
11/16/2010	9.01	14.30	2.92	0.013	0.21	6.28	6.29	0.057	0.906	82	1.74
11/23/2010	9.00	13.50	3.10	0.013	0.20	6.30	6.15	0.053	0.862	78	1.79
11/30/2010	8.99	12.00	3.46	0.011	0.19	6.38	6.04	0.052	0.861	101	1.69
12/7/2010	8.79	12.60	3.30	0.012	0.11	5.44	5.12	0.050	0.977	362	1.69
12/14/2010	8.83	12.50	3.21	0.012	0.16	5.32	5.01	0.049	0.978	210	1.57

Table A2. Fargo 1 sampling data (continued).

Date	рН	Temp. C°	Cl ₂	NO ₂ ⁻ N	NH4 ⁺ -N	TOC	DOC	UVA 1/am	SUVA	HPC CFU/ml	NO ₃ ⁻ N
Date	рп	C	ррт	ppm	ppm	ppm	ppm	₂₅₄ 1/cm	L/mg-M		ppm
12/21/2010	8.86	12.60	3.05	0.011	0.20	5.19	4.95	0.049	0.990	99	1.58
12/28/2010	8.83	11.40	2.95	0.013	0.26	4.95	4.79	0.045	0.940	156	1.46
1/4/2011	8.82	9.80	2.78	0.015	0.36	4.88	4.73	0.041	0.867	107	1.44
1/11/2011	8.86	10.60	3.34	0.010	0.19	4.94	4.73	0.051	1.079	75	1.48
1/18/2011	8.83	10.70	3.25	0.011	0.26	4.90	4.80	0.035	0.729	69	1.56
1/25/2011	8.85	9.80	3.22	0.011	0.18	4.88	4.85	0.039	0.803	70	1.64
2/1/2011	8.91	9.60	3.21	0.015	0.13	4.97	5.19	0.045	0.867	65	1.66
2/8/2011	8.92	9.70	3.22	0.014	0.13	4.94	4.92	0.044	0.894	65	1.68
2/15/2011	8.89	9.60	3.20	0.015	0.13	5.05	5.02	0.046	0.916	67	1.68
2/22/2011	8.88	9.50	3.19	0.015	0.14	5.11	5.10	0.046	0.902	66	1.69
3/1/2011	8.83	9.56	2.23	0.022	0.18	5.29	5.29	0.046	0.870	115	1.67
3/8/2011	8.82	9.70	2.55	0.021	0.18	5.29	5.28	0.046	0.871	125	1.64
3/15/2011	8.89	9.80	2.65	0.021	0.19	5.35	5.35	0.046	0.861	122	1.61
3/22/2011	8.82	9.90	2.78	0.023	0.30	5.72	5.72	0.046	0.805	145	1.58
3/29/2011	8.97	10.00	2.92	0.024	0.35	5.76	5.75	0.045	0.783	175	1.58

Table A2. Fargo 1 sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
6/10/2010	9.02	18.20	3.08	0.015	0.36	4.97	5.07			57	
6/16/2010	8.90	18.90	3.04	0.004	0.23	4.64	4.63	0.044	0.950	0	
6/23/2010	9.15	17.50	3.12	0.015	0.20	4.74	4.65	0.047	1.012	13	
6/30/2010	9.13	19.20	3.07	0.014	0.22	4.66	4.65	0.044	0.946	41	
7/6/2010	9.00	20.00	3.19	0.009	0.26	4.78	4.70	0.045	0.958	84	
7/13/2010	9.16	20.20	3.70	0.011	0.17	4.43	4.39	0.045	1.025	16	
7/20/2010	9.02	20.40	3.06	0.015	0.14	4.39	4.30	0.043	1.000	21	
7/27/2010	8.96	21.10	2.66	0.020	0.22	4.46	4.50	0.038	0.845	41	0.62
8/3/2010	8.98	21.20	2.90	0.021	0.20	4.35	4.30	0.039	0.907	75	0.66
8/10/2010	9.05	21.40	3.05	0.022	0.17	4.22	4.14	0.039	0.941	110	0.42
8/17/2010	9.03	21.10	3.10	0.018	0.19	4.42	4.31	0.042	0.976	85	0.49
8/24/2010	9.00	21.90	2.93	0.019	0.17	4.02	4.00	0.030	0.749	34	0.35
8/31/2010	9.02	21.30	3.19	0.019	0.13	4.22	4.00	0.041	1.026	42	0.31

Table A3. Fargo 2 sampling data.

