

WATER QUALITY VARIATIONS DURING NITRIFICATION IN DRINKING WATER
DISTRIBUTION SYSTEMS

by

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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_2 residual dosed at 4.5:1 $\text{Cl}_2:\text{NH}_3\text{-N}$. 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_2 at 5:1 $\text{Cl}_2:\text{NH}_3\text{-N}$ 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.

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LIST OF ABBREVIATIONS

Awwa	American Water Works Association
AwwaRF:	American Water Works Association Research Foundation
AOB	Ammonia oxidizing bacteria
DBP	Disinfection by-product
DO	Dissolved oxygen
HPC	Heterotrophic plate count
HRT	Hydraulic residence time
NOB	Nitrite oxidizing bacteria
PDS	Pilot distribution system
TKN	Total Kjeldahl nitrogen

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.

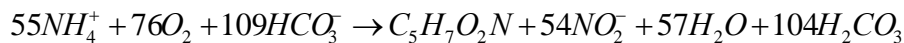
2 LITERATURE REVIEW

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2.1 Theoretical Aspects of Nitrification in Chloraminated Water Systems

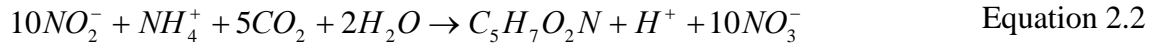
2.1.1 Nitrification Biology

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.



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.



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

	NH ₄	O ₂	HCO ₃	NO ₂	H ₂ CO ₃
AOB NH ₄	1 ↓	3.45 ↓	8.63 ↓	0.99 ↑	8.37 ↑
	NO ₂	NH ₄	H ₂ CO ₃	HCO ₃	NO ₃
NOB NO ₂	1 ↓	0.0025 ↓	0.044 ↓	0.011 ↓	1 ↑

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

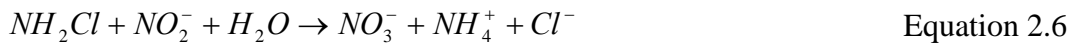
Chloramination has been implemented in the United States by many utilities since chloramines are less reactive than free chlorine and produce less disinfection-by-products (DBPs). Chloramines formed by the reaction of ammonia and chlorine, can produce three different compounds: monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramine (NCl_3).



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 ($\text{Cl}_2:\text{NH}_3$), 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.



For each 1 mg/L of NO₂-N, 5 mg/L of NH₂Cl as Cl₂ 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.



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.

$$V_{T_1} = V_{T_2} \exp(k(T_1 - T_2)) \quad \text{Equation 2.8}$$

$$\ln(\text{ammonia removal}) = 0.058T + 3.161 \quad \text{Equation 2.9}$$

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 $\text{pH} > \text{pK} = 9.3$ (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 CaCO_3 , 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 3-1: Source Water and Treatment Identification

Source	Type	Treatment
G1	Groundwater	Conventional
G2	Groundwater	Softening
G3	Blend	Softening
G4	Blend	Nanofiltration
S1	Surface	Coagulation, Ozonation, BAC
S2	Surface	Coagulated, Nanofiltration
RO	Seawater	Reverse Osmosis

**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

PDS ID	Materials	Sources (Source, %)	
		Phases I and III	Phases II and IV
PDS01	Hybrid	G1 (100)	G2 (100)
PDS02	Hybrid	G2 (100)	G1 (100)
PDS03	Hybrid	S1 (100)	S2 (100)
PDS04	Hybrid	G4 (100)	G3 (100)
PDS05	Hybrid	RO (100)	S1 (100)
PDS06	Hybrid	G1 (55), S1 (45)	G1 (68), RO (32)
PDS07	Hybrid	G1 (68), RO (32)	G1 (55), S1 (45)
PDS08	Hybrid	G1 (23), S1 (45), RO (32)	G1 (60), S2 (30), RO (10)
PDS09	Hybrid	G1 (60), S2 (30), RO (10)	G1 (23), S1 (45), RO (32)
PDS10	Hybrid	G2 (50), S1 (50)	G2 (62), S1 (24), RO (14)
PDS11	Hybrid	G2 (62), S1 (24), RO (14)	G2 (50), S1 (50)
PDS12	Hybrid	G3 (100)	G4 (100)
PDS13	Hybrid	S2 (100)	RO (100)
PDS14	Hybrid	G1, S1, RO(% varied daily)	G1, S1, RO (% varied daily)
PDS15	Unlined Cast Iron	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)
PDS16	Lined Cast Iron	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)
PDS17	PVC	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)
PDS18	Galvanized	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)

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

		Free	Total	Free NH ₃	pH	PHs	Alk	Ca ²⁺	TH	Mg ²⁺	UV-254	Color	Turbidity	D.O.	Conductivity	TDS	T	Cl ⁻	SO ₄ ²⁻	Iron
	Source	as Cl ₂		mg/L N			mg/L as CaCO ₃			cm ⁻¹	CPU	NTU	mg/L	mS/cm	mg/L	oC	mg/L	mg/L	mg/L	
Phase I	G1	0.1	3.9		8.1	7.2	194	211	245	34	0.073	5	0.5	8.2	485	323	20	0.1		
	G2	0.2	4.4		8.2	7.8	95	85	117	32	0.067	4	0.4	8.6	266	177	19	0.0		
	G3	0.2	3.7		8.3	8.0	51	111	136	25	0.069	2	0.7	9.7	423	282	17	0.0		
	G4	0.1	3.7		8.2	8.1	65	68	78	10	0.028	0	0.2	9.2	291	193	18	0.0		
	S1	0.1	4.1		8.0	7.7	59	204	241	36	0.027	1	0.2	13.0	551	368	18	0.0		
	S2	0.2	4.3		8.2	8.1	68	60	71	11	0.025	2	0.3	9.2	308	204	18	0.1		
	RO	0.1	4.2		8.2	8.1	66	61	69	8	0.019	0	0.2	8.7	400	265	21	0.0		
Phase II	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	0.05
	G2	0.1	4.9		7.9	7.8	97	93	126	33	0.067	1	0.1	7.5	305	203	25			
	G3	0.1	4.5		8.2	8.1	51	94	124	30	0.050	0	0.2	8.5	389	258	24			
	G4	0.1	4.7		8.2	7.7	106	96	113	16	0.029	0	0.1	8.1	323	215	25			
	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	0.02
	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	0.02
	RO	0.2	4.5		8.3	8.1	67	66	72	6	0.022	0	0.2	7.9	398	265	25	80.7	4	0.01
Phase III	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	0.05
	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			
	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			
	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			
	S1	0.1	4.8	0.1	8.1	7.9	61	131	156	25	0.033	1	0.4	8.3	580	386	26	31.1	163	0.04
	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	0.01
	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	0.01
Phase IV	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	0.06
	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			
	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			
	G4	0.1	5.0	0.2	8.2	7.8	103	81	92	12	0.036	0	0.1	8.5	317	211	22			
	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	0.07
	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	0.02
	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	0.01

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

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

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.

