Water Quality Variations During Nitrification In Drinking Water Distribution Systems

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WATER QUALITY VARIATIONS DURING NITRIFICATION IN DRINKING WATER DISTRIBUTION SYSTEMS

by

DAVID WEBB JR
B.S. University of Central Florida, 2001

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Civil and Environmental Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Spring Term
2004
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ABSTRACT

This thesis documents the relationship among the major water quality parameters during a nitrification episode. Nitrification unexpectedly occurred in a chloraminated pilot drinking water distribution system practicing with a 4.0 mg/L as Cl\textsubscript{2} residual dosed at 4.5:1 Cl\textsubscript{2}:NH\textsubscript{3}-N. Surface, ground and sea water were treated and disinfected with monochloramines to produce finished water quality similar to regional utility water quality. PVC, galvanized, unlined cast iron and lined iron pipes were harvested from regional distribution systems and used to build eighteen pilot distribution systems (PDSs). The PDSs were operated at a 5-day hydraulic residence time (HRT) and ambient temperatures.

As seasonal temperatures increased the rate of monochloramine dissipation increased until effluent PDS residuals were zero. PDSs effluent water quality parameters chloramines residual, dissolved oxygen, heterotrophic plate counts (HPCs), pH, alkalinity, and nitrogen species were monitored and found to vary as expected by stoichiometry associated with theoretical biological reactions excepting alkalinity. Nitrification was confirmed in the PDSs. The occurrence in the PDSs was not isolated to any particular source water. Ammonia for nitrification came from degraded chloramines, which was common among all finished waters. Consistent with nitrification trends of dissolved oxygen consumption, ammonia consumption, nitrite and nitrate production were clearly observed in the PDSs bulk water quality profiles. Trends of pH and alkalinity were less apparent. To control nitrification: residual was increased to 4.5 mg/L as Cl\textsubscript{2} at 5:1 Cl\textsubscript{2}:NH\textsubscript{3}-N dosing ratio, and the HRT was reduced from 5 to 2 days. Elimination of the nitrification episode was achieved after a 1 week free chlorine burn.
ACKNOWLEDGEMENTS

My Parents – Thank you for always being there for me in my endeavors.

Honey Lynn – You were right, I did do it. Thank you.

My Family and Friends – Thanks for your support.

Dr Taylor – Thanks for: pushing me to learn as painful as it was, the many lessons that may ease my transition into the real world, and the opportunity to contribute in a world class organization.

Dr. Dietz, Dr. Randall, Dr. Cooper – Thank you for your efforts that have helped me become a master student

UCF Civil and Environmental Engineering Department, Dr Norris, Nancy, Carol Ann, Margarida and my colleagues – Thank you for your involvement, making my experience in the program at UCF a successful one.
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<td>4.8</td>
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# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Awwa</td>
<td>American Water Works Association</td>
</tr>
<tr>
<td>AwwaRF:</td>
<td>American Water Works Association Research Foundation</td>
</tr>
<tr>
<td>AOB</td>
<td>Ammonia oxidizing bacteria</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection by-product</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>HPC</td>
<td>Heterotrophic plate count</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic residence time</td>
</tr>
<tr>
<td>NOB</td>
<td>Nitrite oxidizing bacteria</td>
</tr>
<tr>
<td>PDS</td>
<td>Pilot distribution system</td>
</tr>
<tr>
<td>TKN</td>
<td>Total Kjeldahl nitrogen</td>
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1 INTRODUCTION

Nitrification is a biological process that occurs in the natural environment. In the nitrogen cycle, it is responsible for the conversion of ammonia to nitrite and ultimately nitrate. Because of its effectiveness, the process has been utilized in water and wastewater treatment for years. However, the uncontrolled presence of nitrification in drinking water systems is undesirable. Although nitrification has been proven to be beneficial in water treatment, the focus of this paper is on undesired, uncontrolled nitrification in chloraminated water systems. When chloramines are used to maintain a disinfection residual in a drinking water distribution system, there is potential for nitrification. An estimated two-thirds of medium and large systems in the United States that chloraminate experience nitrification to some degree (AWWA, 1995). The uncontrolled presence of nitrification is undesirable due to its adverse effects on water quality, aesthetics, and associated health risks (AWWA, 1995).

UCF conducted research in the Tampa Bay Water AwwaRF TCP “Required Treatment and Water Quality Criteria for Distribution System Blending Of Treated Surface, Ground and Saline Sources” project. During the project, nitrification unintentionally occurred. This presentation examines nitrification occurrence, control, and bulk water quality variations in the pilot distribution system.
2 LITERATURE REVIEW

Nitrification is a biological process that occurs in the natural environment. In the nitrogen cycle, it is responsible for the conversion of ammonia to nitrite and ultimately nitrate. Because of its effectiveness, the process has been utilized in water and wastewater treatment for years. However the uncontrolled presence of nitrification in drinking water systems is undesirable. This discussion reviews the theoretical aspects of nitrification, chloramines, and reports on selected case studies. Several references are made to a literature survey publication by AWWA (1995), a detailed compilation of nitrification occurrence and control in chloraminated water systems.

2.1 Theoretical Aspects of Nitrification in Chloraminated Water Systems

2.1.1 Nitrification Biology

Complete nitrification is a sequential two-step biological process carried out by chemoautotrophic bacteria. Nitrosomonas, considered the major ammonia oxidizing bacteria (AOB) is responsible for the conversion of ammonia to nitrite and will be represented by the following the stoichiometric reaction.

\[
5 NH_4^+ + 109 O_2 + 109 HCO_3^- \rightarrow C_5 H_7 O_2 N + 54 NO_2^- + 57 H_2 O + 10 H_2 CO_3
\]  

Equation 2.1
The inorganic carbon source in the proposed reaction is bicarbonate. Nitrobacter is the major nitrite oxidizing bacteria (NOB) and will be characterized by the following stoichiometric reaction.

\[ 10NO_2^- + NH_4^+ + 5CO_2 + 2H_2O \rightarrow C_2H_7O_2N + H^+ + 10NO_3^- \]  

Equation 2.2

In an aqueous closed system, uninhibited nitrification will change bulk water quality. Table 2-1 is an example of the effects AOB and NOB activity could have on associated parameters based on stoichiometry.

<table>
<thead>
<tr>
<th></th>
<th>NH₄</th>
<th>O₂</th>
<th>HCO₃</th>
<th>NO₂</th>
<th>H₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOB NH₄</td>
<td>↓</td>
<td>3.45</td>
<td>8.63</td>
<td>0.99</td>
<td>8.37</td>
</tr>
<tr>
<td>NOB NO₂</td>
<td>1</td>
<td>0.0025</td>
<td>0.044</td>
<td>0.011</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2-1: Stoichiometric Mass Change Due to Nitrification (mg/L)

Based on the stoichiometry of nitrification ammonia substrate, dissolved oxygen, inorganic carbon source must be present in order to nitrify. A certain environment is required for bacteria to proliferate. Environmental conditions include: temperature and pH.