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
9/7/2010	9.00	19.80	3.07	0.022	0.18	4.43	4.29	0.036	0.839	61	0.51
9/14/2010	8.99	19.80	3.00	0.021	0.17	4.67	4.45	0.042	0.944	40	0.50
9/21/2010	8.96	18.60	2.78	0.024	0.16	4.45	4.24	0.038	0.897	45	0.59
9/28/2010	9.01	18.70	3.21	0.025	0.21	4.70	4.40	0.044	1.000	65	0.75
10/5/2010	8.86	19.20	3.02	0.017	0.16	6.42	6.04	0.052	0.861	79	0.89
10/12/2010	8.88	17.90	2.85	0.022	0.16	6.28	6.19	0.052	0.840	154	0.95
10/19/2010	8.82	17.20	3.15	0.017	0.14	6.29	6.13	0.052	0.849	39	1.16
10/26/2010	8.86	15.70	3.05	0.019	0.17	6.28	6.11	0.053	0.867	55	1.20
11/2/2010	8.88	15.10	3.10	0.020	0.16	6.29	6.16	0.054	0.877	30	1.55
11/9/2010	9.01	14.50	3.05	0.021	0.15	6.29	6.21	0.056	0.901	35	1.66
11/16/2010	9.03	14.00	3.06	0.021	0.15	6.30	6.29	0.056	0.891	3	1.73
11/23/2010	9.01	13.40	3.15	0.020	0.15	6.28	6.15	0.052	0.846	30	1.80
11/30/2010	9.02	11.60	3.23	0.017	0.15	6.28	6.05	0.051	0.844	46	1.70
12/7/2010	8.82	12.30	3.21	0.011	0.11	5.63	5.42	0.050	0.923	2	1.69
12/14/2010	8.81	12.70	3.15	0.012	0.13	5.44	5.13	0.049	0.956	25	1.58

Table A3. Fargo 2 sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
12/21/2010	8.81	13.10	3.09	0.010	0.14	5.31	4.88	0.049	1.004	15	1.58
12/28/2010	8.82	11.30	3.15	0.009	0.20	5.15	4.87	0.045	0.923	15	1.47
1/4/2011	8.84	9.70	3.28	0.009	0.26	5.02	4.79	0.041	0.856	0	1.45
1/11/2011	8.89	9.70	3.30	0.011	0.20	5.03	4.80	0.051	1.063	0	1.49
1/18/2011	8.91	8.80	3.32	0.011	0.23	4.98	4.80	0.035	0.729	3	1.56
1/25/2011	8.95	8.30	3.33	0.011	0.21	4.89	4.88	0.039	0.800	0	1.66
2/1/2011	8.96	8.40	3.33	0.011	0.11	5.03	4.94	0.045	0.911	2	1.67
2/8/2011	8.95	8.30	3.32	0.011	0.12	5.03	5.01	0.045	0.898	3	1.68
2/15/2011	8.96	8.20	3.31	0.011	0.14	5.07	5.02	0.046	0.916	0	1.68
2/22/2011	8.95	8.20	3.32	0.011	0.15	5.12	5.11	0.046	0.901	0	1.69
3/1/2011	8.89	8.21	3.30	0.011	0.07	5.53	5.52	0.047	0.851	107	1.67
3/8/2011	8.88	8.31	3.31	0.012	0.10	5.31	5.30	0.046	0.868	22	1.64
3/15/2011	8.91	8.45	3.32	0.011	0.18	5.34	5.40	0.046	0.852	21	1.61
3/22/2011	8.88	8.55	3.29	0.013	0.26	5.42	5.40	0.047	0.871	28	1.58
3/29/2011	8.96	8.60	3.35	0.013	0.27	5.46	5.45	0.045	0.826	19	1.58

Table A3. Fargo 2 sampling data (continued).

		Temp.	Cl ₂	NO ₂ ⁻ N	NH4 ⁺ -N	тос	DOC	UVA	SUVA	HPC	NO ₃ ⁻ N
Date	pН	C°	ppm	ppm	ppm	ppm	ppm	₂₅₄ 1/cm	L/mg-M	CFU/ml	ppm
6/10/2010	8.80	17.20	2.26	0.024	0.49	4.84	4.83			92	
6/16/2010	8.92	18.80	2.10	0.011	0.40	5.02	5.05	0.045	0.892	0	
6/23/2010	9.00	16.40	2.24	0.024	0.20	4.85	4.90	0.048	0.980	248	
6/30/2010	9.12	17.30	2.44	0.026	0.24	4.60	4.54	0.043	0.948	91	
7/6/2010	9.11	17.40	2.18	0.017	0.20	4.93	4.84	0.049	1.013	356	
7/13/2010	9.13	17.10	2.91	0.018	0.20	4.36	4.37	0.045	1.031	224	
7/20/2010	9.14	17.80	3.01	0.020	0.18	4.44	4.47	0.045	1.006	121	
7/27/2010	9.02	17.50	2.76	0.020	0.15	4.54	4.51	0.042	0.932	138	0.71
8/3/2010	9.01	18.40	2.51	0.029	0.16	4.27	4.21	0.042	0.998	289	0.67
8/10/2010	8.95	20.00	2.34	0.030	0.18	4.08	3.94	0.041	1.041	426	0.58
8/17/2010	9.06	19.60	2.38	0.024	0.23	3.95	3.88	0.038	0.980	342	0.55
8/24/2010	9.06	19.30	2.88	0.021	0.16	4.02	3.95	0.030	0.759	347	0.40
8/31/2010	9.05	20.00	2.61	0.023	0.20	4.07	3.88	0.039	1.005	585	0.33