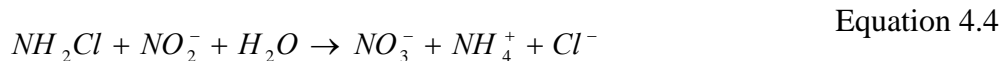
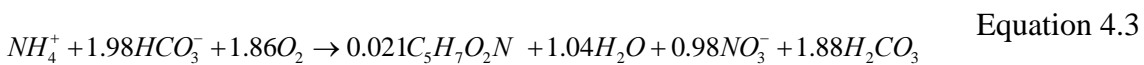
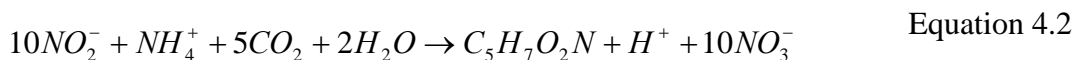
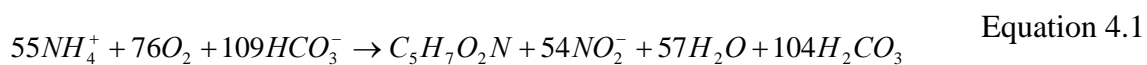
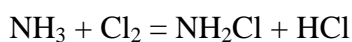


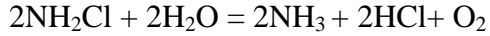
Table 4-1: Stoichiometric Mass Change Due to Nitrification (mg/L)

	NH ₄	O ₂	HCO ₃	NO ₂	H ₂ CO ₃
AOB NH ₄	1 ↓	3.45 ↓	8.63 ↓	0.99 ↑	8.37 ↑
	NO ₂	NH ₄	H ₂ CO ₃	HCO ₃	NO ₃
NOB NO ₂	1 ↓	0.0025 ↓	0.044 ↓	0.011 ↓	1 ↑
	NH ₂ Cl	NO ₂	NO ₃	NH ₄	
NH ₂ Cl NO ₂	1 ↓	0.2 ↓	0.2 ↑	0.2 ↑	

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.



Equation 4.5



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

Source	Type	Treatment
G1	Groundwater	Conventional
G2	Groundwater	Softening
G3	Blend	Softening
G4	Blend	Nanofiltration
S1	Surface	Coagulation, Ozonation, BAC
S2	Surface	Coagulated, Nanofiltration
RO	Seawater	Reverse Osmosis

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

Table 4-3: PDS Material and Source Water

PDS ID	Materials	Sources (Source, %)	
		Phases I and III	Phases II and IV
PDS01	Hybrid	G1 (100)	G2 (100)
PDS02	Hybrid	G2 (100)	G1 (100)
PDS03	Hybrid	S1 (100)	S2 (100)
PDS04	Hybrid	G4 (100)	G3 (100)
PDS05	Hybrid	RO (100)	S1 (100)
PDS06	Hybrid	G1 (55), S1 (45)	G1 (68), RO (32)
PDS07	Hybrid	G1 (68), RO (32)	G1 (55), S1 (45)
PDS08	Hybrid	G1 (23), S1 (45), RO (32)	G1 (60), S2 (30), RO (10)
PDS09	Hybrid	G1 (60), S2 (30), RO (10)	G1 (23), S1 (45), RO (32)
PDS10	Hybrid	G2 (50), S1 (50)	G2 (62), S1 (24), RO (14)
PDS11	Hybrid	G2 (62), S1 (24), RO (14)	G2 (50), S1 (50)
PDS12	Hybrid	G3 (100)	G4 (100)
PDS13	Hybrid	S2 (100)	RO (100)
PDS14	Hybrid	G1, S1, RO(% varied daily)	G1, S1, RO (% varied daily)
PDS15	Unlined Cast Iron	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)
PDS16	Lined Cast Iron	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)
PDS17	PVC	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)
PDS18	Galvanized	G1 (23), S1 (45), RO (32)	G1 (60), S1 (30), RO (10)

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

		Free	Total	Free NH ₃	pH	PHs	Alk	Ca ²⁺	TH	Mg ²⁺	UV-254	Color	Turbidity	D.O.	Conductivity	TDS	T	Cl ⁻	SO ₄ ²⁻	Iron
	Source	as Cl ₂		mg/L N				mg/L as CaCO ₃			cm ⁻¹	CPU	NTU	mg/L	mS/cm	mg/L	oC	mg/L	mg/L	mg/L
Phase I	G1	0.1	3.9		8.1	7.2	194	211	245	34	0.073	5	0.5	8.2	485	323	20	0.1		
	G2	0.2	4.4		8.2	7.8	95	85	117	32	0.067	4	0.4	8.6	266	177	19	0.0		
	G3	0.2	3.7		8.3	8.0	51	111	136	25	0.069	2	0.7	9.7	423	282	17	0.0		
	G4	0.1	3.7		8.2	8.1	65	68	78	10	0.028	0	0.2	9.2	291	193	18	0.0		
	S1	0.1	4.1		8.0	7.7	59	204	241	36	0.027	1	0.2	13.0	551	368	18	0.0		
	S2	0.2	4.3		8.2	8.1	68	60	71	11	0.025	2	0.3	9.2	308	204	18	0.1		
	RO	0.1	4.2		8.2	8.1	66	61	69	8	0.019	0	0.2	8.7	400	265	21	0.0		
Phase II	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	0.05
	G2	0.1	4.9		7.9	7.8	97	93	126	33	0.067	1	0.1	7.5	305	203	25			
	G3	0.1	4.5		8.2	8.1	51	94	124	30	0.050	0	0.2	8.5	389	258	24			
	G4	0.1	4.7		8.2	7.7	106	96	113	16	0.029	0	0.1	8.1	323	215	25			
	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	0.02
	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	0.02
	RO	0.2	4.5		8.3	8.1	67	66	72	6	0.022	0	0.2	7.9	398	265	25	80.7	4	0.01
Phase III	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	0.05
	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			
	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			
	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			
	S1	0.1	4.8	0.1	8.1	7.9	61	131	156	25	0.033	1	0.4	8.3	580	386	26	31.1	163	0.04
	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	0.01
	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	0.01
Phase IV	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	0.06
	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			
	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			
	G4	0.1	5.0	0.2	8.2	7.8	103	81	92	12	0.036	0	0.1	8.5	317	211	22			
	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	0.07
	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	0.02
	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	0.01