Nitrification has been observed at temperatures between 5-30°C (Brazos et al., 1996), yet it is more commonly seen above 15°C (AWWA, 1995). Nitrification has occurred in systems within a wide pH range, 6.5-10, though the optimum range is 7.2-8.5 (AWWA, 1995).
2.1.2 Chloramine Chemistry

Chloramination has been implemented in the United States by many utilities since chloramines are less reactive than free chlorine and produce less disinfection-by-products (DBPs). Chloramines formed by the reaction of ammonia and chlorine, can produce three different compounds: monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (NCl₃).

\[
\begin{align*}
NH_3 + HOCl & \leftrightarrow NH_2Cl + H_2O & \text{Equation 2.3} \\
NH_3 + 2HOCl & \leftrightarrow NHCl_2 + 2H_2O & \text{Equation 2.4} \\
NH_3 + 3HOCl & \leftrightarrow NCl_3 + 3H_2O & \text{Equation 2.5}
\end{align*}
\]

The predominant chloramines species formed would depend on factors such as pH, temperature, contact time, and chlorine to ammonia ratio. Monochloramines are formed at a 1:1 molar ratio (Cl₂:NH₃), or 5:1 by weight and a pH of around 8.0. At higher chlorine to ammonia ratios and lower pHs, it is possible to obtain the other two species, but they are unstable and quickly decompose at pH values above 7.0. Organic chloramines could also be formed if organic nitrogen compounds are present in the water being chloraminated. Organic chloramines have a poor disinfection efficacy and may contribute to residual measurement thus overestimating the disinfection capacity in the water.

A problem with chloramines in drinking water systems is the introduction of ammonia. Free ammonia is present upon dosing and present in amounts depending on the dosing ratio of chlorine to ammonia. Monochloramines are an unstable product and decay releasing
ammonia (AWWA, 2003). The reduction of monochloramines by NOM produces 1 mole of free ammonia for each mole of monochloramine reduced. The auto decomposition of monochloramines releases 1 mole of ammonia for every 3 moles of monochloramine consumed. By comparison more ammonia is released during the oxidation of NOM suggesting the presence of higher concentrations of NOM may increase a distribution system’s nitrification potential (AWWA, 2003). The free ammonia becomes substrate for AOBs and can lead to the production of nitrite. The presence of nitrite may accelerate the destruction of residual. Nitrite is unstable and readily reacts with strong oxidants such as chlorine and monochloramine. The reaction of monochloramine with nitrite to produce nitrate is shown in Equation 2.6.

\[
\text{NH}_2\text{Cl} + \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NH}_4^+ + \text{Cl}^- \\
\text{Equation 2.6}
\]

For each 1 mg/L of NO\(_2\)-N, 5 mg/L of NH\(_2\)Cl as Cl\(_2\) is consumed. The chlorine demand by nitrites can lead to the rapid loss of residual and proliferation of bacteria. Once nitrifiers establish as biofilm, they are more resistant to disinfection by increased chloramine residual (AWWA, 1995). Nitrifiers are more resistant to chloramines than free chlorine. Nitrification episodes are often controlled by the application of free chlorine though the application of breakpoint chlorination. Breakpoint chlorination is the addition of excess chlorine to an ammonia containing water at a mass ratio of about 7.5:1 to completely oxidize ammonia to nitrogen gas.

\[
3\text{Cl}_2 + 2\text{NH}_3 \leftrightarrow \text{N}_2(g) + 6\text{HCl} \\
\text{Equation 2.7}
\]
Free chlorine residual can be established after all ammonia is oxidized along with any other chlorine demand. Chlorine dissipation rates in a drinking water system may vary. Typically rates are dependant on time, temperature, and organic content among other factors. These factors are related to a drinking water system through hydraulic retention time (HRT), seasonal temperature changes and fluctuations of organic content in source water. Common occurrences of dissipation in distribution systems due to HRT are dead ends or lower flows. Seasonal temperature increases of 5 to 10°C may double the dissipation rate. Organic content may directly react with chloramines or catalyze the decomposition increasing the rate of dissipation. Chloramines chemistry is also affected by pH. High pH (pH > 8.7) has been used to maintain residual and control nitrification in several utilities (Cates et al, 1999; Skadsen, 2002).

2.2 Nitrification in Drinking Water Systems

An estimated two-thirds of medium and large systems in the United States that chloraminate experience nitrification to some degree (AWWA, 1995). Methods of quantifying the bacteria responsible for nitrification are available and can be used to confirm its presence; though they typically are not used to monitor the extent of nitrification. Instead nitrification is usually detected and monitored through certain water quality parameters, which are commonly referred to as indicators (AWWA, 1995). Parameters that have been used as indicators and the trends expected during nitrification include: the loss of chloramine residual, an increase in heterotrophic plate counts (HPCs), the decrease in ammonia concentration, increase of nitrite and nitrate concentrations, and decreased dissolved oxygen (DO) concentration (AWWA, 1995, Wolfe et al, 1988). Other parameters can be considered
indicators such as pH, alkalinity and temperature, though correlations typically are not as strong as those previously mentioned (AWWA, 1995; Cates et al, 1999).

2.2.1 Chloramine Residual

Disinfectant residual monitoring is regulated by US EPA and must be monitored by all utilities. Because it is monitored so frequently it is often the first indication of nitrification in a system. Wolfe et al observed a 0.6 mg/L residual decrease from August 13 to 14th 1986 during a nitrification episode at the Orange County Reservoir. Residual loss and maintenance problems associated with nitrification have also been observed by Wolfe et al at the Garvey Reservoir, Negrin et al Los Angeles Department of Water and Power, by Skadsen et al at Ann Arbor Utilities Department, at the Philadelphia Water Department, and Broward County Environmental Services (AWWA, 1995).

There is some question about whether nitrification began and caused the chloramine residual to drop or, as may be more likely, whether the chloramine residual dropped in the system and allowed nitrification to occur (AWWA, 1995).

2.2.2 HPC Trends

Nitrifiers are autotrophs and are not directly measured by HPCs though many findings have noted a large increase in HPCs during nitrification. Possible explanation for this occurrence is the nitrifiers become primary producers. Autotrophs die, becoming substrate for heterotrophs and in areas of low disinfectant residual the bacteria can proliferate.
Elevated HPCs has been observed in many systems, but amounts varied widely. HPC may be a fairly good indicator of nitrification occurrence, but interpretation is required (AWWA, 1995)

2.2.3 Temperature Correlations

Temperature has a strong influence on nitrification. Temperature affects the growth rate and biological activity of nitrifiers. The optimum temperature for nitrification is 25-30 °C (AWWA, 1995). Most nitrification episodes occur during the summer (AWWA, 1995, 2003). The impact of temperature on biological activity and ammonia removal in biologically activated carbon filters was studied by Andersson et al, 2001. Equation 2.8 and Equation 2.9 show the increasing relationship between temperature and ammonia removal.