Table A4. Fargo 3 sampling data.

Dete	T	Temp.	Cl ₂	NO ₂ -N	$\mathbf{NH_4^+}$ -N	TOC	DOC	UVA	SUVA	HPC	NO ₃ ⁻ N
Date	pН	C°	ppm	ppm	ppm	ppm	ppm	₂₅₄ 1/cm	L/mg-M	CFU/ml	ppm
9/7/2010	9.03	19.40	2.30	0.028	0.19	4.28	4.15	0.026	0.627	417	0.46
9/14/2010	9.01	17.60	2.34	0.034	0.10	4.30	4.05	0.037	0.914	457	0.43
9/21/2010	8.96	18.40	2.40	0.027	0.25	4.42	4.10	0.036	0.878	420	0.50
9/28/2010	9.01	18.70	2.35	0.029	0.31	4.36	4.12	0.039	0.947	479	0.60
10/5/2010	8.96	18.40	2.02	0.027	0.21	4.78	4.59	0.048	1.045	525	0.75
10/12/2010	8.86	18.50	2.05	0.029	0.24	5.59	6.02	0.053	0.880	720	0.82
10/19/2010	8.85	17.70	2.16	0.028	0.29	5.59	5.79	0.053	0.916	812	0.87
10/26/2010	8.84	16.10	1.99	0.029	0.32	5.58	5.80	0.053	0.914	786	1.20
11/2/2010	8.89	15.90	2.01	0.028	0.31	5.88	5.86	0.052	0.888	721	1.39
11/9/2010	8.95	15.80	2.03	0.030	0.35	6.02	5.89	0.050	0.849	688	1.64
11/16/2010	8.98	15.70	1.99	0.030	0.36	6.05	5.88	0.049	0.833	672	1.71
11/23/2010	9.00	13.50	2.14	0.023	0.26	6.01	5.80	0.050	0.861	578	1.81
11/30/2010	9.02	12.70	2.75	0.023	0.22	5.99	5.76	0.050	0.868	554	1.70
12/7/2010	8.99	13.30	2.49	0.024	0.26	6.49	6.21	0.054	0.870	456	1.71
12/14/2010	8.85	14.00	2.35	0.029	0.29	5.64	5.54	0.051	0.920	487	1.60

Table A4. Fargo 3 sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
12/21/2010	8.78	15.20	2.32	0.037	0.32	5.30	5.04	0.051	1.011	425	1.60
12/28/2010	8.74	13.20	2.32	0.030	0.32	5.13	5.10	0.047	0.922	543	1.47
1/4/2011	8.74	11.90	2.06	0.022	0.31	5.31	5.13	0.047	0.780	620	1.44
1/11/2011	8.79	11.40	1.83	0.055	0.36	5.09	4.86	0.052	1.069	539	1.49
1/18/2011	8.82	12.00	2.11	0.033	0.29	4.97	4.82	0.040	0.830	680	1.57
1/25/2011	8.80	11.80	1.99	0.035	0.30	4.91	4.90	0.040	0.817	599	1.65
2/1/2011	8.77	11.50	1.78	0.036	0.27	4.87	4.92	0.044	0.894	601	1.68
2/8/2011	8.80	11.20	1.77	0.035	0.29	5.09	5.05	0.044	0.871	565	1.69
2/15/2011	8.77	11.10	1.84	0.038	0.29	5.13	5.09	0.047	0.923	575	1.69
2/22/2011	8.80	11.00	1.83	0.037	0.28	5.17	5.13	0.047	0.916	599	1.70
3/1/2011	8.89	11.20	2.35	0.026	0.11	5.07	5.10	0.047	0.921	522	1.70
3/8/2011	8.89	11.30	2.32	0.025	0.10	5.30	5.30	0.048	0.906	455	1.64
3/15/2011	8.89	11.40	2.28	0.024	0.21	5.29	5.28	0.047	0.890	410	1.61
3/22/2011	8.89	11.40	2.31	0.022	0.36	5.28	5.27	0.047	0.892	455	1.58
3/29/2011	8.89	11.50	2.29	0.019	0.40	5.31	5.21	0.045	0.864	409	1.61

Table A4. Fargo 3 sampling data (continued).