Process and PDS water quality was routinely monitored in the field and laboratory.

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

Parameter	Location	Reference
Alkalinity	Field	SM 2320 B
Ammonia-N	Field	SM 4500-NH ₃ C
Chlorine, free	Field	SM 4500-Cl G or Hach 8021
Chlorine, total	Field	SM 4500-Cl-G or Hach 8167
Hardness (total, calcium)	Field	SM 2340 C
Nitrate	Field	Hach 8192
Nitrite	Field	Hach 8507
Oxygen, dissolved (DO)	Field	SM 4500-O G
pH	Field	SM 4500-H ⁺ B
Phosphate, ortho	Field	SM 4500-P E
Temperature	Field	
Turbidity	Field	SM 2130 B
TKN-Nitrogen-(trivalent)	UCF	SM 4500-Norg Macro-Kjeldahl Method
Coliforms (Fecal, Total)	UCF	SM Membrane Filtration Technique
HPC	UCF	SM 9215B Pour Plate Method

SM = Standard Methods of Water and Wastewater Analysis, 19th Ed (1995)

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_2Cl was practically constant at approximately 4 mg/L as Cl_2 . The effluent NH_2Cl 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_2Cl 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 $\text{NH}_3\text{-N}$ in the PDS feed stream. However there was no indication of excessive HPC growth until mid March when the NH_2Cl residual was essentially lost.

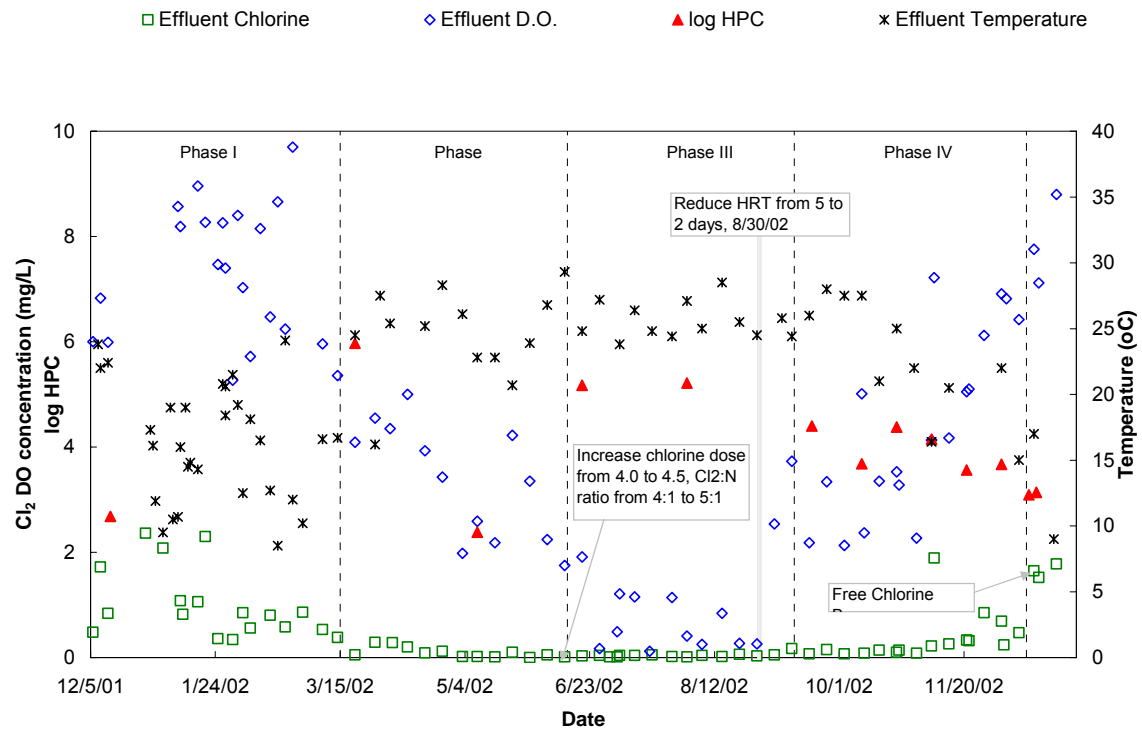


Figure 4.1: Monochloramine Residual Degradation in PDS 15

After the chloramine residual was lost in PDS 15, nitrite and nitrate concentrations increased as shown in Figure 4.2.