\[ V_{T1} = V_{T2} \exp(k(T_1 - T_2)) \]  
Equation 2.8

\[ \text{Ln(ammonia removal)} = 0.058T + 3.161 \]  
Equation 2.9

During the study, the effect of drastic temperature changes on rates and biomass concentrations were evaluated. As temperature decreased, 16 to 3 °C, biological activity decreased resulting in ammonia removal reduction from 90% to 10%. The biomass concentrations were not significantly affected. When the temperature increased quickly after three weeks of cold temperatures the biological activity and ammonia removal rates returned to high removal (Andersson et al, 2001).
2.2.4 Nitrogen Trends

A nitrogen balance is a useful tool in understanding nitrification episodes in drinking water systems. Components of the balance include chloramine nitrogen, ammonia, organic nitrogen, nitrite and nitrate. Theoretically ammonia levels decrease and nitrite and nitrate increase. The ammonia decrease is not always observable in distribution systems (AWWA, 1995). Ammonia feed systems and sampling has been suspected as sources of variation. At Ann Arbor ammonia correlations with other parameter were not significant, although ammonia concentrations did approach zero at the location in the distribution system where maximum nitrite levels were observed (Skadsen, 1993). In laboratory studies the decreasing ammonia trend during nitrification has been consistently observed (AWWA, 1995).

The sum of all the components is the total nitrogen. The total nitrogen in a closed system should not change. However, a small amount of nitrogen gas may be lost due to chloramine auto decomposition (AWWA, 2003). Significant conversion to nitrogen gas would occur during microbial denitrification, but requires an anoxic environment which is not typical in drinking water systems. If the system were open, total nitrogen may decrease as free ammonia was lost to the atmosphere, especially at pH > pK = 9.3 (AWWA, 2003).
2.2.5 Dissolved Oxygen Trends

According to theory, dissolved oxygen decreases with nitrification. The decrease in dissolved has been observed in many nitrification episodes (AWWA, 1995). Dissolved oxygen appears to be a good indicator of nitrification.

2.2.6 pH Changes

According to theory, pH should decrease with nitrification. Few systems noted pH trends with nitrification. pH changes are not a good indicator of nitrification (AWWA, 1995).

2.2.7 Alkalinity Changes

According to theory, alkalinity decreases with nitrification. Alkalinity changes in water systems are not a good indicator of nitrification. This may be due to the distribution impacts on nitrification, through the deposition as CaCO₃, or the dissolution of scales and cement linings (AWWA, 1995).
3 METHODOLOGY

The project’s experimental system was setup to vary the source water provided to 18 pilot distribution systems (PDS) composed either of PVC, cast iron lined, cast iron, or galvanized iron material and monitor the water quality changes. The pilot distribution system (PDS) consists of 18 parallel operating lines. There were 14 hybrid lines and 4 single material lines. The hybrid lines had a total length of 90 ft and were composed of 20 ft of 6in diameter PVC, 20 ft of 6 inch diameter cast iron lined, 12 ft of 6 inch diameter cast iron and 40 ft of 2 inch diameter galvanized. The single material lines had a total length of 90 ft except for 2 inch galvanized material, which had a total length of 140 ft. There were seven different treated waters used as sources to the PDSs shown in Table 3-1

<table>
<thead>
<tr>
<th>Source</th>
<th>Type</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>Groundwater</td>
<td>Conventional</td>
</tr>
<tr>
<td>G2</td>
<td>Groundwater</td>
<td>Softening</td>
</tr>
<tr>
<td>G3</td>
<td>Blend</td>
<td>Softening</td>
</tr>
<tr>
<td>G4</td>
<td>Blend</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>S1</td>
<td>Surface</td>
<td>Coagulation, Ozonation, BAC</td>
</tr>
<tr>
<td>S2</td>
<td>Surface</td>
<td>Coagulated, Nanofiltration</td>
</tr>
<tr>
<td>RO</td>
<td>Seawater</td>
<td>Reverse Osmosis</td>
</tr>
</tbody>
</table>

*Primary disinfection with free chlorine and final disinfectant for all waters.

The operating lines received a blend of the seven different source waters. The source waters supplied to the PDSs were varied over the course of one year. The source waters were stored in plastic white opaque tanks and the chloramine residual was maintained at 4.0 mg/L.
as Cl₂. The frequency of modification of the blends was once every three months, or phase, with the exception of the high frequency line (PDS14) that experienced a change in blend twice per day. Blends of the primary waters G1, S1, and RO were supplied in different ratios to the PDSs in four consecutive phases. The Phases were as follows: Phase I December 2001 – March 2002, Phase II March 2002 – June 2002, Phase III June 2002 – September 2002, Phase IV September 2002 – December 2002. G3 and G4 were treated blends at ratios of 45% G1, 32% S1, and 23% in Phases I and III and 60% G1, 30% S1, and 10% RO in Phases II and IV. The PDSs received 100% of source water or a blend of the source waters throughout a phase as shown in Table 3-2.

Table 3-2: PDS Material and Source Water

<table>
<thead>
<tr>
<th>PDS ID</th>
<th>Materials</th>
<th>Phases I and III</th>
<th>Phases II and IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDS01</td>
<td>Hybrid</td>
<td>G1 (100)</td>
<td>G2 (100)</td>
</tr>
<tr>
<td>PDS02</td>
<td>Hybrid</td>
<td>G2 (100)</td>
<td>G1 (100)</td>
</tr>
<tr>
<td>PDS03</td>
<td>Hybrid</td>
<td>S1 (100)</td>
<td>S2 (100)</td>
</tr>
<tr>
<td>PDS04</td>
<td>Hybrid</td>
<td>G4 (100)</td>
<td>G3 (100)</td>
</tr>
<tr>
<td>PDS05</td>
<td>Hybrid</td>
<td>RO (100)</td>
<td>S1 (100)</td>
</tr>
<tr>
<td>PDS06</td>
<td>Hybrid</td>
<td>G1 (55), S1 (45)</td>
<td>G1 (68), RO (32)</td>
</tr>
<tr>
<td>PDS07</td>
<td>Hybrid</td>
<td>G1 (68), RO (32)</td>
<td>G1 (55), S1 (45)</td>
</tr>
<tr>
<td>PDS08</td>
<td>Hybrid</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S2 (30), RO (10)</td>
</tr>
<tr>
<td>PDS09</td>
<td>Hybrid</td>
<td>G1 (60), S2 (30), RO (10)</td>
<td>G1 (23), S1 (45), RO (32)</td>
</tr>
<tr>
<td>PDS10</td>
<td>Hybrid</td>
<td>G2 (50), S1 (50)</td>
<td>G2 (62), S1 (24), RO (14)</td>
</tr>
<tr>
<td>PDS11</td>
<td>Hybrid</td>
<td>G2 (62), S1 (24), RO (14)</td>
<td>G2 (50), S1 (50)</td>
</tr>
<tr>
<td>PDS12</td>
<td>Hybrid</td>
<td>G3 (100)</td>
<td>G4 (100)</td>
</tr>
<tr>
<td>PDS13</td>
<td>Hybrid</td>
<td>S2 (100)</td>
<td>RO (100)</td>
</tr>
<tr>
<td>PDS14</td>
<td>Hybrid</td>
<td>G1, S1, RO(% varied daily)</td>
<td>G1, S1, RO (% varied daily)</td>
</tr>
<tr>
<td>PDS15</td>
<td>Unlined Cast Iron</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S1 (30), RO (10)</td>
</tr>
<tr>
<td>PDS16</td>
<td>Lined Cast Iron</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S1 (30), RO (10)</td>
</tr>
<tr>
<td>PDS17</td>
<td>PVC</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S1 (30), RO (10)</td>
</tr>
<tr>
<td>PDS18</td>
<td>Galvanized</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S1 (30), RO (10)</td>
</tr>
</tbody>
</table>
The pilot distribution system was operated at flow rates to achieve a hydraulic residence time of five days. Due to the limited length of the pipe (PDS lines range from approximately 90 to 140 feet), the experienced velocities were almost zero. A flushing event was included in PDS operation to simulate representative velocities that would be experienced in a full-scale operating system. The flushing operation was completed on a weekly cycle. Appropriate quantities of the different source waters were used to flush each PDS. The flow rate during the flush cycle was selected to achieve a velocity of approximately 1.0 ft/sec. The duration of the flush cycle was regulated to pass a volume equal to five pipe volumes. The final disinfectant for all waters was monochloramines. Typical water quality for source waters is shown in Table 3-3.
### Table 3-3: Typical Source Water Qualities for Phase 1-4

