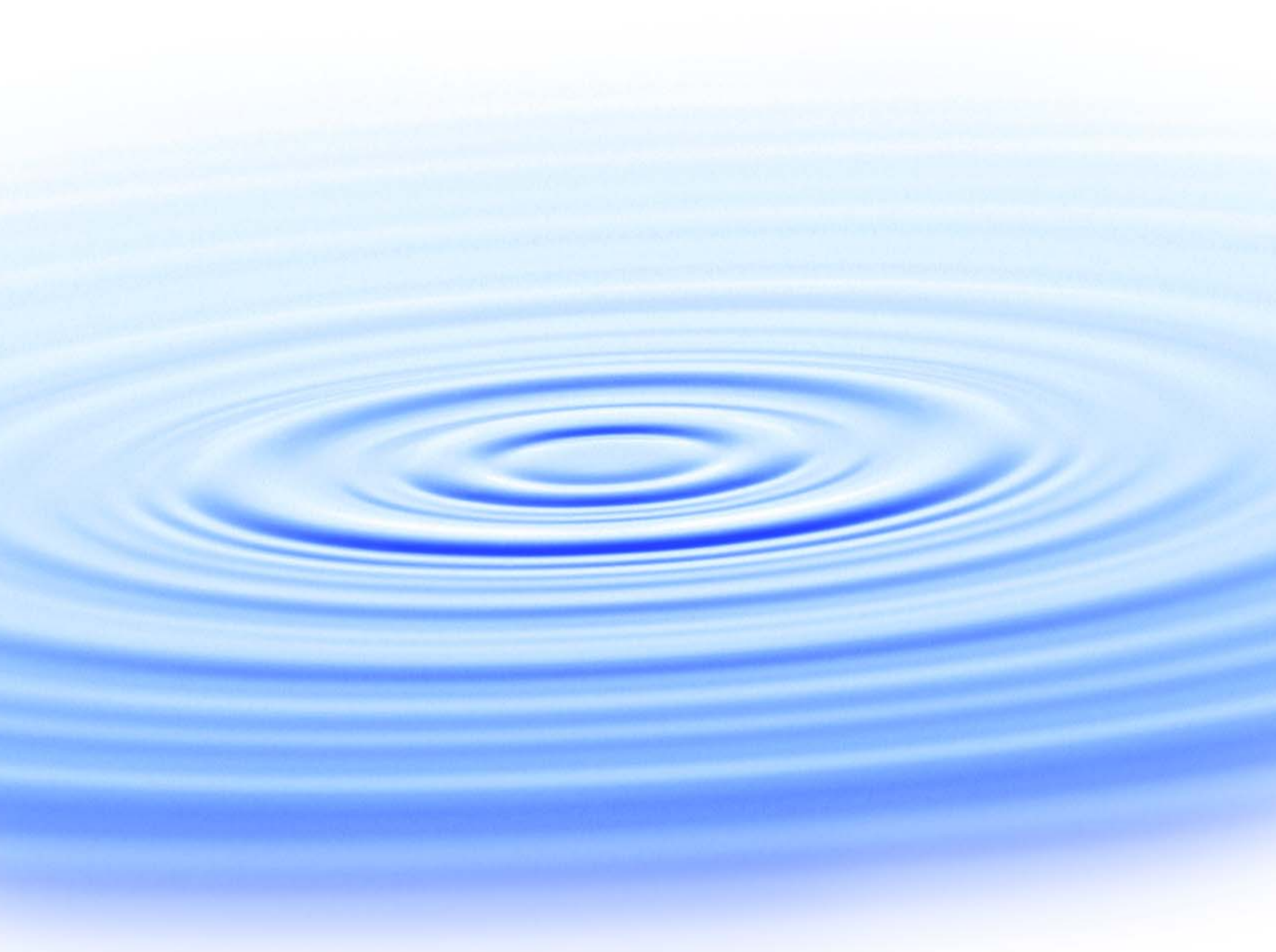
WateReuse

Establishing Nitrification Reliability Guidelines for Water Reuse



WateReuse Research Foundation

Establishing Nitrification Reliability Guidelines for Water Reuse

About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water for various uses through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, reduction of energy requirements, concentrate management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of providing a reliable, safe product for its intended use.

The Foundation's funding partners include the supporters of the California Direct Potable Reuse Initiative, Water Services Association of Australia, Pentair Foundation, and Bureau of Reclamation. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations.

Establishing Nitrification Reliability Guidelines for Water Reuse

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WATEREUSE

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Acronyms

AOB	ammonia-oxidizing bacteria
BNR	biological nutrient removal
BOD	biological oxygen demand
CAS	conventional activated sludge
CCB	chlorine contact basin
CT	product of chlorine concentration (C) and contact time (T)
DBP	disinfection by-product
DFB	chlorine-demand-free buffer
DO	dissolved oxygen
EPA	Environmental Protection Agency
MBR	membrane bioreactor
MGD	million gallons per day
MLE	modified Ludzack-Ettinger
NDMA	N-nitrosodimethylamine
NDN	nitrification-denitrification
O&M	operation and maintenance
SCADA	supervisory control and data acquisition (i.e., plant control)
SRT	solids retention time
TDS	total dissolved solids
TSS	total suspended solids
UF	ultrafiltration
WAS	waste activated sludge
WRF	water reclamation facility or water recycling facility
WRP	water reclamation plant

Foreword

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide sustainable sources of high-quality water, protect public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse and desalination research topics including:

- Defining and addressing emerging contaminants, including chemicals and pathogens
- Determining effective and efficient treatment technologies to create 'fit for purpose' water
- Understanding public perceptions and increasing acceptance of water reuse
- Enhancing management practices related to direct and indirect potable reuse
- Managing concentrate resulting from desalination and potable reuse operations
- Demonstrating the feasibility and safety of direct potable reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project to provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The objectives of this research project are to (1) document the reliability of nitrification processes used in water reuse, and (2) develop guidelines for ensuring nitrification reliability at recycled water treatment facilities. The intended outcome of this research is to build a foundation for developing revised disinfection guidelines for water reuse.

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Executive Summary

Water recycling offers a cost-effective option to expand the water portfolios of many communities. Given the wastewater origin of recycled water, however, recycled water disinfection practices for both non-potable and potable reuse scenarios typically exceed the requirements of more traditional water supplies. Chlorine disinfection—the most widely practiced form of disinfection in the United States—offers the potential to inactivate a number of relevant pathogens. Chlorine disinfection of recycled water, however, differs significantly from drinking water applications because of the frequent presence of ammonia in recycled waters. The addition of chlorine to ammonia-containing recycled water transforms the disinfectant from its more potent "free" chlorine form to the less potent "combined" chlorine (or chloramine) form. Because of this reduction in potency, the chlorine dose needed to achieve a given level of inactivation is significantly higher for combined chlorine. This fact has important impacts on the design, cost, footprint, and effectiveness of the system given that combined chlorine requires larger contact tanks [for longer contact times] and is effective against a narrower range of pathogens.

Not all water recycling facilities, however, have ammonia present during the chlorine disinfection step. In particular, recycling facilities that practice nitrification—the biological conversion of ammonia or ammonium to nitrate—frequently reduce ammonia to low levels prior to disinfection. The absence of ammonia allows the dosed chlorine to remain in its free chlorine state, that is, not converted to chloramine. Thus, these facilities disinfect with the more potent disinfectant and should therefore receive the appropriate pathogen credit. Under current water recycling regulations, however, no differentiation is made between free chlorine and combined chlorine disinfection (e.g., see the California Department of Public Health's Water Recycling Criteria).

This practice, rooted in a time when nitrification was not commonly required as it is today, raises a number of important questions and provided the motivation for the current nitrification reliability study. Free chlorine disinfection provides a number of benefits, including smaller and less expensive infrastructure (e.g., chlorine contact tanks) and stronger disinfectant potential. Reconfiguring systems to take advantage of these benefits, however, also places stricter requirements on the nitrification process itself. For example, the smaller chlorine contact tanks used in free chlorine disinfection would not provide sufficient contact times for combined chlorine disinfection. Thus, the consistent and reliable removal of ammonia is critical if free chlorine disinfection is to be practiced. The purpose of this study was to evaluate the potential of nitrifying facilities to achieve the stringent nitrification conditions needed to control a free chlorine disinfection system. The main focus of the study was on nitrification reliability, understood along two key lines: (1) the effectiveness and consistency of the nitrification process itself (process reliability) and (2) the technical capacity to monitor and verify this process (monitoring reliability).

The field studies and historical operations data at four water recycling facilities demonstrated that the nitrification process has the potential to meet the new reliability requirements (Figure ES.1). It is important to note that most nitrifying facilities are not currently operated with the goal of achieving the higher level of reliability needed for free chlorine disinfection. Under the current operating paradigm, even in plants that seek to nitrify, treatment goals typically focus on meeting monthly nutrient discharge limits. Transient ammonia bleed-through events, which occur diurnally with peaks in nutrient levels, organic loading, and flow, are often acceptable under this paradigm because they have little impact on monthly or daily limits. Consequently, many of the facilities did not achieve the consistent performance needed to implement a free chlorine strategy. The fact that they are not *currently* meeting these requirements should not, however, be construed to mean that they do not have the capability to meet them in the future.