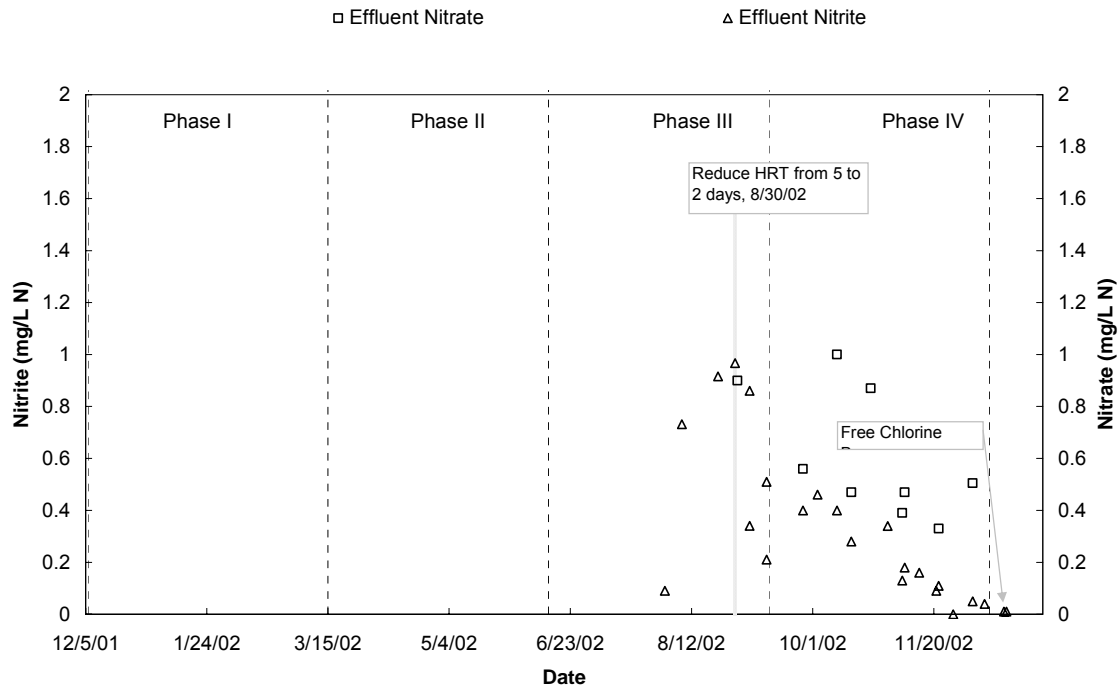


Figure 4.2: PDS 15 Nitrite and Nitrate versus Time

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.

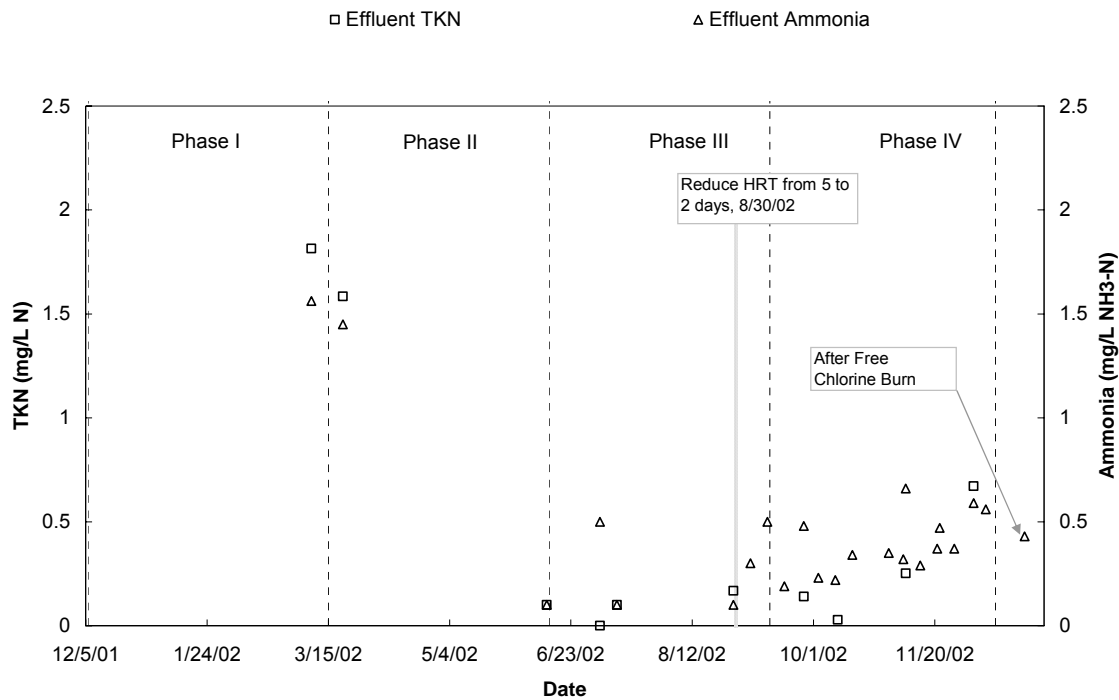


Figure 4.3: PDS TKN and Ammonia versus Time

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.