<table>
<thead>
<tr>
<th>Source</th>
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Routine water quality monitoring included field laboratory and laboratory analysis. Monitoring included analysis of source waters, PDS influent, PDS internal ports, and PDS effluent. A collection of nitrification indicators was selected to monitor nitrification. The water quality analyses methods used in the field lab and UCF lab are shown in Table 3-4.

Table 3-4: Water Quality Analysis Methods

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4 WATER QUALITY VARIATIONS DURING NITRIFICATION IN DRINKING WATER DISTRIBUTION SYSTEMS

4.1 Introduction

Nitrification is undesirable in drinking water distribution systems due to adverse health and aesthetic effects on consumers. Some of those effects include a destruction of residual, increased HPCs, increased nitrite and nitrate concentrations, decreased dissolved oxygen, decreased pH, decreased alkalinity and corrosion (AwwaRF, 1995). Flushing, residual boosting, free chlorine burns and monitoring of nitrites and nitrates are practiced by utilities to control nitrification in distribution systems. Although the general mechanisms of nitrification are known, the interrelationships of key water quality parameters to nitrification need further study. The objective of this work is to identify and discuss the changes and interrelationships among the physical, chemical and water quality parameters before, during and after a nitrification episode in several pilot distribution systems (PDSs). The PDSs were a key component in the Tampa Bay Water (TBW) AwwaRF tailored collaboration project “Required Treatment and Water Quality Criteria for Distribution System Blending of Treated Surface, Ground and Saline Sources” project.
4.2 Literature Review

Biological nitrification in drinking water systems is a sequential two step process. A reduced form of nitrogen must be available for the oxidizing bacteria to biochemically form nitrites and nitrates. Ammonia is considered to be the primary nitrogen source and *Nitrosomonas* bacteria are considered as the primary ammonia oxidizing bacteria (AOB). *Nitrosomonas* bacteria are responsible for the conversion of ammonia to nitrite and is represented Equation 4.1. *Nitrobacter* is the major nitrite oxidizing bacteria (NOB) and is represented by Equation 4.2. The two equations combined represent complete biochemical nitrification. During the intermediate step of biochemical nitrification, nitrites can also react chemically with chloramines as shown in Equation 4.3. The stoichiometric change of water quality parameters involved in the biochemical nitrification reaction is shown in Table 4-1.

\[
55NH_4^+ + 76O_2 + 109HCO_3^- \rightarrow C_4H_7O_2N + 54NO_2^- + 57H_2O + 104H_2CO_3^- \quad \text{Equation 4.1}
\]

\[
10NO_2^- + NH_4^+ + 5CO_2 + 2H_2O \rightarrow C_4H_7O_2N + H^+ + 10NO_3^- \quad \text{Equation 4.2}
\]

\[
NH_4^+ + 1.98HCO_3^- + 1.86O_2 \rightarrow 0.021C_4H_7O_2N + 1.04H_2O + 0.98NO_3^- + 1.88H_2CO_3^- \quad \text{Equation 4.3}
\]

\[
NH_2Cl + NO_2^- + H_2O \rightarrow NO_3^- + NH_4^+ + Cl^- \quad \text{Equation 4.4}
\]
Table 4-1: Stoichiometric Mass Change Due to Nitrification (mg/L)

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</tbody>
</table>

Assuming there is no ammonia in the source water and ammonia is only added to form chloramines, then there are only two sources of ammonia in the distribution system. Ammonia is available from (1) excess ammonia used in the formation of chloramines and (2) the dissipation of chloramines in the distribution system. Based on the simplified formation reaction for chloramines shown in Equation 4.5, very little excess ammonia will remain when a 5/1 chlorine to ammonia-nitrogen ratio (Cl₂/NH₃-N) is used for chloramine formation.

Assuming most utilities would form 4 mg/L NH₂Cl as Cl₂, Cl₂/NH₃-N ratios of 4/1 and 3/1 would result in remaining or excess NH₃-N of approximately 0.3 and 0.7 mg/L NH₃-N.

However the degradation reaction with water or anything as shown in Equation 4.6 will result in approximately 1 mg/L NH₃-N. Hence, any use of chloramines as a residual provides NH₃-N as an energy source for nitrification. Low chloramines residuals and difficulty maintaining residuals are associated with nitrification episodes.

$$\text{NH}_3 + \text{Cl}_2 = \text{NH}_2\text{Cl} + \text{HCl}$$  \hspace{1cm} Equation 4.5
\[2\text{NH}_2\text{Cl} + 2\text{H}_2\text{O} = 2\text{NH}_3 + 2\text{HCl} + \text{O}_2\]  

Equation 4.6

### 4.3 Methods and Materials

Finished water was produced by seven different pilot plants as shown in Table 4-2. These waters were produced to simulate actual water production from surface, ground and sea water by existing and state of the art treatment processes. The finished waters were blended to simulate the variation in finished water quality that would be experienced in the distribution systems of the various member governments receiving these waters. All finished waters were stabilized, disinfected with free chlorine or ozone and chloraminated before blending.

The blended finished waters were provided to 18 pilot distribution systems (PDS) composed either of PVC, cast iron lined, cast iron, or galvanized iron material and monitor the water quality changes. The pilot distribution system (PDS) consists of 18 parallel operating lines. There were 14 hybrid lines and 4 single material lines. The hybrid lines had a total length of 90 ft and were composed of 20 ft of 6 inch diameter PVC, 20 ft of 6 inch diameter cast iron lined, 12 ft of 6 inch diameter cast iron and 40 ft of 2 inch diameter galvanized. The single material lines had a total length of 90 ft except for 2 inch galvanized material, which had a total length of 140 ft. The pilot systems and PDSs were operated from December 2001 to December 2002 in the study. Blends of finished waters to each PDS were varied in three month increments following a ninety day equilibration period. The same blending sequence for the first six months was repeated the following six months to study the
effects of changing water quality and season. The PDSs received 100% of source water or a
blend of the source waters throughout a phase as shown in Table 4-2.