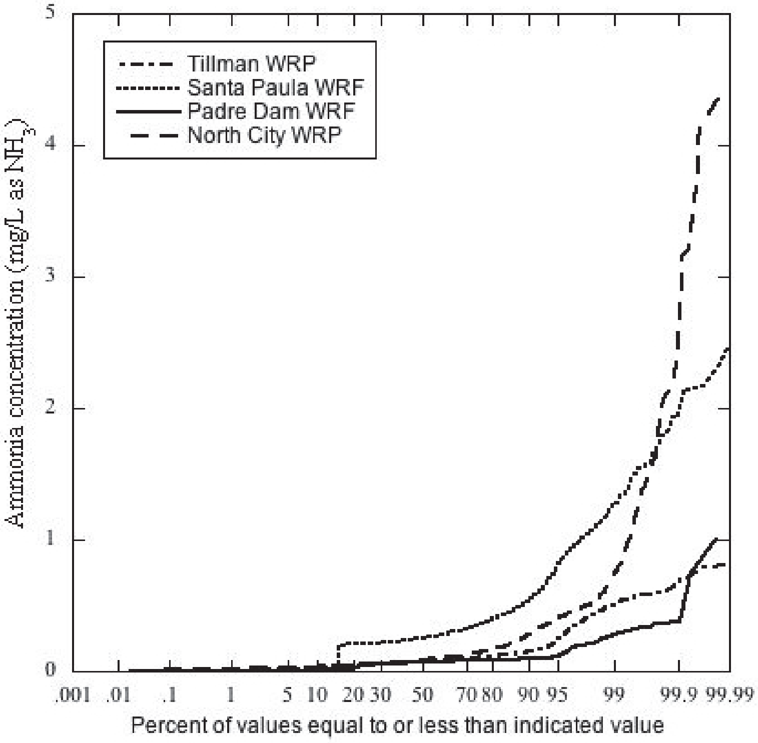

Figure ES.1. Probability distributions of the secondary effluent ammonia concentrations at the four field-test sites.

Note: Distribution functions are based on the average ammonia concentrations detected by the three online analyzers.

If disinfection with free chlorine is to be reliably achieved, a new nitrification reliability paradigm is required in which even transient ammonia events are managed. The most important adaptation required for free chlorine disinfection is therefore an operational paradigm shift that focuses on achieving a consistent, low level of effluent ammonia at all times. This report capitalizes on the knowledge gained from the field studies to create a framework for nitrification reliability and free chlorine disinfection in terms of operation, design, and failure response. This framework provides recommendations for the modification of existing facilities as well as for the design of new or upgraded facilities.

To achieve the operational paradigm shift needed for free chlorine disinfection, the two main elements to be addressed are monitoring and process control. These elements ensure the absence of ammonia prior to chlorination and provide data to control the disinfection system in the event of ammonia breakthrough. Identifying a reliability metric that can continuously monitor compliance was a principal goal of this study. Online ammonia analyzers were the metric used in this study to measure and verify the proper functioning of the nitrification process. Ideal characteristics for monitoring include (1) near-continuous or continuous measurement of ammonia levels in secondary effluents, (2) a high level of accuracy, and (3) acceptable operation and maintenance (O&M) requirements. To test their ability to meet the criteria, the analyzers were subjected to a battery of tests including an initial laboratory verification of performance, a nine month field deployment at four recycling facilities, and a series of field challenge tests. Through this study, it was concluded that all of the analyzers have the potential to monitor and verify nitrification reliability. Each demonstrated sufficient sensitivity to detecting appropriately low levels of ammonia with monitoring frequencies capable of providing near-continuous resolution of effluent ammonia concentrations.

Data from the monitors can also be used for process control. By quantifying ammonia levels in treated effluents, the monitors provide information to regulate chlorine dosing and system response. For example, online measurements could be used to modify chlorine dosing in real time based on the measured ammonia concentrations. When the monitors detect excessive ammonia levels, they could trigger the system to divert water or to initiate backup systems prior to distribution. One option for free chlorine process control is presented in Figure ES.2.

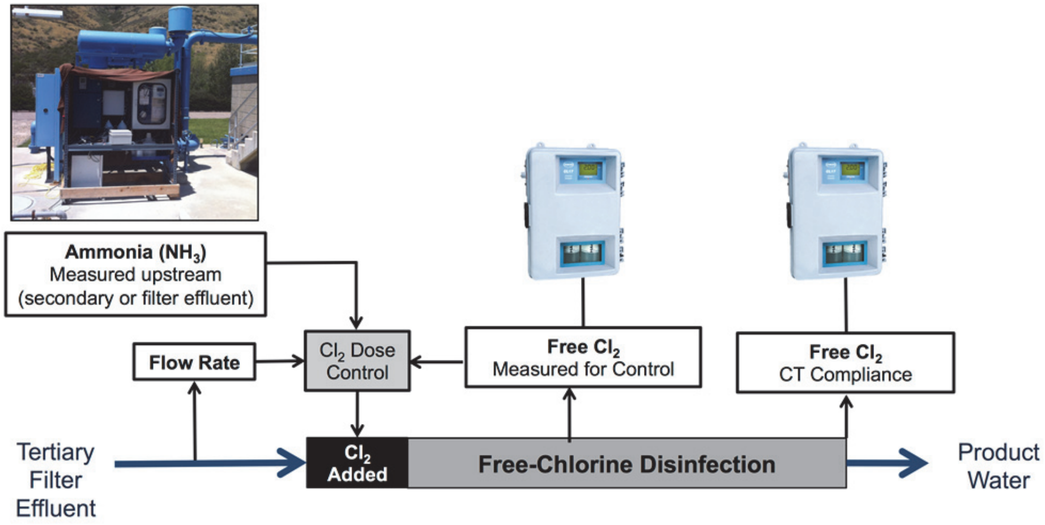

Figure ES.2. Possible configuration of ammonia monitoring and control system for free chlorine disinfection.

One potential shortcoming of the existing monitors was the need to deal with frequent O&M issues. The O&M requirements were not trivial, but the monitors provide important value in the constant verification of nitrification performance. Therefore, improvements that reduce the labor requirements for operation, cleaning, and maintenance will increase the robustness of the monitors (and by extension, the entire nitrification system) and should be sought. In the meantime, these monitors can be used to demonstrate compliance with the new nitrification requirements.

This report also uses the information from the study to provide an economic analysis of the two disinfection schemes. This analysis revealed that free chlorine disinfection is more economical than chloramine disinfection when average ammonia levels are kept low. Although free chlorine dosing strategies require higher chemical consumption (because of the need for breakpoint chlorination), the reduced capital costs outweigh this impact at low ammonia concentrations. On the basis of the assumptions used in this analysis, the ammonia concentration at which the two strategies break even on cost is approximately 0.8 mg/L of ammonia (average). Above this concentration, the higher chemical costs associated with breakpoint chlorination push the total cost of free chlorine disinfection above that of combined chlorine disinfection. The exact ammonia concentration at which the two scenarios break even will vary from site to site depending on plant conditions and flow, among other factors.

The two disinfection strategies (free and combined chlorine) also impact factors beyond cost. Because free chlorine is a more potent oxidant, it can provide demonstrable inactivation of a range of pathogen types including bacteria, viruses, and protozoa (e.g., *Giardia*). Chloramines also provide protection against bacteria but are less effective against viruses, even at longer contact times. They also provide limited to no protection against protozoa such as *Giardia* and *Cryptosporidium*. Pathogen control strategies that use free chlorine disinfection are therefore capable of providing protection against a broader set of contaminants of public health concern. In addition, free chlorine also provides better reduction of trace organic compounds.

On the basis of the results of this study, the nitrification process can be operated, monitored, and verified with sufficient reliability to pursue a free chlorine disinfection strategy. Ensuring consistent free chlorine residuals, however, will require a significant shift from the current operational paradigm. In this new context, reliability is no longer framed in terms of nutrient loading but in achieving consistent, low ammonia levels at all times. Ammonia peaks—both transient and long-term—offer challenges to the free chlorine strategy; therefore, both preventive and responsive strategies need to be incorporated into design and operation.

Through this study, a number of knowledge and technical gaps were identified that should be addressed in future efforts. One of the most important next steps is to engage the relevant regulatory agencies on the issue of free chlorine disinfection credit for recycled water. These discussions should include defining the operating conditions needed to obtain free chlorine disinfection credit. One likely outcome of these discussions is the need to demonstrate the operation of a free chlorine system using a pilot- or full-scale demonstration system.