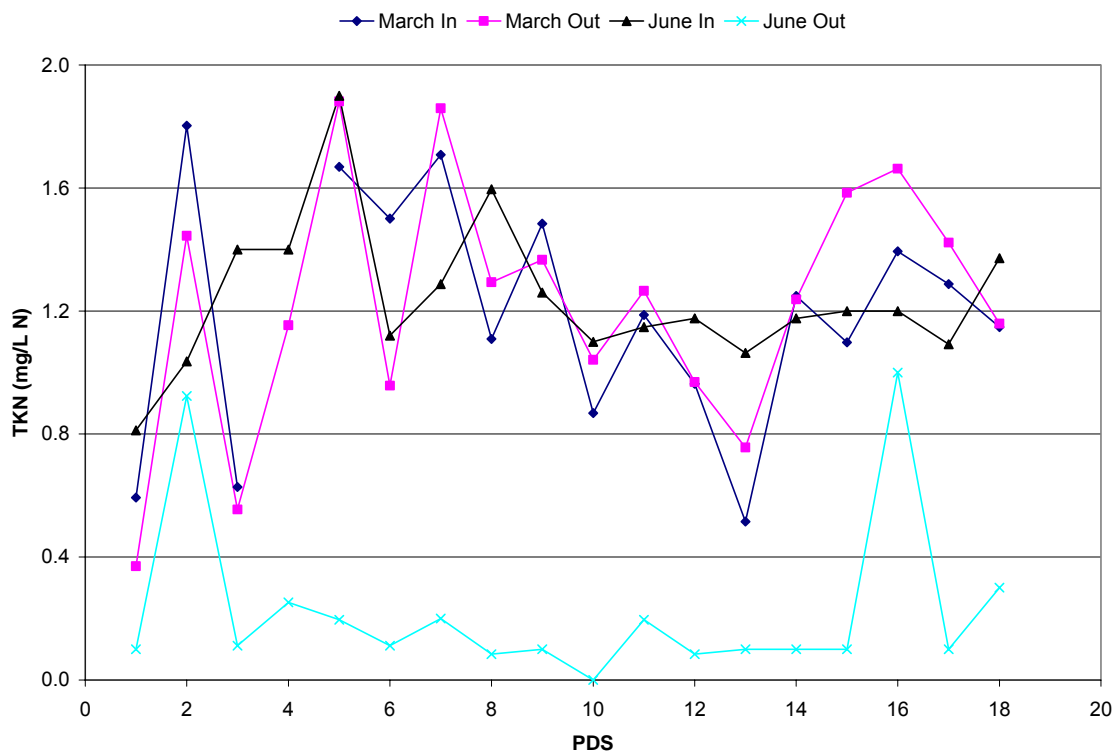


Figure 4.4: PDS TKN Before and After Nitrification

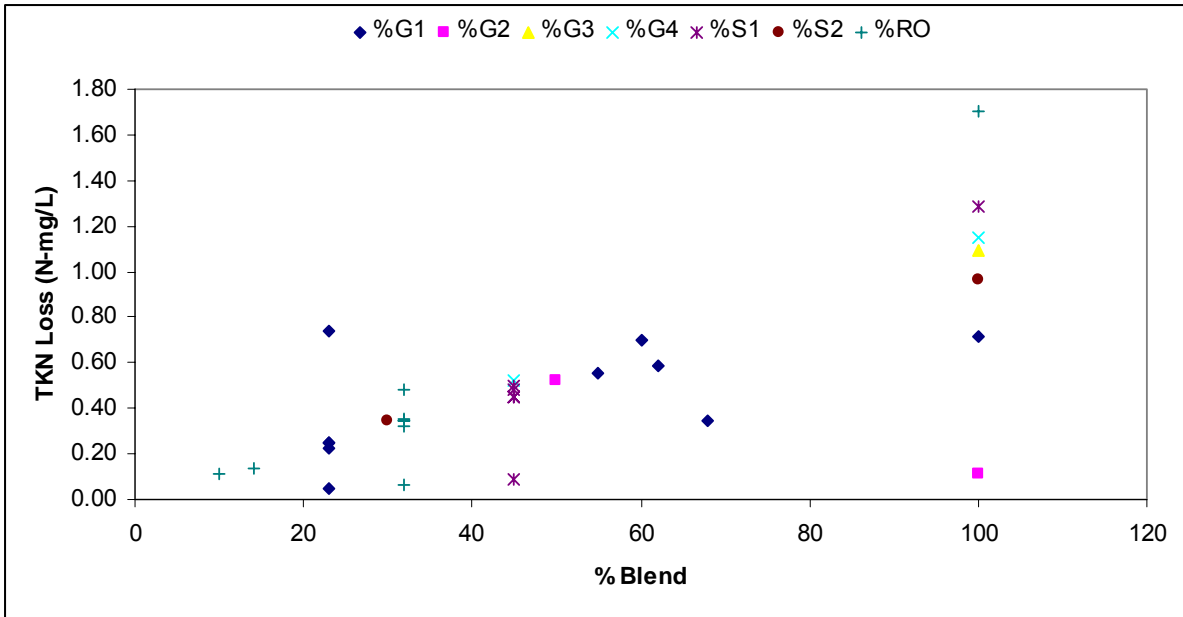


Figure 4.5: Linearly Proportioned TKN Loss by Percent Blend

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 Cl₂, 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 NH₃-N due to chloramine degradation. Nitrites and nitrates concentration increased to more than 0.1 mg/L NO₃-N from 20 to 30 hours, which marked the onset of nitrification. During this period, free ammonia increased less than 0.1 mg/L NH₃-N, much less than the increase of 0.3 mg/L NH₃-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%.

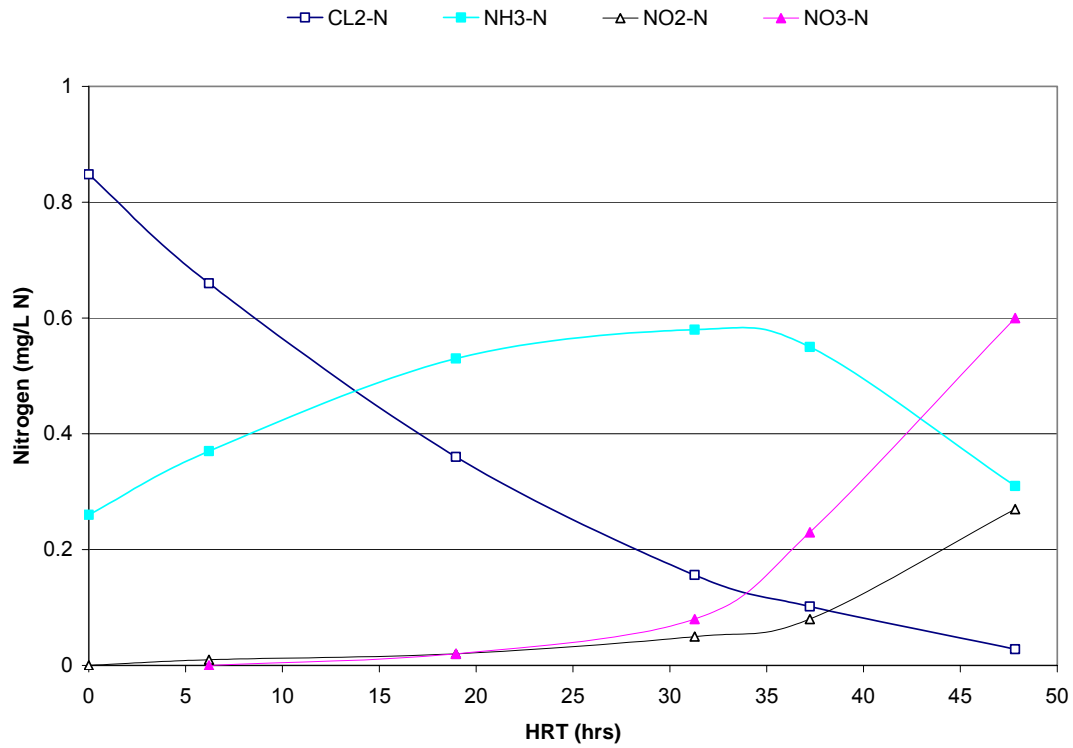


Figure 4.6: PDS 15 N Species

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 O₂ in PDS 15 as shown in Figure 4.7.