Table 4-2: Source Water and Treatment Identification

<table>
<thead>
<tr>
<th>Source Type</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>Groundwater Conventional</td>
</tr>
<tr>
<td>G2</td>
<td>Groundwater Softening</td>
</tr>
<tr>
<td>G3</td>
<td>Blend Softening</td>
</tr>
<tr>
<td>G4</td>
<td>Blend Nanofiltration</td>
</tr>
<tr>
<td>S1</td>
<td>Surface Coagulation, Ozonation, BAC</td>
</tr>
<tr>
<td>S2</td>
<td>Surface Coagulated, Nanofiltration</td>
</tr>
<tr>
<td>RO</td>
<td>Seawater Reverse Osmosis</td>
</tr>
</tbody>
</table>

*Primary disinfection with free chlorine and final disinfectant for all waters.

Table 4-3: PDS Material and Source Water

<table>
<thead>
<tr>
<th>PDS ID</th>
<th>Materials</th>
<th>Phases I and III</th>
<th>Phases II and IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDS01</td>
<td>Hybrid</td>
<td>G1 (100)</td>
<td>G2 (100)</td>
</tr>
<tr>
<td>PDS02</td>
<td>Hybrid</td>
<td>G2 (100)</td>
<td>G1 (100)</td>
</tr>
<tr>
<td>PDS03</td>
<td>Hybrid</td>
<td>S1 (100)</td>
<td>S2 (100)</td>
</tr>
<tr>
<td>PDS04</td>
<td>Hybrid</td>
<td>G4 (100)</td>
<td>G3 (100)</td>
</tr>
<tr>
<td>PDS05</td>
<td>Hybrid</td>
<td>RO (100)</td>
<td>S1 (100)</td>
</tr>
<tr>
<td>PDS06</td>
<td>Hybrid</td>
<td>G1 (55), S1 (45)</td>
<td>G1 (68), RO (32)</td>
</tr>
<tr>
<td>PDS07</td>
<td>Hybrid</td>
<td>G1 (68), RO (32)</td>
<td>G1 (55), S1 (45)</td>
</tr>
<tr>
<td>PDS08</td>
<td>Hybrid</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S2 (30), RO (10)</td>
</tr>
<tr>
<td>PDS09</td>
<td>Hybrid</td>
<td>G1 (60), S2 (30), RO (10)</td>
<td>G1 (23), S1 (45), RO (32)</td>
</tr>
<tr>
<td>PDS10</td>
<td>Hybrid</td>
<td>G2 (50), S1 (50)</td>
<td>G2 (62), S1 (24), RO (14)</td>
</tr>
<tr>
<td>PDS11</td>
<td>Hybrid</td>
<td>G2 (62), S1 (24), RO (14)</td>
<td>G2 (50), S1 (50)</td>
</tr>
<tr>
<td>PDS12</td>
<td>Hybrid</td>
<td>G3 (100)</td>
<td>G4 (100)</td>
</tr>
<tr>
<td>PDS13</td>
<td>Hybrid</td>
<td>S2 (100)</td>
<td>RO (100)</td>
</tr>
<tr>
<td>PDS14</td>
<td>Hybrid</td>
<td>G1, S1, RO (% varied daily)</td>
<td>G1, S1, RO (% varied daily)</td>
</tr>
<tr>
<td>PDS15</td>
<td>Unlined Cast Iron</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S1 (30), RO (10)</td>
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<tr>
<td>PDS16</td>
<td>Lined Cast Iron</td>
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<td>G1 (60), S1 (30), RO (10)</td>
</tr>
<tr>
<td>PDS17</td>
<td>PVC</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S1 (30), RO (10)</td>
</tr>
<tr>
<td>PDS18</td>
<td>Galvanized</td>
<td>G1 (23), S1 (45), RO (32)</td>
<td>G1 (60), S1 (30), RO (10)</td>
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</tbody>
</table>
The PDS hydraulic residence time (HRT) was five and two days. PDS velocity was low and representative of near dead-end conditions. PDS flushing occurred weekly and consisted of five pipe volumes of finished water at 1 ft/sec. Typical water quality for the source waters is shown in Table 4-4.
## Table 4-4: Typical Source Water Qualities for Phase 1-4

<table>
<thead>
<tr>
<th>Source</th>
<th>Free as Cl₂ mg/L N</th>
<th>pH</th>
<th>PH₅</th>
<th>Ca⁰⁺</th>
<th>Mg⁰⁺</th>
<th>UV-254 cm⁻¹</th>
<th>Color</th>
<th>Turbidity NTU</th>
<th>D.O. mg/L</th>
<th>Conductivity mS/cm</th>
<th>TDS mg/L</th>
<th>Cl⁻ mg/L</th>
<th>SO₄²⁻ mg/L</th>
<th>Iron mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.1 3.9</td>
<td>8.1</td>
<td>7.2</td>
<td>194</td>
<td>211</td>
<td>245 34</td>
<td>0.073</td>
<td>5</td>
<td>0.5</td>
<td>8.2</td>
<td>485</td>
<td>323</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>G2</td>
<td>0.2 4.4</td>
<td>8.2</td>
<td>7.8</td>
<td>95</td>
<td>85</td>
<td>117 32</td>
<td>0.067</td>
<td>4</td>
<td>0.4</td>
<td>8.6</td>
<td>266</td>
<td>177</td>
<td>19</td>
<td>0.0</td>
</tr>
<tr>
<td>G3</td>
<td>0.2 3.7</td>
<td>8.3</td>
<td>8.0</td>
<td>51</td>
<td>111</td>
<td>136 25</td>
<td>0.069</td>
<td>2</td>
<td>0.7</td>
<td>9.7</td>
<td>423</td>
<td>282</td>
<td>17</td>
<td>0.0</td>
</tr>
<tr>
<td>G4</td>
<td>0.1 3.7</td>
<td>8.2</td>
<td>8.1</td>
<td>65</td>
<td>68</td>
<td>78 10</td>
<td>0.028</td>
<td>0</td>
<td>0.2</td>
<td>9.2</td>
<td>291</td>
<td>193</td>
<td>18</td>
<td>0.0</td>
</tr>
<tr>
<td>S1</td>
<td>0.1 4.1</td>
<td>8.0</td>
<td>7.7</td>
<td>59</td>
<td>204</td>
<td>241 36</td>
<td>0.027</td>
<td>1</td>
<td>0.2</td>
<td>13.0</td>
<td>551</td>
<td>368</td>
<td>18</td>
<td>0.0</td>
</tr>
<tr>
<td>S2</td>
<td>0.2 4.3</td>
<td>8.2</td>
<td>8.1</td>
<td>68</td>
<td>60</td>
<td>71 11</td>
<td>0.025</td>
<td>2</td>
<td>0.3</td>
<td>9.2</td>
<td>308</td>
<td>204</td>
<td>18</td>
<td>0.1</td>
</tr>
<tr>
<td>RO</td>
<td>0.1 4.2</td>
<td>8.2</td>
<td>8.1</td>
<td>66</td>
<td>61</td>
<td>69 8</td>
<td>0.019</td>
<td>0</td>
<td>0.2</td>
<td>8.7</td>
<td>400</td>
<td>265</td>
<td>21</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Phase I**