Although free chlorine disinfection will have the widest applicability for facilities producing non-potable recycled water, the benefits will be equally or more important for potable reuse. The inactivation and removal of viruses will be one of the important challenges because many physical removal processes (e.g., granular media filtration and microfiltration) are only partially effective at removing particles in the size range of most viruses. Taking advantage of the chlorine disinfection systems that currently exist at many recycling facilities provides an obvious economic advantage over the addition of a new disinfection process, such as UV or ozone. As the country moves toward potable reuse, free chlorine disinfection has the potential to play an important role in meeting pathogen goals for both direct and indirect potable reuse applications

Chapter 1

Introduction

1.1 Background

1.1.1 Recycled Water and Reuse Regulations

The growing demand for water is motivating many communities across the world to increase the reclamation and reuse of water. Water recycling can supplement dwindling freshwater resources with a renewable and drought-proof source, the availability of which increases with increasing potable water use. Water recycling is a cost-effective way to expand the water portfolios of many municipalities, and the practice is expected to increase rapidly in the near future.

A comparison of the recycled water requirements of four of the states most actively involved in water reclamation—CA, FL, TX, and AZ—is provided in Table 1.1. Some of the most stringent requirements for recycled, non-potable water for unrestricted access uses are found within California's Title 22 Water Recycling Criteria. These criteria require that recycled water be well-oxidized water that has undergone both filtration and disinfection. Whereas Florida, Texas, and Arizona have disinfection requirements based on bacterial indicators (typically fecal coliform), California bases its disinfection requirements on the inactivation of virus. Because viruses are typically more resistant to chlorine than bacteria are, viral requirements are deemed to be stricter or more demanding.

Table 1.1. Requirements for Recycled Water for Unrestricted Access Uses

Parameter	California	Florida[b]	Texas[c]	Arizona[d]
Legislation	Title 22, CA Code of Regulations	F.A.C. Chapter 62-610	T.A.C. Title 30, Chapter 210	A.A.C. Title 18, Chapter 11
Treatment requirements	Filtration, disinfection	Filtration, “high-level disinfection”		Filtration, disinfection
Disinfection	Chlorine: 450 CT with 90-min modal contact time *or* Alternative technologies: provide 5-log virus reduction when combined with filtration	Chlorine: 1 mg/L minimum residual for ≥ 15 min If FC < 10 MPN/mL: CT = 25 If FC = 10–100 MPN/mL: CT = 40 If FC > 100 MPN/mL[a]: CT = 120		
Performance	TC testing Weekly: median MPN < 2.2/100 mL Monthly: No more than one sample MPN > 23/100 mL Any 1 sample MPN not > 240/100 mL Turbidity (*coagulation & media filtration*) (1) Daily average < 2 NTU, (2) 5 NTU < 5% of samples in 24 h period, (3) No sample > 10 NTU Turbidity (*membrane filtration*) (1) 0.2 NTU < 5% of time in 24 h, (2) No sample > 0.5 NTU	For monthly FC testing 75% samples < determined limit for FC Any 1 sample not > 25 MPN/100 mL Any 1 sample not > 5 mg/L of TSS	30 day averages BOD_5: 5 mg/L Turbidity: 3 NTU FC: 20 CFU/mL (geometric mean) FC: 75 CFU/mL (single grab sample)	FC: below detection for 4 of last 7 daily samples with single sample max FC of < 23/100 mL Turbidity: 24 h average ≤ 2 NTU; never > 5 NTU

Notes: [a] CT values (the product of chlorine concentration and contact time) calculated using total chlorine residual at peak hourly flow. [b] Strictest treatment requirements from 62-610 (and from 62-600-440); intended for “public access areas, residential irrigation, and edible crops.” [c] Requirements for “Type 1 Reclaimed Water Use” including irrigation or other uses in areas where the public may be present during the time when irrigation takes place or other uses where the public may come in contact with the reclaimed water. [d] Requirements for “Class A Reclaimed Water,” that is, for reuse applications where there is a relatively high risk of human exposure to potential pathogens in the reclaimed water.

F.A.C. = Florida Administrative Code, T.A.C. = Texas Administrative Code, A.A.C. = Arizona Administrative Code, BOD = biological oxygen demand, CFU = colony forming unit, FC = fecal coliform, MPN = most probable number, NTU = nephelometric turbidity unit, TSS = total suspended solids

1.1.2 Free Chlorine Disinfection Versus Combined Chlorine Disinfection

Of the various disinfection methods available (chlorine, UV, ozone, pasteurization), chlorine is by far the most common. The two forms of chlorine that are most commonly used for disinfection are free chlorine (which is the combination of HOCl and OCl^-; pKa = 7.53) and combined chlorine (typically monochloramine, NH_2Cl). These two disinfectants are intimately connected in that combined chlorine is produced via the reaction of free chlorine with ammonia. The total chlorine residual is composed of both free and combined chlorine species, which include monochloramine, dichloramine ($NHCl_2$), and trichloramine (NCl_3). When adding free chlorine to an ammonia-containing water, the amount and composition of the chlorine residual depends on the chlorine-to-ammonia nitrogen ratio (Cl_2:NH_3-N), which increases as more chlorine is added.

When chlorine is initially added to an ammonia-containing water (Zone A of Figure 1.1), the increase in the total chlorine residual is nearly proportional to the amount of chlorine added. This occurs because of the rapid formation of monochloramine according to the following reaction (Crittenden et al., 2012):

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \qquad (1.1)$$

Depending on the pH, dichloramine may also form within Zone A as follows:

$$NH_2Cl + H^+ \Leftrightarrow NH_3Cl^+ \qquad (1.2)$$

$$NH_3Cl^+ + NH_2Cl \Leftrightarrow NHCl_2 + NH_4^+ \qquad (1.3)$$

The dichloramine formation reactions are catalyzed by H^+; therefore, significant dichloramine formation occurs below pH 7; above pH 7, monochloramine is typically the only combined chlorine species present. Trichloramine formation is minimal unless the pH is below 4.

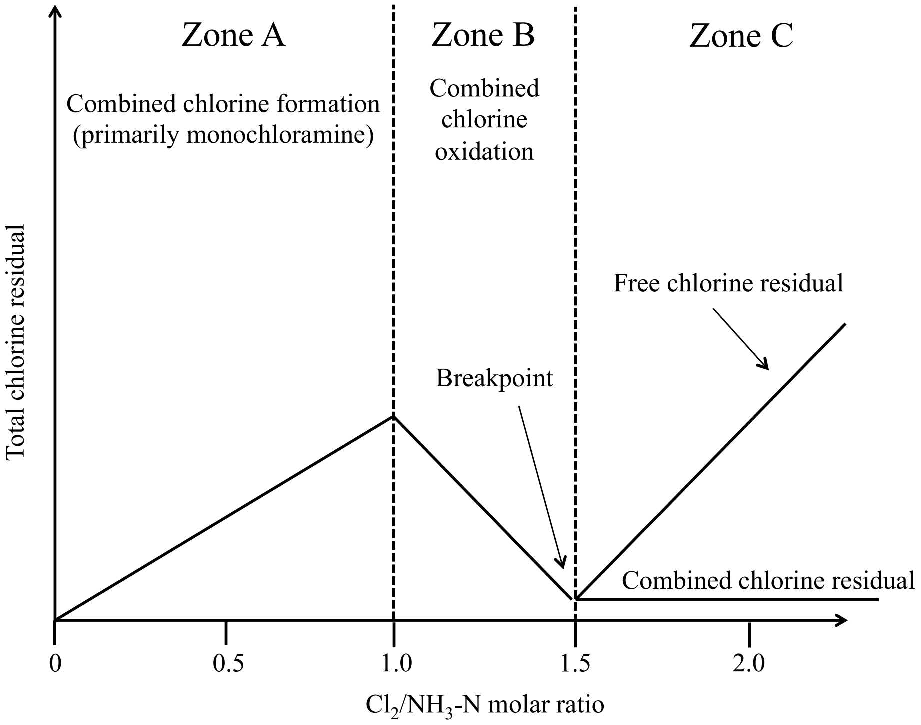

Figure 1.1. Schematic representation of the chlorine residual versus chlorine dosage during breakpoint chlorination.

As the $Cl_2:NH_3$-N ratio increases, the total chlorine residual approaches a maximum value that is reached at a 1:1 molar $Cl_2:NH_3$-N ratio, equivalent to a 5.07:1 mass ratio. As the $Cl_2:NH_3$-N ratio continues to increase (Zone B), there is no further free ammonia to react with the free chlorine. Consequently, free chlorine begins to react with other less-reactive constituents in the water, such as monochloramine. As additional chlorine is added in Zone B, a net decrease in the total chlorine residual occurs because of the following reaction (Snoeyink and Jenkins, 1980):

$$2NH_2Cl + HOCl \Leftrightarrow N_2(g) + 3H^+ + 3Cl^- + H_2O \qquad (1.4)$$

The decrease in the total chlorine residual is coupled with the oxidation of ammonia to nitrogen gas [$N_2(g)$]. The mechanisms of chloramine oxidation are not fully understood, and other reactions may also occur to form NO_3^- and other nitrogen-containing chlorine-free species.

The point at which the chlorine residual reaches a minimum is called the breakpoint. The chlorine dose required to reach the breakpoint is a 7.6:1 mass ratio of $Cl_2:NH_3$-N. In actual practice chlorine is often added in a 10:1 mass ratio to ensure breakpointing is complete. After the breakpoint (Zone C), the further addition of chlorine results in a proportional increase in the total chlorine residual in the form of free chlorine. A low level of combined chlorine residual also remains in the form of dichloramine and trichloramine.