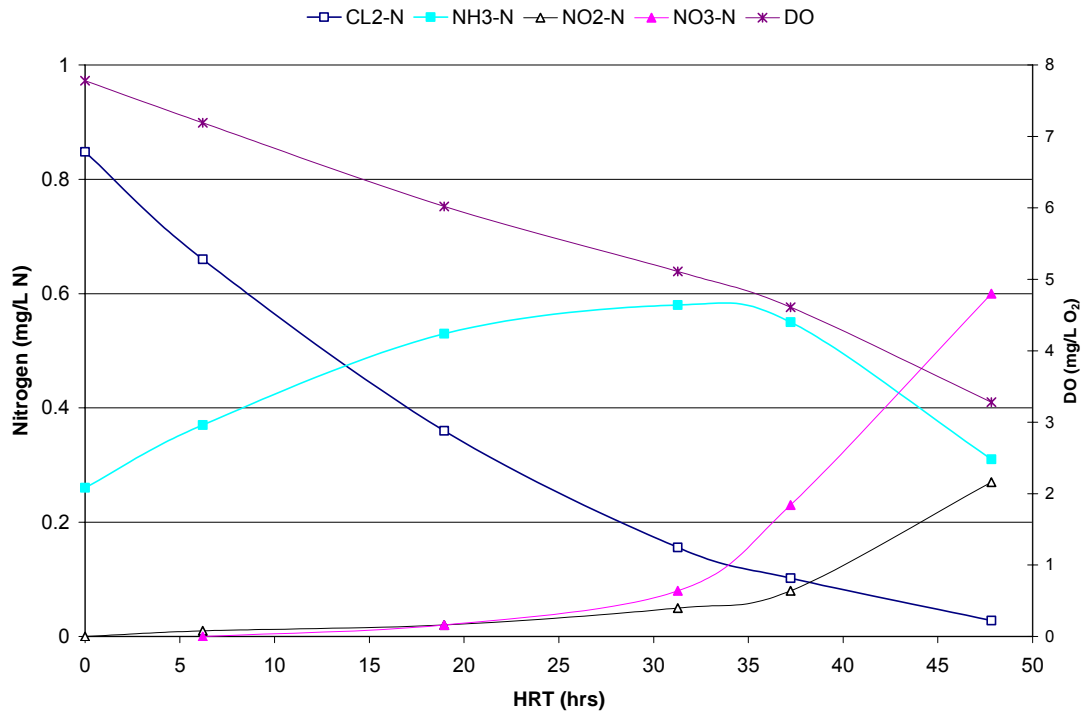


Figure 4.7: PDS 15 Dissolved Oxygen (10/25/02)

Consistent decreasing trends of pH and alkalinity were not observed during nitrification shown in Figure 4.8 and Figure 4.9.

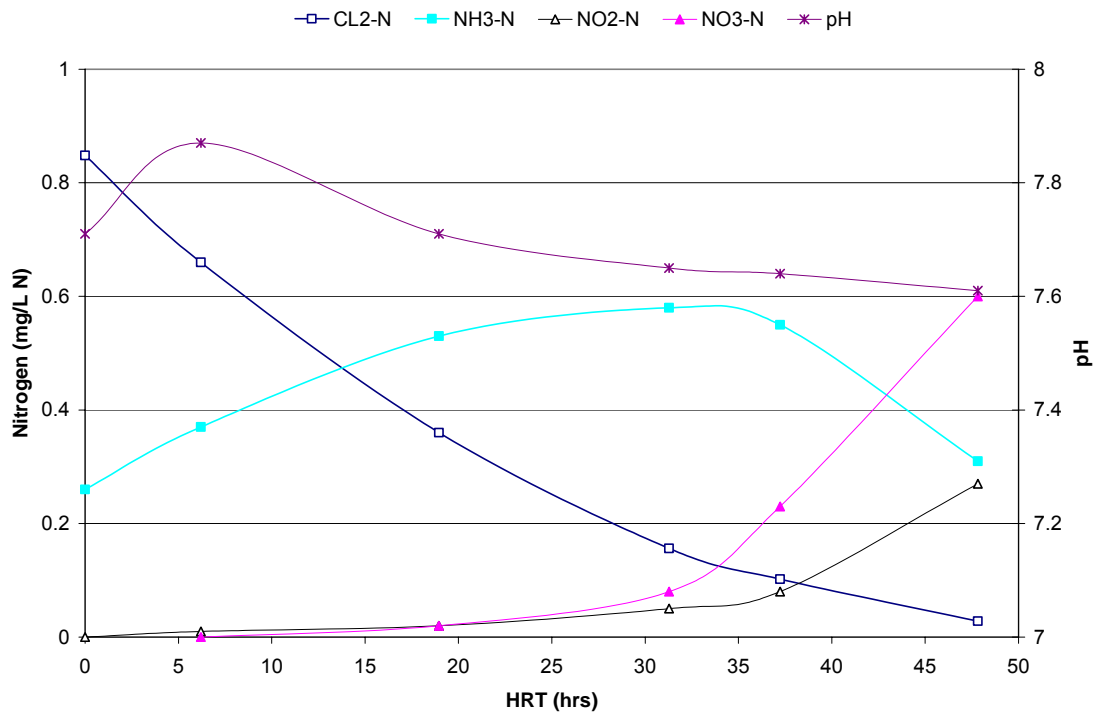


Figure 4.8: PDS 15 pH (10/25/02)