		Temp.	Cl ₂	NO ₂ ⁻ -N	NH4 ⁺ -N	TOC	DOC	UVA	SUVA	HPC	NO ₃ -N
Date	pН	C°	ppm	ppm	ppm	ppm	ppm	₂₅₄ 1/cm	L/mg-M	CFU/ml	ppm
6/10/2010	9.28	19.50	2.57	0.220	0.27	3.20	3.28			0	
6/16/2010	9.20	20.20	2.49	0.086	0.09	3.02	3.08	0.028	0.908	0	
6/23/2010	9.30	21.00	2.58	0.147	0.08	2.92	2.96	0.032	1.080	0	
6/30/2010	9.30	21.80	2.49	0.228	0.10	3.14	3.13	0.031	0.990	1	
7/6/2010	9.22	21.80	2.48	0.168	0.10	2.78	2.81	0.027	0.960	0	
7/13/2010	9.33	21.50	2.52	0.152	0.09	2.68	2.65	0.029	1.095	0	
7/20/2010	9.24	21.80	2.51	0.145	0.12	2.73	2.77	0.029	1.048	0	
7/27/2010	9.28	21.70	2.75	0.066	0.12	2.47	2.46	0.026	1.058	0	0.36
8/3/2010	9.25	22.20	2.65	0.068	0.12	2.54	2.47	0.027	1.094	0	0.37
8/10/2010	9.19	23.30	2.55	0.099	0.14	2.64	2.52	0.028	1.110	0	0.46
8/17/2010	9.27	21.10	2.57	0.075	0.20	2.48	2.47	0.028	1.132	0	0.52
8/24/2010	9.24	21.90	2.65	0.069	0.13	2.42	2.47	0.018	0.728	0	0.39
8/31/2010	9.26	21.60	2.59	0.039	0.13	2.61	2.54	0.029	1.143	0	0.44

Table A5. Moorhead WTP sampling data.

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
9/7/2010	9.27	19.50	2.55	0.023	0.13	2.82	2.76	0.024	0.869	6	0.42
9/14/2010	9.22	18.80	2.55	0.056	0.11	2.88	2.89	0.026	0.901	0	0.37
9/21/2010	9.22	17.50	2.61	0.023	0.11	2.96	2.85	0.026	0.914	0	0.42
9/28/2010	9.22	17.60	2.56	0.026	0.23	3.24	3.14	0.029	0.923	0	0.49
10/5/2010	9.24	17.60	2.56	0.012	0.09	3.24	3.10	0.027	0.870	0	0.55
10/12/2010	9.25	17.70	2.39	0.014	0.11	3.41	3.43	0.027	0.787	0	0.71
10/19/2010	9.16	15.60	2.41	0.019	0.13	3.41	3.40	0.027	0.794	0	0.76
10/26/2010	9.21	14.10	2.46	0.017	0.15	3.50	3.45	0.029	0.840	0	1.01
11/2/2010	9.20	13.80	2.45	0.017	0.12	3.56	3.47	0.030	0.865	0	1.25
11/9/2010	9.18	13.20	2.44	0.026	0.10	3.62	3.49	0.032	0.918	0	1.55
11/16/2010	9.18	12.80	2.41	0.045	0.07	3.66	3.53	0.034	0.962	0	1.70
11/23/2010	9.15	12.00	2.51	0.045	0.10	3.96	3.77	0.034	0.903	0	1.70
11/30/2010	9.06	11.10	2.58	0.046	0.12	4.56	3.95	0.034	0.860	0	1.69
12/7/2010	9.20	10.90	2.44	0.045	0.11	4.37	4.08	0.038	0.932	0	1.70
12/14/2010	9.19	11.60	2.30	0.042	0.11	4.40	4.15	0.038	0.915	0	1.54