Chlorine disinfection doses are typically quantified in terms of the product of the residual concentration of the free or combined chlorine (C) and the contact time (T); this product is often expressed as "CT" with units of mg-min/L. Free chlorine is a more powerful oxidant than monochloramine; this allows it to react more readily with chlorine-reactive substances (Dhaliwal and Baker, 1983). Because it is stronger, free chlorine achieves a given level of inactivation at lower doses than combined chlorine (Sobsey, 1989). Typical CT values required to inactivate various classes of pathogens are listed in Table 1.2. For example, a 4-log reduction of viruses can be achieved with free chlorine at doses in the range of 5–10 mg/L. Combined chlorine achieves the same level at CTs that are one to more than two orders of magnitude higher.

Table 1.2. CT Values (in mg Cl_2-min/L) Required To Inactivate Various Classes of Pathogens with Free Chlorine and Combined Chlorine

Log_{10} Reduction	**Bacteria**		**Viruses**		**Protozoa (*Giardia* cysts)**	
	Free	**Combined**	**Free**	**Combined**	**Free**	**Combined**
1-log_{10}	0.1–0.2	4–6			20–30	400–650
2-log_{10}	0.4–0.8	12–20	2.5–3.5	300–400	35–45	700–1000
3-log_{10}	1.5–3.0	30–75	4.0–5.0	500–800	70–80	1100–2000
4-log_{10}	10.0–12.0	200–250	6.0–7.0	200–1200		

Note: Assumes disinfection at approximately pH 7 and 20 °C

Source: Adapted from Metcalf & Eddy, Inc., et al., 2003

Despite the effectiveness of free chlorine, the California Title 22 regulations require that recycled water receive a dose of 450 mg Cl_2-min/L for any form of chlorine. No differentiation is made between disinfection with free chlorine and with combined chlorine despite the differences in their oxidative strengths. The following section explores the historical basis of the regulations.

1.1.3 History of Disinfection Requirements in California Water Recycling Criteria

The disinfection requirements of California's Water Recycling Criteria were developed in the 1970s and based largely on disinfection studies undertaken at that time. During that period, nitrification was less reliable than it is today (e.g., there was a lack of source control programs), and appropriate tools to properly monitor and control nitrification were not in place [e.g., online dissolved oxygen (DO) and ammonia analyzers]. Given this uncertainty, the more conservative regulatory approach was to assume that all facilities—including nitrifying facilities—would have moments when ammonia was present in the secondary effluents. As discussed, the presence of ammonia generally precludes disinfection by free chlorine (barring breakpoint chlorination). By assuming the presence of combined chlorine, the disinfection regulations were conservatively constructed. Advances in both the control and monitoring of the nitrification process (e.g., improved source control and online analyzers) have brought the reliability of nitrification to the point where these conservative assumptions should be revisited.

The second factor that influenced this regulatory strategy was the results of an important virus inactivation study undertaken at that time: the Pomona Virus Study (Sanitation Districts of Los Angeles County, 1977). The Pomona Virus Study was conducted at a critical time in the development of the California Water Recycling Criteria and served as the basis of many of the regulatory requirements in place today, including the 450 mg-min/L CT requirement. Based on our current understanding of viral disinfection, the use of free chlorine typically requires doses that are two orders of magnitude lower than those of combined chlorine. The Pomona Virus Study that was completed in the 1970s, however, reported only minor differences in the viral disinfection properties of free and combined chlorine. In the Pomona Virus Study, an approximately 3.9-log inactivation of polio was observed with a free chlorine CT of approximately 390 mg-min/L, whereas a 3.7-log inactivation was achieved with a 510 mg-min/L chloramine CT (Figure 1.2; black bars). It is important to note that the 390 mg-min/L free chlorine CT value was the only free chlorine CT tested. Had lower CTs been tested, it is possible (as indicated by more recent studies) that the researchers would have met the 4-log virus inactivation at significantly lower CTs. These results are compared with eight subsequent studies evaluating the potency of the two disinfectants in Figure 1.2. Two points are clear from this comparison: (1) the combined chlorine results from the Pomona Virus Study are supported by all of the subsequent studies on combined chlorine disinfection, but (2) the free chlorine results are markedly different.

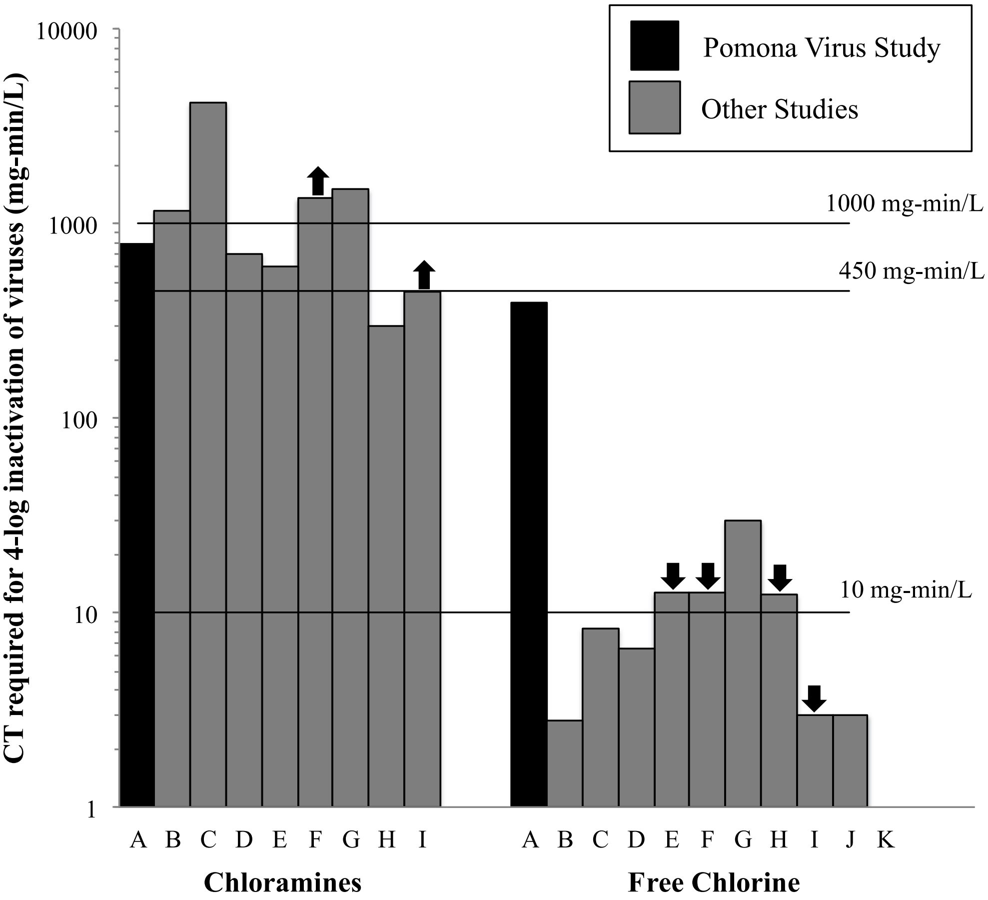

Figure 1.2. Comparison of studies evaluating chloramine and free chlorine CTs required for 4-log virus inactivation.

Note: Arrows represent values below detection limits (downward-pointing arrows) or sparse data (upward-pointing arrows).

Source: A: Sanitation Districts of Los Angeles County, 1977, poliovirus, filtered effluent; B and C: Sobsey et al., 1988, poliovirus and MS2, respectively, chlorine-demand-free buffer (DFB); D: Metcalf & Eddy, Inc., et al., 2003, estimate, filtered effluent; E and F: Soroushian et al., 2010, filtered effluent; G: Asano, 2007, DFB; H, I, and K: Tang et al., 2011, filtered effluent; J: Hirani, 2012, membrane bioreactor (MBR) effluent.

With the exception of the Pomona Virus Study, nearly all of the free chlorine studies required CTs of 10 mg-min/L or less for 4-log inactivation. Compared with chloramine (which has CTs ranging from hundreds to thousands of mg-min/L), free chlorine has the potential to greatly reduce CT requirements. For example, a CT of 10 mg-min/L would be 45 times lower than the 450 mg-min/L CT required by the California Title 22 Water Recycling Criteria.

Although the reasons for this discrepancy have not been described, the validity of these findings is called into question given the weight of evidence demonstrating the difference in these two disinfectants. The presence and speciation of nitrogen is not only important in disinfection but also impacts the consequences of wastewater and recycled water discharge on both public and environmental health. The impacts of wastewater nitrogen are discussed in the following section.

1.2 Impact of Nitrogen in Wastewater Effluent

Nitrogen (N) is present in the environment in various forms. Total N typically refers to the sum of the concentrations of ammonium N, organic N, nitrite, and nitrate. Total N concentrations in domestic wastewater typically range from 20–85 mg/L. Of this, approximately 60% is present as ammonium N (NH_3-N) and 40% as organic N, with a small contribution from nitrates. The amount of nitrogen remaining in treated wastewater depends on the type of treatment used. During the activated sludge process, some N is removed because of cell synthesis and solids wasting. Most ammonia, however, is not removed unless the process has been expressly designed for nitrification. Effluent total N levels in non-nutrient removal plants typically range from 15–35 mg/L, with most of the N present as ammonia.