| G1     | 0.1 4.9             | 7.9 | 7.1 | 211  | 214  | 246 32       | 0.077 | 4           | 0.4       | 7.1                 | 520      | 346       | 24        | 25.4     | 28       |
| G2     | 0.1 4.9             | 7.9 | 7.8 | 97   | 93   | 126 33       | 0.067 | 1           | 0.1       | 7.5                 | 305      | 203       | 25        | 30.6     | 29       |
| G3     | 0.1 4.5             | 8.2 | 8.1 | 51   | 94   | 124 30       | 0.050 | 0           | 0.2       | 8.5                 | 389      | 258       | 24        | 30.6     | 29       |
| G4     | 0.1 4.7             | 8.2 | 7.7 | 106  | 96   | 113 16       | 0.029 | 0           | 0.1       | 8.1                 | 323      | 215       | 25        | 30.6     | 29       |
| S1     | 0.1 4.5             | 8.0 | 7.8 | 55   | 195  | 230 36       | 0.025 | 0           | 0.2       | 9.1                 | 633      | 420       | 24        | 39.2     | 217      |
| S2     | 0.2 4.7             | 8.2 | 8.1 | 65   | 61   | 66 5         | 0.028 | 1           | 0.2       | 7.8                 | 339      | 225       | 25        | 59.7     | 15       |
| RO     | 0.2 4.5             | 8.3 | 8.1 | 61   | 66   | 72 6         | 0.022 | 0           | 0.2       | 7.9                 | 398      | 265       | 25        | 80.7     | 4        |

**Phase II**

| G1     | 0.1 5.2             | 0.2 | 7.8 | 7.1 | 214  | 215 246 31  | 0.072 | 4           | 0.4       | 7.2                 | 539      | 359       | 25        | 30.6     | 29       |
| G2     | 0.2 5.0             | 0.2 | 8.0 | 7.9 | 88   | 81   119 38  | 0.065 | 1           | 0.2       | 7.5                 | 302      | 200       | 26        | 30.6     | 29       |
| G3     | 0.1 5.0             | 0.3 | 8.0 | 8.0 | 66   | 94   117 23  | 0.046 | 0           | 0.1       | 8.0                 | 464      | 307       | 26        | 30.6     | 29       |
| G4     | 0.1 5.1             | 0.3 | 8.1 | 8.1 | 77   | 58   71 13   | 0.032 | 0           | 0.1       | 7.7                 | 313      | 208       | 26        | 30.6     | 29       |
| S1     | 0.1 4.8             | 0.4 | 8.1 | 7.9 | 61   | 131 156 25  | 0.033 | 1           | 0.4       | 8.3                 | 580      | 386       | 26        | 31.1     | 163      |
| S2     | 0.2 5.7             | 0.2 | 8.3 | 8.1 | 66   | 62   68 6    | 0.035 | 0           | 0.2       | 7.7                 | 387      | 257       | 27        | 65.4     | 11       |
| RO     | 0.1 5.0             | 0.3 | 8.2 | 8.1 | 68   | 64   71 7    | 0.025 | 0           | 0.1       | 7.9                 | 414      | 275       | 25        | 80.7     | 2        |

**Phase III**

| G1     | 0.2 4.8             | 0.2 | 7.9 | 7.1 | 212  | 213 244 31  | 0.075 | 6           | 0.4       | 7.6                 | 528      | 351       | 23        | 24.4     | 31       |
| G2     | 0.1 4.9             | 0.2 | 8.0 | 7.8 | 93   | 93   122 30  | 0.063 | 1           | 0.2       | 7.6                 | 299      | 199       | 23        | 24.4     | 31       |
| G3     | 0.1 4.9             | 0.3 | 7.9 | 7.8 | 85   | 95   118 23  | 0.063 | 0           | 0.1       | 8.5                 | 430      | 287       | 23        | 24.4     | 31       |
| G4     | 0.1 5.0             | 0.2 | 8.2 | 7.8 | 103  | 91   92 12   | 0.036 | 0           | 0.1       | 8.5                 | 317      | 211       | 22        | 24.4     | 31       |
| S1     | 0.1 4.8             | 0.1 | 8.3 | 8.1 | 59   | 89   102 14  | 0.067 | 1           | 0.6       | 9.1                 | 517      | 345       | 23        | 27.7     | 142      |
| S2     | 0.2 5.4             | 0.1 | 8.6 | 8.1 | 69   | 64   70 6    | 0.033 | 0           | 0.2       | 8.3                 | 402      | 269       | 23        | 72.1     | 8        |
| RO     | 0.2 4.8             | 0.2 | 8.4 | 8.1 | 67   | 64   70 6    | 0.023 | 0           | 0.2       | 8.3                 | 419      | 283       | 23        | 78.9     | 2        |
Process and PDS water quality was routinely monitored in the field and laboratory.

Table 4-5: Water Quality Analyses by Location and Method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>Field</td>
<td>SM 2320 B</td>
</tr>
<tr>
<td>Ammonia-N</td>
<td>Field</td>
<td>SM 4500-NH3 C</td>
</tr>
<tr>
<td>Chlorine, free</td>
<td>Field</td>
<td>SM 4500-Cl G or Hach 8021</td>
</tr>
<tr>
<td>Chlorine, total</td>
<td>Field</td>
<td>SM 4500-Cl-G or Hach 8167</td>
</tr>
<tr>
<td>Hardness (total, calcium)</td>
<td>Field</td>
<td>SM 2340 C</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Field</td>
<td>Hach 8192</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Field</td>
<td>Hach 8507</td>
</tr>
<tr>
<td>Oxygen, dissolved (DO)</td>
<td>Field</td>
<td>SM 4500-O G</td>
</tr>
<tr>
<td>pH</td>
<td>Field</td>
<td>SM 4500-H B</td>
</tr>
<tr>
<td>Phosphate, ortho</td>
<td>Field</td>
<td>SM 4500-P E</td>
</tr>
<tr>
<td>Temperature</td>
<td>Field</td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>Field</td>
<td>SM 2130 B</td>
</tr>
<tr>
<td>TKN-Nitrogen-(trivalent)</td>
<td>UCF</td>
<td>SM 4500-Norg Macro-Kjeldahl Method</td>
</tr>
<tr>
<td>Coliforms (Fecal, Total)</td>
<td>UCF</td>
<td>SM Membrane Filtration Technique</td>
</tr>
<tr>
<td>HPC</td>
<td>UCF</td>
<td>SM 9215B Pour Plate Method</td>
</tr>
</tbody>
</table>