Table A5. Moorhead WTP sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
12/21/2010	9.16	12.40	2.21	0.040	0.11	4.42	4.21	0.039	0.926	0	1.55
12/28/2010	9.20	11.90	2.22	0.036	0.13	4.40	4.15	0.035	0.844	0	1.45
1/4/2011	9.23	11.20	2.27	0.028	0.15	4.25	4.11	0.031	0.754	0	1.44
1/11/2011	9.27	10.70	2.22	0.018	0.17	4.31	4.14	0.032	0.772	0	1.44
1/18/2011	9.14	10.10	2.33	0.014	0.09	3.74	3.74	0.028	0.750	0	1.55
1/25/2011	9.15	10.30	2.33	0.013	0.10	3.89	3.88	0.033	0.849	0	1.64
2/1/2011	9.18	10.60	2.33	0.012	0.12	4.09	3.92	0.032	0.816	0	1.65
2/8/2011	9.20	10.50	2.31	0.012	0.12	4.10	3.96	0.032	0.809	0	1.63
2/15/2011	9.21	10.20	2.33	0.012	0.12	4.10	4.00	0.032	0.800	0	1.66
2/22/2011	9.21	10.00	2.31	0.013	0.11	4.15	4.06	0.033	0.813	0	1.68
3/1/2011	9.29	7.70	2.65	0.008	0.10	4.37	4.33	0.032	0.740	0	1.63
3/8/2011	9.28	8.00	2.65	0.008	0.10	4.35	4.35	0.032	0.736	0	1.59
3/15/2011	9.29	8.30	2.66	0.008	0.11	4.21	4.21	0.032	0.760	0	1.62
3/22/2011	9.28	9.10	2.65	0.008	0.10	4.12	4.11	0.031	0.754	0	1.64
3/29/2011	9.32	10.80	2.66	0.008	0.11	3.94	4.10	0.030	0.732	0	1.58

Table A5. Moorhead WTP sampling data (continued).

		Temp.	Cl ₂	NO ₂ ⁻ N	NH ₄ ⁺ -N	тос	DOC	UVA	SUVA	HPC	NO ₃ ⁻ N
Date	pН	C°	ppm	ppm	ppm	ppm	ppm	₂₅₄ 1/cm	L/mg-M	CFU/ml	ppm
6/10/2010	9.22	20.20	2.09	0.225	0.39	3.31	3.20			0	
6/16/2010	9.16	18.90	2.44	0.086	0.09	3.07	3.09	0.028	0.906	0	
6/23/2010	9.32	18.50	2.51	0.152	0.08	3.04	3.00	0.033	1.102	199	
6/30/2010	9.34	19.00	2.48	0.235	0.09	3.19	3.15	0.032	1.016	142	
7/6/2010	9.28	19.10	2.33	0.165	0.09	2.77	2.78	0.027	0.972	156	
7/13/2010	9.36	19.00	2.37	0.150	0.09	2.66	2.66	0.031	1.165	126	
7/20/2010	9.28	19.80	2.50	0.145	0.11	2.74	2.73	0.029	1.062	273	
7/27/2010	9.25	20.50	2.71	0.068	0.11	2.45	2.32	0.027	1.166	282	0.34
8/3/2010	9.23	21.00	2.60	0.069	0.11	2.53	2.32	0.027	1.163	445	0.36
8/10/2010	9.22	21.10	2.44	0.097	0.12	2.63	2.55	0.031	1.214	546	0.45
8/17/2010	9.26	20.30	2.52	0.075	0.14	2.61	2.57	0.029	1.127	335	0.50
8/24/2010	9.25	20.60	2.52	0.073	0.12	2.46	2.41	0.020	0.832	205	0.40
8/31/2010	9.29	20.00	2.55	0.040	0.13	2.61	2.57	0.032	1.246	117	0.45

Table A6. Moorhead 1 sampling data.

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
9/7/2010	9.28	18.60	2.55	0.022	0.13	2.89	2.91	0.025	0.860	205	0.41
9/14/2010	9.23	17.90	2.56	0.058	0.09	2.93	2.84	0.027	0.952	64	0.38
9/21/2010	9.22	16.70	2.51	0.023	0.12	3.06	2.87	0.027	0.939	65	0.40
9/28/2010	9.23	16.30	2.52	0.027	0.20	3.26	3.16	0.030	0.950	75	0.48
10/5/2010	9.25	16.10	2.48	0.016	0.10	3.23	3.12	0.027	0.865	114	0.54
10/12/2010	9.27	16.60	2.34	0.015	0.11	3.38	3.38	0.027	0.799	458	0.69
10/19/2010	9.15	15.20	2.51	0.019	0.12	3.34	3.35	0.027	0.805	48	0.78
10/26/2010	9.24	13.70	2.43	0.024	0.18	3.45	3.39	0.029	0.857	45	1.01
11/2/2010	9.20	11.20	2.43	0.035	0.15	3.55	3.49	0.030	0.861	43	1.26
11/9/2010	9.21	10.90	2.44	0.041	0.11	3.61	3.50	0.032	0.914	40	1.56
11/16/2010	9.20	10.10	2.41	0.047	0.08	3.73	3.52	0.034	0.965	46	1.71
11/23/2010	9.14	8.10	2.42	0.048	0.10	3.93	3.85	0.034	0.882	39	1.71
11/30/2010	9.15	6.70	2.58	0.048	0.12	4.53	4.33	0.035	0.808	25	1.69
12/7/2010	9.30	6.10	2.34	0.050	0.12	4.27	4.10	0.038	0.927	13	1.69
12/14/2010	9.24	7.00	2.20	0.047	0.13	4.32	4.13	0.038	0.921	27	1.56