The principal reason that plants undertake nitrification processes is to minimize the harmful effects of ammonia discharges on environmental and human health or to reduce nutrient loadings. The nitrification process can also be coupled with an anoxic denitrification step that converts nitrate into nitrogen gas (N_2). Nitrification-denitrification (NDN) allows N_2 gas to escape into the atmosphere, effectively removing the nitrogen from the wastewater. The main effects of nitrogen, including ammonia, on environmental and human health are the following:

1. Reduction in DO concentrations
2. Eutrophication
3. Toxicity for aquatic life
4. Public health concerns
5. Decreased suitability of water for reuse

1.2.1 DO Concentrations

Ammonia discharges to the environment affect the DO concentrations in two ways. Firstly, organisms can utilize ammonia directly as an energy source. In aerobic waters, ammonia oxidation is coupled with oxygen consumption, using 4.57 mg of O_2 per mg of ammonia. In addition to this direct pathway, ammonia can also indirectly lead to decreasing oxygen concentrations. Aquatic plant growth is often limited by the absence of nitrogen, so an input of nitrogen from wastewater can cause a rapid growth of plants, for example, algal blooms. When these large algal masses die, bacterial decomposition of the remaining organic matter consumes DO. The fate of numerous aquatic species depends on the presence of sufficient levels of DO; thus, inputs that reduce DO need to be controlled.

1.2.2 Eutrophication

As described previously, nitrogen is often the nutrient that limits the growth of plant life in aquatic systems. The introduction of new nitrogen sources can lead to eutrophication, which is the excessive growth of plants or algae because of over-fertilization. In addition to lowering the DO level, eutrophication causes aesthetic deterioration by increasing the turbidity of previously clear waters and by producing foul odors associated with the decomposition of plant growth.

1.2.3 Aquatic Toxicity

Uncharged, free ammonia (NH_3) causes toxicity in a wide range of organisms, from terrestrial to aquatic. This ammonia is the N-containing compound that is most responsible for toxicity in aquatic species. The less toxic, charged ammonium species (NH_4^+) deprotonates to form the more toxic, uncharged NH_3 species at pH levels above its pK_a of 9.3. The pK_a can shift to lower values because of changes in temperature and salinity, but ammonia is mainly present in the NH_4^+ form under most environmental conditions. Even though most of the total ammonia in waters is present as NH_4^+, low concentrations of NH_3 can exert toxic effects. The Environmental Protection Agency (EPA) has found acute toxicity effects at concentrations between 0.1 and 10 mg/L of uncharged NH_3 for both salmonid and nonsalmonid fish. Accordingly, the maximum 1-hour average for in-stream concentrations of NH_3 is less than 1.0 mg/L, and the maximum 4-day average is less than 0.1 mg/L.

1.2.4 Public Health

The presence of excessive nitrites and nitrates in drinking water can also affect human health. The most cited health effect is methemoglobinemia, or “blue baby syndrome.” Nitrates are converted to nitrites in the bloodstream, and nitrites affect oxygen exchange in infants. Excess nitrite in the blood leads to a bluish coloring of the skin because of asphyxiation.

1.2.5 Wastewater Reuse

The presence of high levels of N is especially problematic when the reclaimed water is destined for potable reuse (both direct and indirect) because of potential human health concerns. High N levels are less problematic, and potentially even favorable, when the reclaimed water is used for agricultural irrigation given that supplemental N sources are often applied in the form of fertilizers. The presence of N in reclaimed water can offset those demands.

Given these impacts, effluent discharge standards are becoming increasingly stringent. Consequently, there is a growing interest in controlling N by converting ammonium to nitrate with the process of nitrification.

1.3 Basics of Biological Nitrification

The widespread use of wastewater nitrification began in the late 1960s in the United States and increased even more after the 1972 Clean Water Act required more facilities to remove ammonia from their effluents. The primary goal of the treatment was to alleviate the environmental consequences of ammonia discharge into receiving waters, especially those consequences related to fish toxicity and eutrophication. At this time, biological and physical-chemical processes were considered equally viable options for ammonia removal.

Since that time, advances in biological nitrogen control have outpaced advances in physical-chemical methods, allowing for a more dependable and economical treatment. Biological nitrification serves as the key process in overall nitrogen control. Nitrification advanced to such an extent that when the EPA updated its Nitrogen Control Manual in 1993 (originally published in 1975), biological nitrification was the recommended method of ammonia removal. Physical-chemical processes, such as ion exchange, ammonia stripping, and breakpoint chlorination, continue to be used, but they are typically reserved for situations in which biological control is more difficult (e.g., industrial pretreatment, cold climates).

Nitrification is the biological conversion of ammonia or ammonium to nitrate. This process occurs in two steps: (1) the conversion of ammonium to nitrite, and (2) the conversion of nitrite to nitrate. These steps are mediated by ammonia-oxidizing bacteria (AOB) of the genus *Nitrosomonas* and nitrite-oxidizing bacteria of the genus *Nitrobacter*. The presence of both groups is necessary for nitrification. Both genera are classified as *autotrophic* organisms because they use inorganic nitrogen as their energy source (in contrast to *heterotrophic* organisms, which use organic carbon as their energy source).

The chemical reactions that take place during nitrification are the following:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \qquad \textbf{(1.5)}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad \textbf{(1.6)}$$

Combining the two equations and expressing the hydrogen ion in terms of carbonate species yields

$$NH_4^+ + 2HCO_3^- + 2O_2 \rightarrow NO_3^- + 2CO_2 + 3H_2O \qquad \textbf{(1.7)}$$

In this form, both the oxygen and alkalinity requirements of ammonia oxidation are clear. Specifically, 4.57 mg O_2 and 7.14 mg of alkalinity are required per mg of nitrified ammonia.

1.3.1 Factors Affecting the Efficiency of Biological Nitrification

Many factors are involved in the efficiency and rate of the nitrification process. The most important factors are discussed in detail in the following.

Solids Retention Time (SRT)

The rate of ammonia removal is linked to the growth of nitrifying bacteria. Under most conditions, the growth rate of nitrifying bacteria is limited by the AOB, which can be modeled with the Monod equation:

$$\mu_N = \frac{\hat{\mu}_N N}{K_N + N} \tag{1.8}$$

where μ_N is the specific growth rate of AOB in day^{-1}, $\hat{\mu}_N$ is the maximum specific growth rate in day^{-1}, N is the NH_4^+-N concentration in mg/L, and K_N is the half-saturation coefficient of the AOB in mg/L of NH_4^+-N.

Typical nitrifying systems contain populations of both carbon-utilizing heterotrophic bacteria and nitrifying autotrophic bacteria. The growth rate of the nitrifying bacteria, however, is often 10–20 times lower than that of the heterotrophs. Given the lower autotrophic growth rates, conditions need to be controlled to ensure that the autotrophic bacteria can maintain their populations within the reactor. If autotrophic populations do not reside within the reactor for a sufficient time to reproduce, they will be washed out of the system.

The SRT quantifies the amount of time that bacteria reside in a reactor and is defined as

$$SRT = \frac{Biomass\ inventory}{Biomass\ wasting\ rate} \tag{1.9}$$

where biomass inventory is the total mass of bacterial solids in the reactor (in units of mass) and biomass wasting rate is the rate at which the solids are removed from the system (in units of mass per time).

The minimum SRT for the nitrifying populations (SRT_N) can be simplified as

$$SRT_N = 1 / \mu_{\square} \tag{1.10}$$

To maintain their numbers within the reactor, the bacteria need sufficient time to reproduce. Therefore, the design SRT (SRT_D) of a nitrifying reactor should be chosen such that $SRT_D \geq SRT_N$. The design of a nitrification reactor can be based either on the minimum SRT or on the rate of ammonium oxidation.

Temperature

Nitrification is strongly influenced by temperature, though it can occur at temperatures ranging from 4 to 45 ˚C. Predicting the effect of a change in temperature is difficult given that temperature affects many variables involved in the process, including the maximum growth rate and the half-saturation coefficient. Therefore, nitrification rates are expected to vary depending on geographic location (warm vs cool regions) and seasonal fluctuations in temperature.

DO Concentration

DO is required for the oxidation of ammonia to nitrite and of nitrite to nitrate (Equations 1.5 and 1.6). Nitrification becomes limited below a certain DO level. This level ranges from 0.5 to 2.5 mg/L and varies depending on the conditions in the nitrification reactor. Attached growth reactors, for example, typically have higher diffusional resistance and therefore require higher DO concentrations than suspended growth systems to maintain suitable nitrification conditions. Recent design criteria for suspended growth systems suggest maintaining an optimum DO level of at least 2.0 mg/L to prevent ammonia bleed-through during peak loading; however, lower DO levels may be sufficient in some cases.