Hach = DR4000 Spectrometer Method Handbook
4.4 Results and Discussion

4.4.1 Occurrence

Nitrification occurred in several PDSs. The water quality changes in PDS 15, a pure material line made using cast iron pipe, are used to represent the changes during nitrification throughout all PDSs. As shown in Figure 4.1, the PDS effluent temperature increased from 10°C to 30°C from the beginning of January 2003 to the beginning of May 2003. During this period the feed stream NH$_2$Cl was practically constant at approximately 4 mg/L as Cl$_2$. The effluent NH$_2$Cl residual decreased from approximately 2 mg/L as Cl$_2$ to zero. Although the HPC data is limited, the corresponding HPCs increased by approximately four orders of magnitude. The D.O. also decreased from approximately 8 mg/L as O$_2$ to 2 mg/L as O$_2$. These events occurred simultaneously and would be expected of a system that was experiencing aerobic bacterial growth with no restrictions on food sources or D.O. The PDSs were initially operated with a 5 day HRT, 4.0 mg/L NH$_2$Cl as Cl$_2$ at 4.5:1, Cl$_2$/N ratio, and biweekly PDS flushing. At a Cl$_2$/N ratio of 4.5:1, there was initially a 0.1 mg/L of excess NH$_3$-N in the PDS feed stream. However there was no indication of excessive HPC growth until mid March when the NH$_2$Cl residual was essentially lost.
Figure 4.1: Monochloramine Residual Degradation in PDS 15
After the chloramine residual was lost in PDS 15, nitrite and nitrate concentrations increased as shown in Figure 4.2.

Figure 4.2: PDS 15 Nitrite and Nitrate versus Time

Effluent ammonia decreased from greater than 1.5 mg/L before nitrification, to less than 0.5 mg/L N after nitrification shown in Figure 4.3.
Nitrification was not specific to any source water in the PDSs nor was any source water protected from nitrification. TKNs in PDSs 1 thru 18 from March to June 2002 are shown in Figure 4.4. TKNs were the primary method of measuring ammonia and organic nitrogen. There was no change from influent to effluent TKNs in any of the PDSs in March 2002. There was a decrease in effluent TKNs in 16 of the 18 PDSs in June 2002, which was due to the conversion of ammonia to nitrites and nitrates by nitrification. The finished waters were either unblended or blended combinations of the seven sources and as shown in Figure 4.4, there was no difference among source waters. As shown in Figure 4.5, the TKN loss was proportionally distributed by blend and is shown to increase linearly with blend percentage although there is some variation.
among the data. Figure 4.5 also indicates no difference in nitrification among sources. The reason for the lack of difference among processes for nitrification is the ammonia for nitrification came from the chloramine dose which was constant among processes. The blend of source waters by PDS is shown Table 4-3, and the feed stream water quality of each PDS is shown in Table 4-4.

Figure 4.4: PDS TKN Before and After Nitrification
4.4.2 Incremental PDS Sampling During Nitrification

After nitrification was confirmed in the PDSs, incremental port sampling of nitrate, nitrite, ammonia-N, alkalinity, pH, D.O. and temperature was conducted to determine the change of these key water quality variables during nitrification. These parameters were selected because of the expected changes from biochemical reactions during the nitrification process. PDSs that continued to experience nitrification after residual and HRT changes were selected for the study. Samples were taken from influent, internal, and effluent ports from the selected PDSs.
The nitrogen species, chloramines N, ammonia N, nitrate N, and nitrite N varied through the PDSs as shown for PDS 15 in Figure 4.6. Points on the graph represent values at sample ports and lines are drawn to simulate actual water quality trends. Monochloramine residual decreased from 4.2 to 1.8 mg/L as Cl\textsubscript{2}, and nitrite and nitrate concentrations remained below 0.1 mg/L as N from 0 to 19 hours. During this period ammonia nitrogen increased to 0.5 mg/L NH\textsubscript{3}-N due to chloramine degradation. Nitrites and nitrates concentration increased to more than 0.1 mg/L NO\textsubscript{3}-N from 20 to 30 hours, which marked the onset of nitrification. During this period, free ammonia increased less than 0.1 mg/L NH\textsubscript{3}-N, much less than the increase of 0.3 mg/L NH\textsubscript{3}-N during the initial 19 hours. As monochloramine residuals continued to decrease the rate of nitrification increased and free ammonia was oxidized to nitrites and nitrates. The average nitrogen balance recovery for observations in the incremental study on PDS 15 was 96.7% with a standard deviation of 9.4%.
The variations of related parameters with nitrification are shown for PDS 15 in the following figures. Dissolved oxygen decreased from 7.8 to 3.3 mg/L O$_2$ in PDS 15 as shown in Figure 4.7.
Figure 4.7: PDS 15 Dissolved Oxygen (10/25/02)

Consistent decreasing trends of pH and alkalinity were not observed during nitrification shown in Figure 4.8 and Figure 4.9.
Figure 4.8: PDS 15 pH (10/25/02)
Figure 4.9: PDS 15 Alkalinity (10/25/02)

Nitrate and nitrite levels were plotted versus temperature in an attempt to develop a correlation. There is an obvious increasing trend between temperature and nitrite and nitrate shown in Figure 4.10.
To explain the water quality changes seen in PDS 15, biological nitrification was considered to be the primary source of nitrates and nitrates and a comparison was made between actual and theoretical water quality variations due to nitrification. Theoretical water quality changes based on biological reactions were calculated and compared to observed water quality changes in PDS 15 in Table 4-6. The comparison illustrates the difference between theoretical and actual water quality changes. Actual nitrite and nitrate concentrations were used to determine the expected theoretical change in HCO$_3^-$, pH, O$_2$, and NH$_3$-N based on Equation 4.1 and Equation 4.3 stoichiometry. To determine the expected theoretical water quality at a
specific HRT the theoretical parameter change was added (production) or subtracted (consumption) to the feed stream water quality. An additional adjustment was made for free ammonia. Assuming all nitrogen released from monochloramine degradation is available as free ammonia, released ammonia was added to the theoretical ammonia calculation.

Table 4-6: Theoretical and Actual Water Quality Associated with Biochemical Nitrification in PDS 15 (mg/L)

<table>
<thead>
<tr>
<th>HRT</th>
<th>ID</th>
<th>NH₃Cl-N</th>
<th>NH₃-N</th>
<th>O₂</th>
<th>HCO₃ as CaCO₃</th>
<th>NO₂-N</th>
<th>NO₃-N</th>
<th>pH</th>
<th>ΣN</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>Actual</td>
<td>0.85</td>
<td>0.26</td>
<td>7.8</td>
<td>154</td>
<td>0</td>
<td>0.00</td>
<td>7.71</td>
<td>1.11</td>
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<tr>
<td>6</td>
<td>Actual</td>
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<td>0.37</td>
<td>7.2</td>
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<td>0.01</td>
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<td>7.69</td>
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<tr>
<td></td>
<td>Difference</td>
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<td>-0.18</td>
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The theoretical and actual values are not equal, however some observations can be made. Actual and theoretical ammonia increase as chloramines degrade for the initial 31 hrs, and decrease after 31 hrs as the rate of nitrite and nitrate production becomes greater than the rate of monochloramine degradation and corresponding ammonia release. Hence ammonia is an intermediate product during nitrification when chloramines are used for residual maintenance.
There is increasing oxygen demand throughout the PDS for each observation to 31 hrs, which is probably due to utilization of DO by aerobic microorganisms. The difference between the actual and expected DO concentrations also increases during this period. More oxygen is consumed than required by the nitrification reactions. After 31 hrs the differences decrease, indicating actual oxygen demand is not increasing at the same rate biological nitrification increases. The conversion of nitrites to nitrates by monochloramines would contribute to this effect by reducing the actual oxygen demand. The production of 0.60 and 0.27 nitrates and nitrites should reduce bicarbonate alkalinity from 154 to 148 as mg/L as CaCO\(_3\) and pH from 7.71 to 7.39 according to theory. Actual alkalinity and pH decreased but less than and was less consistent than expected.