Table A6. Moorhead 1 sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
12/21/2010	9.18	10.90	2.01	0.044	0.14	4.37	4.19	0.039	0.931	29	1.55
12/28/2010	9.24	8.60	2.07	0.035	0.16	4.20	4.01	0.035	0.872	30	1.46
1/4/2011	9.28	7.60	2.16	0.028	0.17	4.16	4.00	0.031	0.775	84	1.44
1/11/2011	9.37	5.40	2.25	0.018	0.15	4.32	4.13	0.032	0.774	35	1.45
1/18/2011	9.24	4.90	2.45	0.014	0.07	3.88	3.74	0.029	0.775	73	1.55
1/25/2011	9.24	4.40	2.40	0.012	0.06	3.90	3.90	0.033	0.846	55	1.64
2/1/2011	9.25	4.30	2.32	0.011	0.05	4.06	4.00	0.033	0.824	60	1.66
2/8/2011	9.24	4.20	2.30	0.011	0.06	4.09	3.97	0.032	0.807	57	1.64
2/15/2011	9.24	4.20	2.32	0.011	0.06	4.09	4.10	0.032	0.781	56	1.67
2/22/2011	9.25	4.10	2.30	0.011	0.06	4.16	4.07	0.033	0.812	59	1.68
3/1/2011	9.34	5.30	2.61	0.012	0.06	4.38	4.38	0.032	0.731	79	1.63
3/8/2011	9.34	5.30	2.64	0.012	0.07	4.36	4.36	0.032	0.735	65	1.59
3/15/2011	9.35	5.29	2.65	0.010	0.07	4.24	4.24	0.032	0.756	50	1.62
3/22/2011	9.31	5.30	2.64	0.009	0.08	4.12	4.11	0.031	0.754	44	1.64
3/29/2011	9.40	5.30	2.66	0.008	0.08	3.93	4.11	0.031	0.755	7	1.58

Table A6. Moorhead 1 sampling data (continued).

		Temp.	Cl ₂	NO ₂ ⁻ N	NH4 ⁺ -N	TOC	DOC	UVA	SUVA	HPC	NO ₃ ⁻ N
Date	pН	C°	ppm	ppm	ppm	ppm	ppm	₂₅₄ 1/cm	L/mg-M	CFU/ml	ppm
6/10/2010	9.20	20.30	1.82	0.182	0.36	3.32	3.33			6	
6/16/2010	9.25	18.30	2.32	0.089	0.10	3.03	3.02	0.029	0.962	0	
6/23/2010	9.32	18.10	2.43	0.154	0.09	3.01	2.98	0.033	1.106	29	
6/30/2010	9.23	20.10	1.84	0.211	0.17	3.18	3.10	0.032	1.033	13	
7/6/2010	9.26	19.50	2.32	0.170	0.10	2.77	2.71	0.027	0.996	212	
7/13/2010	9.33	20.30	2.35	0.152	0.09	2.65	2.62	0.033	1.259	79	
7/20/2010	9.27	20.40	2.43	0.144	0.13	2.72	2.82	0.029	1.029	39	
7/27/2010	9.24	20.70	2.53	0.068	0.12	2.34	2.38	0.027	1.133	72	0.35
8/3/2010	9.22	21.00	2.51	0.070	0.12	2.56	2.39	0.028	1.172	65	0.41
8/10/2010	9.20	21.00	2.43	0.096	0.11	2.61	2.54	0.031	1.219	37	0.47
8/17/2010	9.24	19.80	2.50	0.079	0.13	2.52	2.50	0.030	1.199	29	0.52
8/24/2010	9.22	20.20	2.51	0.075	0.11	2.42	2.42	0.020	0.826	23	0.40
8/31/2010	9.27	19.80	2.53	0.046	0.13	2.66	2.52	0.032	1.268	20	0.46

Table A7. Moorhead 2 sampling data.