Water Quality (including the C:N ratio)

The influent water quality plays a critical role in determining nitrification efficiency. The EPA's Nitrogen Control Manual states that the C:N ratio is the most fundamental water quality parameter. When the heterotrophs in the reactor are exposed to the organics in the wastewater, they use the organics both for energy and biomass production. The autotrophs are not maintained at appreciable concentrations until a minimum critical SRT is achieved. Once this SRT is reached, the nitrifier growth is related to the amount of residual nitrogen that is available for oxidation. The C:N ratio has an important impact on the relative percentages of the heterotrophic and autotrophic populations: to obtain a higher percentage of nitrifiers requires either a reduction in carbon sources or an increase in available nitrogen sources. Typically, raw wastewater contains high concentrations of organic, carbonaceous material and low concentrations of unoxidized nitrogen. Typical ratios of chemical oxygen demand to total Kjeldahl nitrogen (COD:TKN) are in the range of 10:1 to 15:1. Altering this ratio can have important consequences on nitrification efficiency.

pH and Alkalinity

As shown in Equation 1.7, nitrification consumes significant amounts of alkalinity in the form of bicarbonate (7.14 mg of alkalinity as $CaCO_3$ per mg of ammonia as N). The concentration of bicarbonate present in the water is a function of both the alkalinity and the pH. The reactor setup will also influence the amount of alkalinity required; for example, systems open to the atmosphere can release CO_2 via air stripping, reducing the pH. A review of published data shows that a pH of 8 provides optimum efficiency. Acidic pH levels are generally believed to decrease nitrification rates.

Inhibitors

An often cited but infrequently encountered nitrification problem is the presence of inhibitors. The main inhibitors of concern are heavy metals and some nitrogen species, including nonionized, free ammonia (NH_3) and nonionized nitrous acid (HNO_2). The increase in industrial pretreatment of wastewater has further decreased the frequency of nitrification inhibition. The effects are also difficult to predict given that nitrifying populations have been shown to acclimate to constant, low-level exposure to certain inhibitors. Short pulses of concentrated inhibitors pose a larger threat than this low basal exposure. One current research priority is to create assays to determine when nitrifying populations are affected by inhibitory compounds.

Methods have been developed to understand the importance of these various parameters on nitrification efficiency. One recent Water Environment Research Foundation (WERF) study utilized modeling to determine that the most important parameters contributing to high effluent ammonia concentrations were the maximum autotrophic growth rates and the ammonia half-saturation constants (Cox, 2003). These conclusions were based on data from a given wastewater treatment plant and therefore should not be assumed to be generally applicable.

1.3.2 Upsets of Biological Nitrification

Nitrification is a biologically mediated process, which means that its efficiency is affected by all of the factors that affect bacterial growth and metabolism. Changes to any of the parameters listed previously can impact the process or cause upsets. Nitrification upsets result in the incomplete transformation of ammonia or ammonium to nitrate and can be broadly categorized into transient and massive upsets. Transient upsets are defined as short periods of incomplete nitrification and are upsets from which the system typically can recover quickly. Massive upsets are the result of large process upsets, are longer in duration, and require longer recovery times.

One common situation that leads to temporary bleed-through is the presence of diurnal peaks in ammonia loads. Peaks of ammonia that enter in the morning have been shown to cause ammonia levels to exceed the maximum levels of nitrification available in the activated sludge, even when the aeration is set at its highest level (Kaelin et al., 2008).

For systems that are properly designed with regard to SRT, temporary ammonia breakthroughs can also be associated with (1) inadequate mass (oxygen) transfer, (2) inadequate alkalinity, (3) excessive ammonia concentrations, (4) solids washout, and (5) toxicity (United States Environmental Protection Agency, 1993). These upsets can be resolved either by readjusting the parameters to their optimal levels (e.g., DO) or by the acclimation of the populations (e.g., to low levels of toxic compounds or to shifts in pH).

The washout or death of nitrifying populations in the reactor can also potentially cause massive upsets of nitrification. Temporary inputs of inhibitory compounds that are toxic to the microbiota can provoke such a massive upset, as can insufficient SRTs that lead to the reduction of nitrifying populations. Recovery from such upsets requires sufficient time to reestablish the nitrifying populations.

1.3.3 Types of Nitrification Systems

Today, a number of different types of treatment systems may be used to achieve nitrification. Both suspended growth (e.g., conventional activated sludge [CAS] processes, step-feed processes, sequencing batch reactors) and attached growth (e.g., trickling filters, rotating biological contactors) treatment processes are used for nitrification, often in conjunction with the removal of biological oxygen demand (BOD; e.g., Parker et al., 2004; Daigger and Parker, 2000; Metcalf & Eddy, Inc., et al., 2003). Newer technologies such as membrane bioreactors (MBRs), integrated fixed-film activated sludge processes, and bioaugmentation are also being used to achieve nitrification (e.g., Li et al., 2005; Nelson and Renner, 2008; Leu and Stenstrom, 2010).

Conventional Activated Sludge

Most often, nitrification systems are incorporated into a CAS system. CAS systems are typically composed of three components, beginning with a suspended growth system in which biomass is mixed with sewage in an aerated basin [Figure 1.3(A)]. Biochemical reactions in this basin lead to the degradation of organics and the transformation of reduced nitrogen (NH_3) to nitrate. The aeration basin is followed by a secondary clarifier that separates the biomass in the effluent from the liquid stream. A recycle system redirects biomass either back to the aeration tank or to a downstream waste sludge treatment.

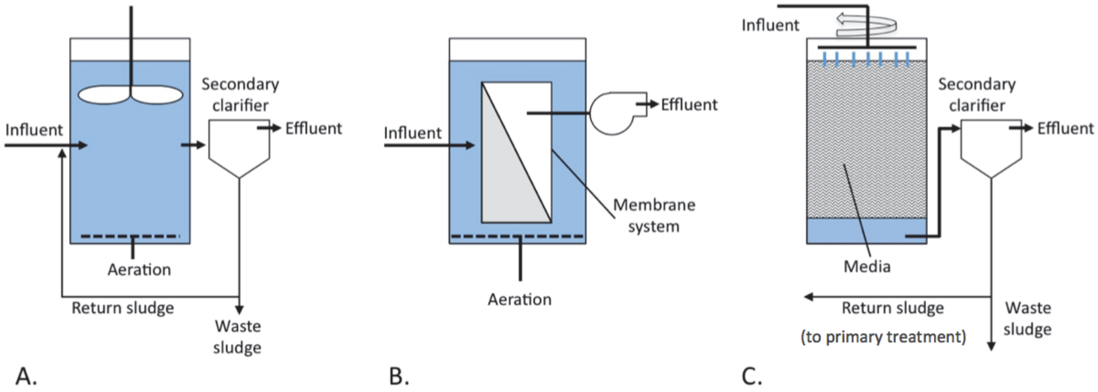

Figure 1.3. Configurations of three systems used for biological nitrification: CAS (A), MBR (B), and trickling filter (C).

Membrane Bioreactor

MBRs also utilize suspended growth bioreactors, but they replace the sedimentation processes with low-pressure membranes for solid-liquid separation [Figure 1.3(B)]. The MBR configuration can be either integrated (with the MBR unit situated within the aerobic bioreactor) or external (with the MBR outside of the bioreactor). Negative pressure pulls water through the membranes and leaves the solids within the reactor. Compressed air is applied at the base of the MBR to provide oxygen for the system and also physical agitation of the membranes. This mechanical scouring helps to control the fouling of the membranes by biomass growth. By decoupling the volumetric loading rate and solids separation, MBRs allow for shorter hydraulic residence times and longer SRTs. Consequently, MBRs benefit from having smaller footprints and lower sludge productions. The longer SRTs favor the development of nitrifying bacterial populations.

Trickling Filter

The trickling filter is an attached growth process that utilizes support media (stones, plastic, wood) as a surface for the development of biofilms. The media are placed within a basin or tower, and wastewater is applied over the media (Figure 1.3[C]). As the wastewater passes over the media and diffuses into the biofilm, the microorganisms oxidize both organic matter and ammonia. Most of the volume within the basin is occupied by air, as the wastewater does not submerge the loosely packed media. Accordingly, the natural flow of air through the filter is typically sufficient to ensure sufficient oxygen at the surface of the biofilms. Biofilms increase in thickness as they develop, leading to sloughing. As with CAS, the sloughed solids are typically removed from the liquid stream via secondary clarification.

Combined Processes

Trickling filters can be combined with an activated sludge (TF/AS) or a solids contact (TF/SC) process to form a hybrid process. The solids contact process is a suspended growth system with a short aeration period. In a combined process, the trickling filter precedes the activated sludge or solids contact process, and the clarifier follows the activated sludge or solids contact process.