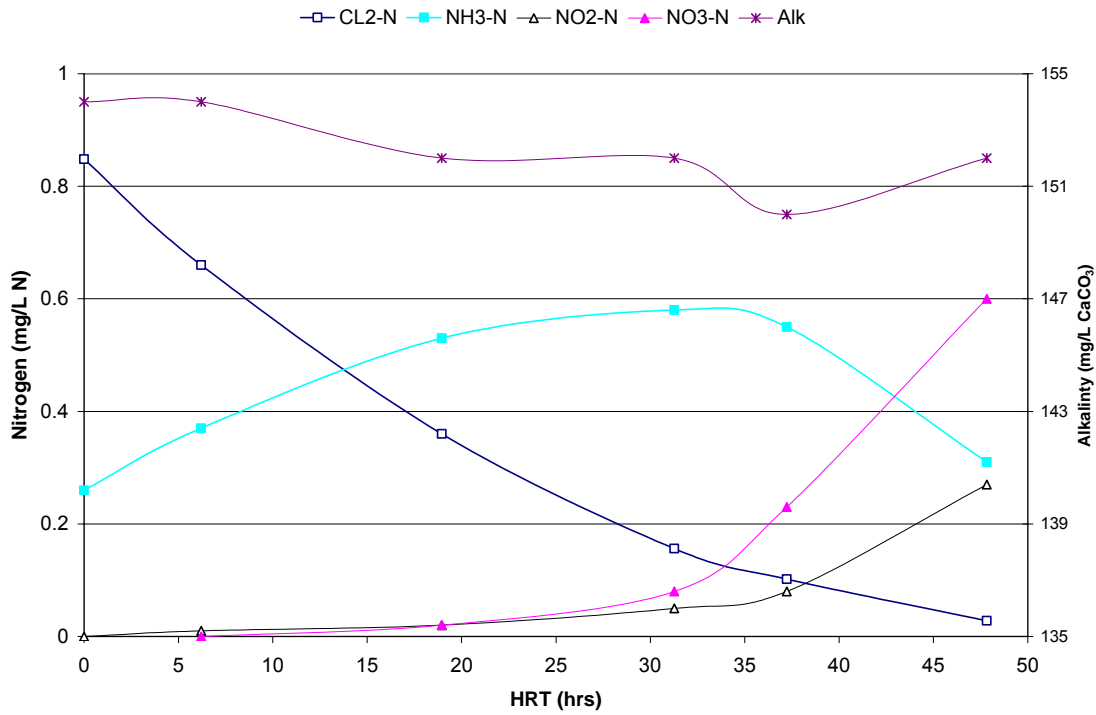


Figure 4.9: PDS 15 Alkalinity (10/25/02)

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.

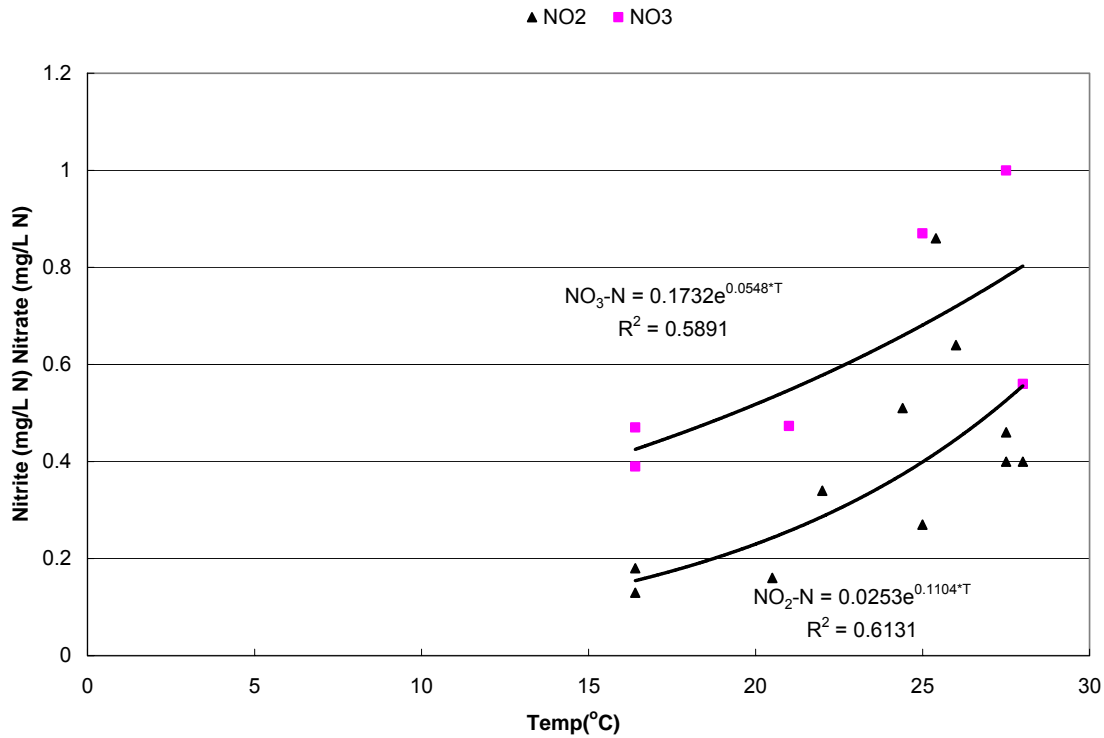


Figure 4.10: PDS 15 Temperature Correlation (9/5/02-11/13/02)

To explain the water quality changes seen in PDS 15, biological nitrification was considered to be the primary source of nitrates and nitrites 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 $\text{NH}_3\text{-N}$ 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)