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
9/7/2010	9.26	18.60	2.57	0.025	0.13	3.06	2.85	0.025	0.876	35	0.49
9/14/2010	9.18	18.10	2.49	0.052	0.10	2.97	2.86	0.027	0.943	29	0.42
9/21/2010	9.18	17.00	2.44	0.025	0.13	2.95	2.84	0.027	0.951	18	0.41
9/28/2010	9.15	16.50	2.49	0.030	0.16	3.20	3.11	0.030	0.965	21	0.52
10/5/2010	9.23	16.80	2.43	0.018	0.25	3.24	3.15	0.028	0.890	16	0.58
10/12/2010	9.24	16.50	2.29	0.019	0.13	3.37	3.16	0.027	0.854	35	0.65
10/19/2010	9.11	15.40	2.46	0.023	0.14	3.36	3.13	0.027	0.864	39	0.78
10/26/2010	9.17	14.20	2.18	0.023	0.19	3.41	3.26	0.029	0.890	38	1.02
11/2/2010	9.18	11.50	2.19	0.032	0.17	3.59	3.46	0.030	0.867	29	1.26
11/9/2010	9.17	11.60	2.22	0.041	0.13	3.62	3.69	0.032	0.868	10	1.56
11/16/2010	9.17	10.60	2.34	0.042	0.10	3.73	3.82	0.035	0.915	5	1.70
11/23/2010	9.08	10.60	2.30	0.043	0.15	3.99	3.87	0.035	0.905	6	1.70
11/30/2010	9.07	10.60	2.24	0.049	0.16	4.54	4.35	0.035	0.805	2	1.66
12/7/2010	9.23	7.30	2.27	0.048	0.13	4.36	4.06	0.039	0.960	7	1.67
12/14/2010	9.20	7.80	2.01	0.043	0.14	4.30	4.06	0.039	0.961	11	1.54

Table A7. Moorhead 2 sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
12/21/2010	9.17	9.40	1.76	0.042	0.14	4.27	4.05	0.039	0.962	10	1.56
12/28/2010	9.25	9.10	1.90	0.037	0.16	4.15	4.05	0.035	0.864	15	1.45
1/4/2011	9.26	8.00	2.16	0.029	0.17	4.15	4.06	0.031	0.764	19	1.45
1/11/2011	9.31	7.00	2.15	0.020	0.18	4.32	4.13	0.032	0.774	15	1.45
1/18/2011	9.15	5.50	2.33	0.014	0.08	3.98	3.91	0.030	0.766	29	1.53
1/25/2011	9.16	6.00	2.33	0.012	0.11	3.91	3.90	0.033	0.846	30	1.66
2/1/2011	9.19	5.50	2.32	0.012	0.10	4.10	4.21	0.033	0.783	31	1.67
2/8/2011	9.18	5.50	2.31	0.011	0.11	4.10	3.98	0.033	0.830	29	1.65
2/15/2011	9.17	5.30	2.31	0.011	0.11	4.11	4.10	0.033	0.806	28	1.68
2/22/2011	9.19	5.30	2.31	0.011	0.11	4.16	4.07	0.034	0.836	27	1.69
3/1/2011	9.29	5.90	2.38	0.014	0.10	4.49	4.46	0.032	0.718	54	1.63
3/8/2011	9.30	5.70	2.41	0.012	0.10	4.40	4.39	0.032	0.729	53	1.59
3/15/2011	9.31	5.60	2.42	0.011	0.11	4.35	4.32	0.032	0.742	55	1.62
3/22/2011	9.32	5.60	2.50	0.010	0.10	4.20	4.18	0.031	0.742	45	1.64
3/29/2011	9.34	5.60	2.55	0.008	0.10	3.92	4.15	0.031	0.747	55	1.58

Table A7. Moorhead 2 sampling data (continued).

		Temp.	Cl ₂	NO ₂ ⁻ N	NH ₄ ⁺ -N	TOC	DOC	UVA	SUVA	HPC	NO ₃ -N
Date	pН	C°	ppm	ppm	ppm	ppm	ppm	₂₅₄ 1/cm	L/mg-M	CFU/ml	ppm
6/10/2010	9.26	17.90	2.23	0.196	0.29	3.33	3.32			0	
6/16/2010	9.27	16.70	2.13	0.074	0.12	3.20	3.24	0.029	0.894	0	
6/23/2010	9.34	15.70	2.31	0.177	0.09	3.22	3.20	0.034	1.062	0	
6/30/2010	9.30	16.30	2.08	0.165	0.11	3.00	3.00	0.032	1.065	0	
7/6/2010	9.29	16.10	2.23	0.178	0.09	2.87	2.76	0.027	0.979	14	
7/13/2010	9.35	16.90	2.26	0.163	0.11	2.58	2.54	0.033	1.300	19	
7/20/2010	9.29	17.00	2.42	0.136	0.12	2.71	2.73	0.030	1.098	5	
7/27/2010	9.28	17.20	2.32	0.093	0.12	2.62	2.52	0.031	1.229	0	0.43
8/3/2010	9.27	18.00	2.32	0.096	0.12	2.56	2.53	0.031	1.223	0	0.46
8/10/2010	9.26	18.80	2.20	0.116	0.12	2.42	2.48	0.032	1.291	30	0.46
8/17/2010	9.29	18.00	2.16	0.126	0.11	2.34	2.31	0.030	1.297	3	0.53
8/24/2010	9.15	18.10	1.65	0.242	0.06	2.54	2.49	0.017	0.682	4	0.50
8/31/2010	9.10	18.00	1.40	0.281	0.04	2.93	2.57	0.017	0.663	125	0.58

Table A8. Moorhead 3 sampling data.