Nitrogen was summed in the last column and represents the sum of monochloramine, ammonia, nitrite and nitrate nitrogen for each increment through PDS 15. The N balance for each HRT is reasonable ranging from 0.87 to 1.21 mg/L N. Influent and effluent total nitrogen were 1.11 mg/L and 1.21 mg/L N. The data in Table 4-6 shows the variation of NH\(_2\)Cl-N, NH\(_3\)-N, DO and pH with NO\(_2\)-N and NO\(_3\)-N formation generally followed the variations predicted by microbiological nitrification reactions as shown in Equation 4.1 and Equation 4.3. The variation of alkalinity during nitrification was less than predicted by microbiological nitrification.

**4.4.3 Control of Nitrification**

A series of steps were taken to control nitrification. Beginning on June 13, 2002 the monochloramine residual in all PDS feed streams was increased to 4.5 mg/L as Cl\(_2\) and the
Cl₂:NH₃-N ratio was increased to 5:1. These steps increased residual and reduced the initial and final available NH₃. Effluent NH₂Cl residuals remained at zero with little effect on nitrification from June 13 2002 to August 30 2002 as shown in Figure 4.1. On August 30 2002, the PDS HRT was reduced from 5 to 2 days to restore chloramine residual and stop nitrification. On September 5, 2002, restoration of monochloramine residual was confirmed. The chloramine residual was 0.1 mg/L NH₂Cl as Cl₂ shown in Figure 4.1. The decrease in nitrification can be seen in the comparison of the bulk water quality indicators in the weeks leading up to and immediately following the HRT reduction. Prior to nitrification in PDS 15, all dissolved oxygen observations were greater than 2 mg/L. During nitrification, dissolved oxygen fell below 2 mg/L and near anaerobic conditions until the HRT was reduced from 5 to 2 days. Following the HRT reduction, dissolved oxygen consumption decreased and effluent D.O. concentration increased from 0.3 to 2.5 mg/L as O₂. Biological activity decreased shown in the decrease of HPCs from 5 log to 4.4 log. The oxidation of ammonia to nitrite and nitrate was reduced seen in the increase in effluent free ammonia concentration in Figure 4.1 and decrease in nitrite and nitrate concentrations in Figure 4.2. During this improvement the major change was HRT as other factors remained the same such as temperature remained between 24°C and 26°C, pH 7.6 to 7.7, and alkalinity 84 to 88. Despite the application of these control practices the nitrification episode was occurring in the PDSs. Monochloramines were replaced by free chlorine and was applied to the PDSs for one week, December 13 2002 through December 20 2002. During free chlorination effluent chlorine residuals were above 1 mg/L in 17 of the 18 lines and nitrites were below detection limits shown in Table 4-7. Free chlorination proved to be effective in eliminating nitrification. In PDS 15 effluent chlorine residual increased from 0.5 to 1.6 mg/L as Cl₂ shown
in Figure 4.1 and nitrite concentrations were below detection limits as seen in Table 4-7.

Immediately after free chlorination monochloramines were reapplied at 4.5 mg/L as Cl\textsubscript{2} and on December 27, 2002 effluent residuals remained above 1 mg/L as Cl\textsubscript{2} 17 of the 18 lines confirming the elimination of nitrification and improvement in effluent water quality from free chlorination.

Table 4-7: Free Chlorine and Nitrite Concentrations During Free Chlorination

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* PDSs in bold were undergoing substantial nitrification before free chlorine burn.
4.5 Conclusions

- Monochloramines were sources of ammonia for nitrification. Monochloramine residual degraded due to the temperature increase. Nitrification occurred after the loss of residual in the PDSs. Effluent chloramine residuals decreased to zero, effluent HPCs increased approximately four orders of magnitude, effluent DO decreased and the production of nitrates and nitrites in PDSs confirmed biochemical nitrification. Nitrification did not result due to the use of particular source water; source water was independent of nitrification.

- During nitrification certain water quality trends were observed. At a 5 day HRT, the extent of nitrification was greater than at a 2 day HRT, which was confirmed by lower monochloramine residuals, lower DO and higher nitrate concentrations. As observed in the incremental analysis of PDSs; DO consumption increased during nitrification, free ammonia concentrations increased initially as chloramines decomposed but eventually decreased as nitrite and nitrate increased.

- Control of nitrification was attempted using four methods. The first two methods were slightly increasing chloramine residual from 4 to 4.5 mg/L and changing the Cl2/NH3-N ratio from 4.5/1 to 5/1 and did not reduce nitrification as a PDS residual could not be maintained. The third method was reducing the PDS HRT from 5 to 2 days, which reestablished chloramine residuals and significantly reduced but did not eliminate nitrification. The fourth method was a one week free chlorine burn at 4 mg/L Cl2 and a two day HRT which eliminated nitrification in the PDSs.
5 CONCLUSIONS AND RECOMMENDATIONS

- Monochloramines were source of ammonia for nitrification. Monochloramines residual degraded due to the temperature increase. Nitrification occurred after the loss of residual in the PDSs. Effluent chloramine residuals decreased to zero, effluent HPCs increased approximately four orders of magnitude, effluent DO decreased and the production of nitrates and nitrites in PDSs confirmed biochemical nitrification. Source water was independent of nitrification.

- During nitrification certain water quality trends were observed. At a 5 day HRT the extent of nitrification was greater than at a 2 day HRT, which was confirmed by lower monochloramine residuals, lower DO and higher nitrate concentrations. As observed in the incremental analysis of PDSs: DO consumption increased during nitrification, free ammonia concentrations increased initially as chloramines decomposed but eventually decreased as nitrite and nitrate increased.

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chloramine residuals and significantly reduced but did not eliminate nitrification. The fourth
method was a one week free chlorine burn at 4 mg/L Cl₂ and a two day HRT which
eliminated nitrification in all PDSs.
LIST OF REFERENCES


Pintar K.DM., Slawson R.M., and Huck P.M. A study of conditions leading to nitrification in a model distribution system.

Skadsen J. (2002). Effectiveness of high pH in controlling nitrification. AWWA 94(7), 73-83.