HRT	ID	NH ₂ Cl-N	NH ₃ -N	O ₂	HCO ₃ as		NO ₂ -N	NO ₃ -N	pH	ΣN
					CaCO ₃					
0	Actual	0.85	0.26	7.8	154		0	0.00	7.71	1.11
	Actual	0.66	0.37	7.2	154		0.01	0.01	7.87	1.05
6	Theoretical		0.43	7.7	153.9				7.69	
	Difference		0.06	0.5	-0.1				-0.18	
19	Actual	0.36	0.53	6.0	152		0.02	0.02	7.71	0.93
	Theoretical		0.71	7.6	153.7				7.68	
	Difference		0.18	1.6	1.7				-0.03	
31	Actual	0.16	0.58	5.1	152		0.05	0.08	7.65	0.87
	Theoretical		0.82	7.3	153.1				7.64	
	Difference		0.24	2.2	1.1				-0.01	
37	Actual	0.10	0.55	4.6	150		0.08	0.23	7.64	0.96
	Theoretical		0.69	6.5	151.8				7.57	
	Difference		0.14	1.9	1.8				-0.07	
48	Actual	0.03	0.31	3.3	152		0.27	0.60	7.61	1.21
	Theoretical		0.19	4.3	147.7				7.39	
	Difference		-0.12	1.0	-4.3				-0.22	

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 the 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 CaCO₃ 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 NH₂Cl-N, NH₃-N, DO and pH with NO₂-N and NO₃-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 Cl₂ 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 Cl₂ and on December 27, 2002 effluent residuals remained above 1 mg/L as Cl₂ 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

	Free Chlorine (mg/L Cl ₂)				Nitrite-N (mg/L N)		
	12/17/2002	12/18/2002	12/19/2002	12/20/2002	12/18/2002	12/19/2002	12/20/2002
PDS	Feed	Effluent	Feed	Effluent	Feed	Effluent	Effluent
1	3.25	2.22	5.08	2.36	0.00	0.01	0.01
2	2.95	0.78	4.90	1.12	0.00	0.01	0.01
3	4.90	3.02	5.53	3.18	0.00	0.01	0.01
4	4.60	1.82	5.29	1.66	0.00	0.01	0.01
5	5.47	3.08	5.69	3.30	0.00	0.01	0.01
6	4.66	1.80	5.26	2.36	0.00	0.01	0.01
7	5.33	3.40	5.33	3.60	0.00	0.01	0.01
8	4.86	2.60	5.19	2.60	0.00	0.01	0.01
9	5.36	3.00	5.43	3.44	0.00	0.01	0.01
10	5.26	2.10	5.43	2.56	0.00	0.01	0.01
11	4.96	2.04	5.99	2.50	0.00	0.01	0.01
12	5.76	2.52	5.56	2.72	0.00	0.01	0.01
13	5.00	2.40	6.29	2.52	0.00	0.01	0.01
14	5.06	2.60	6.06	2.34	0.00	0.01	0.01
15	5.29	1.44	5.69	1.10	0.00	0.01	0.01
16	5.29	2.50	5.93	2.90	0.00	0.01	0.01
17	5.06	3.38	5.43	3.84	0.00	0.01	0.01
18	4.66	0.01	5.23	0.03	0.00	0.01	0.01

* 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.
- 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 $\text{Cl}_2/\text{NH}_3\text{-N}$ 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 Cl_2 and a two day HRT which eliminated nitrification in all PDSs.

LIST OF REFERENCES

- AwwaRF. 1995. Nitrification Occurrence and Control in Chloraminated Water Systems. Denver, CO: American Water Works Association Research Foundation.
- AwwaRF. 2003. Ammonia Decay from Monochloramines: Effects on Distribution System Nitrification. Denver, CO: American Water Works Association Research Foundation
- Brazos B.J, O'Conner J.T., and Kiekamp K. (1996). Control of water quality deterioration in water distribution systems. *Public Works* 127, 56-59.
- Cates J., and Lavinder S. (1999). Improving chloramine residuals and minimizing nitrification. *Florida Water Resource Journal*, 26-28.
- Cunliffe D.A. (1991). Bacterial nitrification in chloraminated water supplies. *Applied and Environmental Microbiology* 57(11), 3399-3402.
- Groenweg J., Sellner B., and Tappe W. (1994). Ammonia oxidation in nitrosomonas at NH₃ concentrations near Km: effects of pH and temperature. *Water Research* 28(12), 2561-2566.
- Kirmeyer G., Foust G., and LeChevallier M. Optimization of chloramination for distribution system water quality control. 71-80.
- Lieu N.I., Wolfe R.L., and Means III E.G. (1993). Optimizing Chloramine Disinfection for the Control of Nitrification. *AWWA*, 84-90.
- Odell L.H., Kirmeyer G.J., Wilczak A., Jacangelo J.G., Marcinko J.P., and Wolfe R.L. (1996). Controlling nitrification in chloraminated distribution systems. *AWWA*, 86-98.
- 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.
- Skadsen J. (1993). Nitrification in Distribution System. *AWWA*, 95-103.
- Tokuno S. (1997). Granular activated carbon filtration and nitrification. *Water/Engineering and Management*, 22-25.

Tokuno S., and Baker F. (1997). The effect of nitrification on sampling sites. *Water/Engineering and Management*, 22-27.

Tokuno S. (1999). Granular activated carbon filtration and chloramine. *Water Engineering and Management*, 16-21.

Vahala R., and Laukkanen R. (1998). Nitrification in GAC-filtered, UV disinfected and chlorinated distribution system. *Water Supply* 16, 245-247.

Vikesland P.J., Ozekin K., and Valentine R.L. (2001). Monochloramine decay in model and drinking water distribution systems. *Water Research* 35(7), 1766-1776.

Wilczak A., Jacangelo J.G., Marcinko J.P., Odell L.H., Kirmeyer G.J., and Wolfe R.L. (1996). Controlling nitrification in chloraminated distribution systems. *AWWA*, 86-98.

Wolfe R.L., Lieu N.I., Izaguirre G., and Means E.G. (1990). Ammonia –Oxidizing Bacteria in a Chloraminated Distribution System: Seasonal Occurrence, Distribution, and Disinfection Resistance. *Applied and Environmental Microbiology* 56(2), 451-462.

Wolfe R.L., Means III E.G., Davis M.K., and Barret S.E. (1998). Biological nitrification in covered reservoirs containing chloraminated water. *AWWA*, 109-114.