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
9/7/2010	9.22	17.60	1.55	0.210	0.07	2.66	2.57	0.025	0.973	68	0.74
9/14/2010	9.24	17.20	1.78	0.127	0.07	2.75	2.65	0.028	1.056	18	0.66
9/21/2010	9.25	17.00	2.07	0.094	0.14	2.84	2.76	0.028	1.013	2	0.69
9/28/2010	9.17	17.00	2.33	0.127	0.15	2.99	2.87	0.027	0.940	20	0.70
10/5/2010	9.14	17.20	1.60	0.125	0.13	3.16	3.05	0.026	0.852	13	0.74
10/12/2010	9.23	16.80	1.89	0.064	0.13	3.39	3.29	0.026	0.790	53	0.77
10/19/2010	9.18	16.20	1.28	0.082	0.14	3.36	3.30	0.026	0.789	82	0.77
10/26/2010	9.18	14.90	1.83	0.073	0.17	3.38	3.34	0.028	0.838	30	1.01
11/2/2010	9.19	11.80	1.75	0.081	0.20	3.25	3.41	0.029	0.850	35	1.24
11/9/2010	9.18	12.10	1.55	0.089	0.25	3.10	3.46	0.032	0.926	39	1.54
11/16/2010	9.16	14.70	1.25	0.090	0.27	3.08	3.52	0.035	0.996	65	1.71
11/23/2010	9.10	13.10	1.36	0.086	0.24	3.57	3.65	0.035	0.958	35	1.70
11/30/2010	9.06	12.60	1.59	0.063	0.18	3.93	3.80	0.033	0.868	29	1.66
12/7/2010	9.09	12.10	1.26	0.066	0.25	4.19	3.83	0.038	0.991	37	1.69
12/14/2010	9.10	12.00	1.30	0.062	0.23	4.12	3.95	0.039	0.988	35	1.55

Table A8. Moorhead 3 sampling data (continued).

Date	рН	Temp. C°	Cl ₂ ppm	NO ₂ ⁻ -N ppm	NH4 ⁺ -N ppm	TOC ppm	DOC ppm	UVA 254 1/cm	SUVA L/mg-M	HPC CFU/ml	NO ₃ ⁻ -N ppm
12/21/2010	9.12	12.10	1.39	0.053	0.23	4.02	4.03	0.039	0.967	30	1.55
12/28/2010	9.13	11.30	1.75	0.049	0.23	4.13	4.00	0.036	0.899	36	1.45
1/4/2011	9.15	10.70	1.82	0.033	0.23	4.14	3.92	0.033	0.842	29	1.44
1/11/2011	9.13	10.80	1.60	0.027	0.23	4.23	4.18	0.033	0.790	25	1.47
1/18/2011	9.17	10.50	1.71	0.022	0.17	3.91	3.91	0.031	0.793	28	1.52
1/25/2011	9.18	10.20	1.70	0.023	0.24	3.91	3.91	0.033	0.844	24	1.65
2/1/2011	9.21	10.30	1.67	0.024	0.26	4.10	4.08	0.033	0.809	23	1.65
2/8/2011	9.19	10.20	1.71	0.023	0.25	4.10	3.99	0.033	0.828	23	1.66
2/15/2011	9.19	10.10	1.80	0.023	0.26	4.10	4.10	0.033	0.805	35	1.69
2/22/2011	9.20	10.10	1.78	0.023	0.27	4.15	4.08	0.034	0.834	32	1.69
3/1/2011	9.25	9.40	2.19	0.016	0.25	4.47	4.45	0.034	0.763	19	1.63
3/8/2011	9.26	9.30	2.21	0.016	0.23	4.37	4.36	0.034	0.780	45	1.59
3/15/2011	9.31	9.00	2.25	0.016	0.21	4.31	4.30	0.034	0.790	55	1.62
3/22/2011	9.25	9.10	2.31	0.013	0.21	4.18	4.18	0.032	0.766	88	1.64
3/29/2011	9.24	9.10	2.33	0.013	0.16	3.97	4.26	0.035	0.822	155	1.58

Table A8. Moorhead 3 sampling data (continued).