Many conventional and MBR systems that practice nitrification also couple their systems with biological denitrification—the conversion of nitrate to nitrogen gas. The process of nitrification-denitrification (NDN) not only improves the water quality by removing nitrogen to a great extent from the wastewater but also improves the economics of secondary treatment by reducing the oxygen demand. Aeration for secondary processes is typically the highest cost of wastewater treatment, with DO being used to oxidize wastewater organic material (resulting in BOD). Nitrifying systems typically have higher aeration demands because of the need to also oxidize ammonia to nitrate.[1] NDN systems take advantage of the nitrate formed in the nitrification process to reduce the overall aeration demands. They do this by cycling nitrified effluents from the aerobic zones of the basin back to an upstream anoxic zone. In the anoxic zone, the bacterial populations oxidize BOD by using nitrate as their terminal electron acceptor instead of oxygen. By using nitrate instead of oxygen in these zones, the NDN systems remove the BOD, resulting in lower aeration (oxygen) demands. Both the modified Ludzack-Ettinger (MLE) and Bardenpho secondary processes discussed in Chapter 2 are examples of NDN processes.

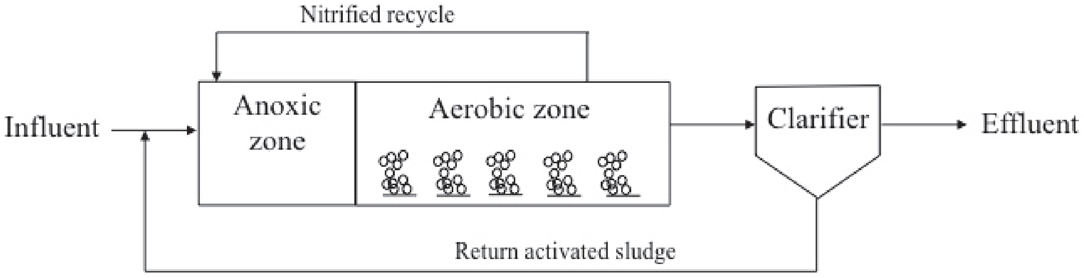

Figure 1.4. Schematic of a secondary process designed for NDN.

Note: Nitrified effluent from the aerobic zone is recycled back to the anoxic zone to promote microbial degradation of organic material with nitrate.

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[1] One major exception is nitrifying trickling filters, which require no aeration blowers and thus have significantly lower operational costs. Such filters cannot, however, perform both nitrification and denitrification.

1.4 Impact of Nitrification on Chlorine Disinfection

1.4.1 Effect of Nitrification on Chlorine Disinfection

The benefits of nitrification extend beyond environmental and public health benefits to include treatment and water quality. Nitrifying plants transform N from its most reduced form (ammonia) to its most oxidized form (nitrate). Although chlorine can combine with ammonia to form chloramines, it cannot further react with nitrate. Therefore, chlorine added to nitrified water remains in the free chlorine form and does not form combined chlorine. When chlorine is present in the more potent free chlorine form, it can achieve inactivation at greatly reduced CT values compared with chloramine.

The benefits of disinfection with free chlorine (vs combined chlorine) are manifold. Most importantly, the lower CT requirements translate to shorter contact times and smaller chlorine contact basins (CCBs). This reduction in basin size allows for important savings in capital costs (i.e., less concrete requirements) and benefits facilities where footprint space is at a premium. For example, satellite reuse facilities could benefit from free chlorine disinfection, especially those situated in highly developed regions where space is the overriding constraint. Smaller contact basins could allow such facilities to consider chlorine disinfection versus other small-footprint alternatives such as UV.

1.4.2 Using Online Ammonia Analyzers to Verify Nitrification Efficiency

As previously discussed, high CT values have been required for recycled water disinfection because current regulations assume that when chlorine is added, disinfection of recycled water occurs via chloramine disinfection. Facilities that fully nitrify, however, are capable of disinfecting with free chlorine. Obtaining regulatory credit for free chlorine disinfection is not straightforward and requires overcoming many hurdles. One of the main regulatory hurdles is providing evidence that nitrifying facilities can consistently and reliably eliminate ammonia prior to disinfection. Studies have shown that changing effluent ammonia concentrations can be successfully modeled, but only over time scales of weeks to months (Cox, 2003). Most ammonia breakthrough events, however, are short-duration events below the temporal resolution of the modeling. In other words, modeling provides information on longer-term events or trends but not on short, discrete changes.

One option for demonstrating nitrification reliability is to monitor ammonia concentrations continuously with online ammonia analyzers. The ideal instrument would be specific for ammonia (free from interference from other species), sensitive (capable of detecting low levels of ammonia), and unaffected by external conditions. The ability to both control and monitor the nitrification process is discussed in detail in Chapter 2.

Chapter 2

Measuring Nitrification Reliability

Two of the primary goals of this study are (1) to document and characterize the reliability of the nitrification process at existing water recycling facilities and (2) to use this information to refine or develop a new definition of reliability in the context of free chlorine disinfection. The focus of Chapter 2 is on the first goal—understanding nitrification reliability at existing facilities. In this chapter, reliability is broken down into two key components: process reliability and monitoring reliability. Process reliability describes the effectiveness and consistency of the nitrification process itself, whereas monitoring reliability refers to the technical capacity to monitor and verify the nitrification process.

To gauge process reliability, we needed to detect both the transient and massive nitrification failures previously discussed. Therefore, it was necessary to look at two different time scales for evidence of both long-term and short-term process failures. For evidence of long-term process reliability, the historical ammonia recordings from different water recycling facilities were obtained and analyzed. These data are typically grab samples taken at a frequency of no more than once per day. Although these data provide evidence of extended, long-term failures, they do not have the temporal resolution to detect failures of shorter duration (e.g., less than a day). To focus on short-term reliability, online ammonia analyzers were installed and operated at four facilities to obtain high resolution data over a shorter period of time.

The field testing of ammonia analyzers also provided an opportunity to assess the second form of reliability: monitoring reliability. One of the main issues in achieving free chlorine disinfection credit is demonstrating the proper functioning of the nitrification process. Online ammonia monitors were tested during the field studies to determine if they could serve as a reliability metric to continuously demonstrate compliance. The following sections describe the testing and the results from the reliability studies, beginning with the online ammonia analyzers.

2.1 Online Ammonia Analyzers

2.1.1 Online Ammonia Analyzer Overview

The three online ammonia analyzers that were used in the field studies underwent a series of tests including laboratory validation, field validation, and field testing. The comparative strengths of the various analyzers had not been documented in head-to-head studies, so this study sought to undertake concurrent testing of the three analyzers to address this unknown. Two minimum criteria for the selected analyzers were that they provide (1) a sufficiently high level of sensitivity and (2) continuous or near-continuous monitoring of ammonia levels. The basic characteristics and layout of the analyzers tested are presented in Table 2.1 and Figure 2.1. All three meet the minimum requirements, but they have significant differences in terms of detection methodologies and measurement frequency. The project team decided a priori that all analyzers provided sufficient temporal resolution to be able to detect transient ammonia upsets, with the caveat that this assumption would be reassessed after the field testing.

Table 2.1. Summary of Online Ammonia Analyzers Used in the Study

Model	Range (ppb)	Detection Method	Detection Frequency	Temporal Sensitivity
Waltron □AI-9046	0–7500[a]	Colorimetric	12 min	12 min
ATI Q45N	50–20,000	Chloramine-specific membrane sensor	1 min	1–2 min
WTW TresCon OA110	128–12,800	Measures NH_3 gas with ammonia ISE	3 min	2–5 min

Note: [a] 750–7500 ppb is by autodilution

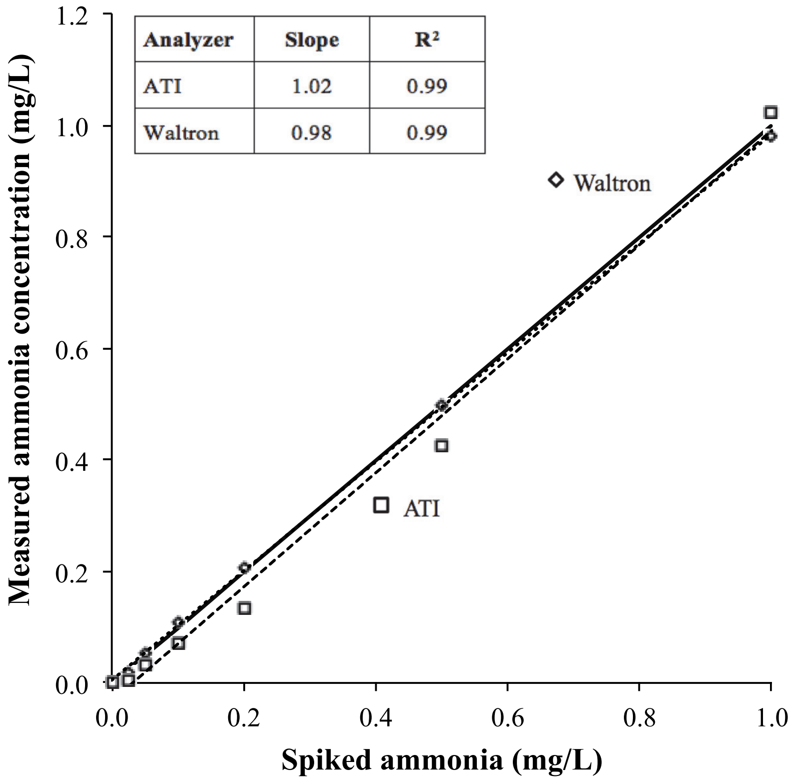
Figure 2.1. Ammonia analyzers tested during the nitrification reliability study: Waltron, ATI, and TresCon instruments (left to right).

One of the principal goals of the study was to assess the monitoring reliability provided by existing technologies, that is, our technical capacity to monitor and verify the nitrification process. To hone in on this question, the analyzers were subjected to a variety of tests meant to assess the following key parameters:

- Accuracy: analyzer accuracy was understood in terms of the closeness of the reported value to the actual value, the ability to maintain accuracy between calibrations, and freedom from interfering compounds
- Sensitivity: analyzers were assessed in terms of both chemical sensitivity (i.e., detection limits) and time sensitivity (i.e., temporal resolution)
- Robustness: analyzer robustness was a measure of the durability of the instruments based on the O&M requirements and the time spent online

2.1.2 Laboratory and Field Assessment of Ammonia Analyzers

Prior to field testing, the ammonia analyzers were tested in the laboratory to determine their accuracy under controlled conditions. In these tests, known concentrations of ammonia were spiked into deionized water and measured using the online analyzers. Results from these laboratory tests are presented in Figure 2.2.



Analyzer	Slope	R^2
ATI	1.02	0.99
Waltron	0.98	0.99

Figure 2.2. Laboratory testing results of the Waltron and ATI analyzers before field deployment.

Note: Each data point represents the average of five replicate samples

As can be seen from the data, both Waltron and ATI analyzers had the sensitivity to detect low concentrations of ammonia (< 0.1 ppm) while providing accurate, linear responses to increasing ammonia concentrations over the range from 0 to 1 ppm.[2] The temporal sensitivity of the monitors was tested by measuring the time it took the monitors to respond to changes in ammonia concentrations (Table 2.1). In general, the measurement frequency was nearly identical to the temporal sensitivity. One explanation for differences between the two—particularly when the temporal sensitivity was longer than the measurement frequency—is the incomplete purging of the sample tubing between measurements. Were this to occur, differences between two samples might be buffered out as a result of dilution with the previous sample.

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[2] The TresCon unit had not yet arrived at the time of lab testing.

In addition to the controlled laboratory conditions, the accuracy of the monitors was also tested through a series of field validation studies conducted during operation at each site. As in the lab validation tests, the field tests evaluated monitor accuracy by exposing the monitors to increasing concentrations of ammonia. The difference between the field and lab tests lies in the sample matrix: whereas the lab tests used deionized water that was essentially ammonia-free, the field validations used nitrified effluents as the matrix. These effluents exhibited low ammonia levels but were not "ammonia-free"; thus, background levels were subtracted from the readings (Figure 2.3).

One difficulty in assessing accuracy during field tests was the presence of ammonia in the background matrix. The accuracy of the monitors is typically listed as a percentage range relative to the measured value, for example, +/- 5% of the measured value. Thus, it is more difficult to differentiate spikes of low ammonia concentration when the background levels are high. Nevertheless, the monitors responded well to the field validation testing, with nearly all values falling within +/- 25% of the spiked value.

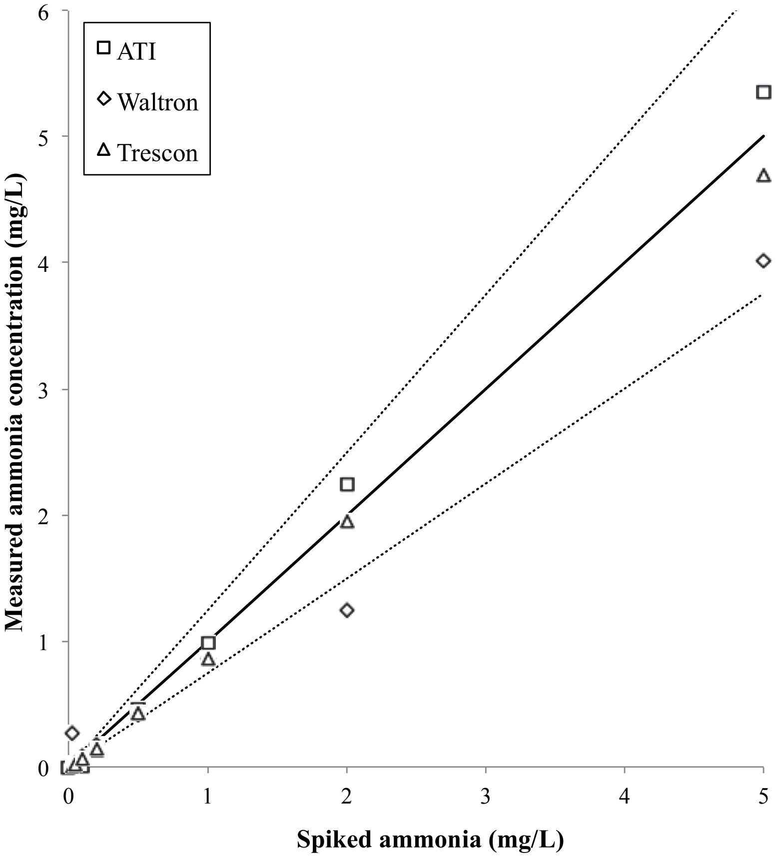

Figure 2.3. Results of field validation for the three ammonia analyzers.

Note: Values shown are averages from validations performed at each of the four test facilities**.**

2.1.3 Online Ammonia Analyzer Operations and Maintenance

Reliability of the monitors was also evaluated based on their robustness in terms of continuous measurement, durability, and O&M requirements. A comparison of the O&M requirements of the different analyzers is provided in Table 2.2.

Table 2.2. Ammonia Analyzer Comparison

Manufacturer	Waltron	ATI	WTW TresCon
Model	mAI-9046	Q45N	OA110
Accuracy/Precision	Performed well in lab and field conditions; accurate at low ammonia concentrations (< 750 µg/L)	Performed well in lab and field conditions	Performed well in lab and field conditions
O&M			
Design	More complex design (less automated)	Simple, robust design (more automated)	Simple, robust design (more automated)
Calibration frequency	Automatic calibration; recommended frequency every 7 days (4 day cycle used during this study)	Manual calibration performed weekly	Automatic calibration every 24 h; option to calibrate every 1, 2, 3, 6, 12, or 24 h
Part replacement frequency	Peristaltic pump tubing requires replacement approximately every 6 months (not replaced during this study) 20 µm filter replaced weekly if there is high TSS in the feed water	Reagent pump tubing requires replacement every 3 months Sample pump tubing requires replacement every 6 months	Reagent pump tubing requires replacement every 2 weeks Membrane requires replacement every 2–3 weeks when measuring high hardness water
Parts cost	No parts were replaced during this study	Reagent pump tubing (package of 10) $100 Sensor electrolyte $40	3 membrane caps $327 Sensor electrolyte $21 Tubing maintenance kit $124
Troubleshooting	Manual calibration required at times System cleaning with hydrochloric acid required if scaling occurs	Calibration failures and inaccurate readings may require - Checking sensor for membrane fouling - Ensuring delivery of chlorine and H_2O_2 - Unclogging of smaller tubing	After calibration alarm - Replace membrane sensor - Replace reagent pump tubing - Replace ammonia standard solution
Estimated frequency of maintenance	Check reagent status and remove scaling (if necessary) daily Check calibration status weekly	Check calibration status weekly	Check status daily (for faulty alarm) Check calibration status weekly

Manufacturer	Waltron	ATI	WTW TresCon
Reagents			
Reagent cost	~ \$420/month (reagents and one standard; additional standard \$70/month)	~ \$70/month (includes reagents but not the cost of weekly NH_3 lab measurement needed for calibration)	~ \$250/month (reagents, standards, and cleaning solution)
Shelf life once opened	1 month for low ammonia standard (< 750 µg/L); 1–2 weeks for high ammonia standard (> 750 µg/L)	1 month	1 month
Other considerations		Peristaltic pump requires long priming period after replacing reagent tubing Most reliable in the field Minimal and easy maintenance	Alarms allow rapid detection of failures but automatically cease ammonia monitoring Minimal and easy maintenance Improvements to operations manual needed

One feature of the TresCon that was noted as a potential reliability issue was the fact that the monitor stops monitoring when one of its automated alarms is triggered. These alarms can serve a beneficial purpose in terms of monitoring nitrification reliability; for example, they could be tied into a facility's supervisory control and data acquisition (SCADA) system with automated alarms to notify operations of an analyzer issue. During this testing, however, the system was not tied into a SCADA system, and so frequently these alarms were not immediately recognized and addressed. Once the alarm was activated, the TresCon stopped monitoring the process stream, resulting in data gaps during periods of testing.

2.2 Donald C. Tillman Water Reclamation Plant

2.2.1 Background

The Donald C. Tillman Water Reclamation Plant (WRP) began continuous operation in 1985 serving the area between Chatsworth and Van Nuys in the western portion of the San Fernando Valley, CA. It was initially designed to treat 40 million gallons per day (MGD) of wastewater but was later expanded to treat up to 80 MGD, of which approximately 40% is from commercial operations and 60% from residential.

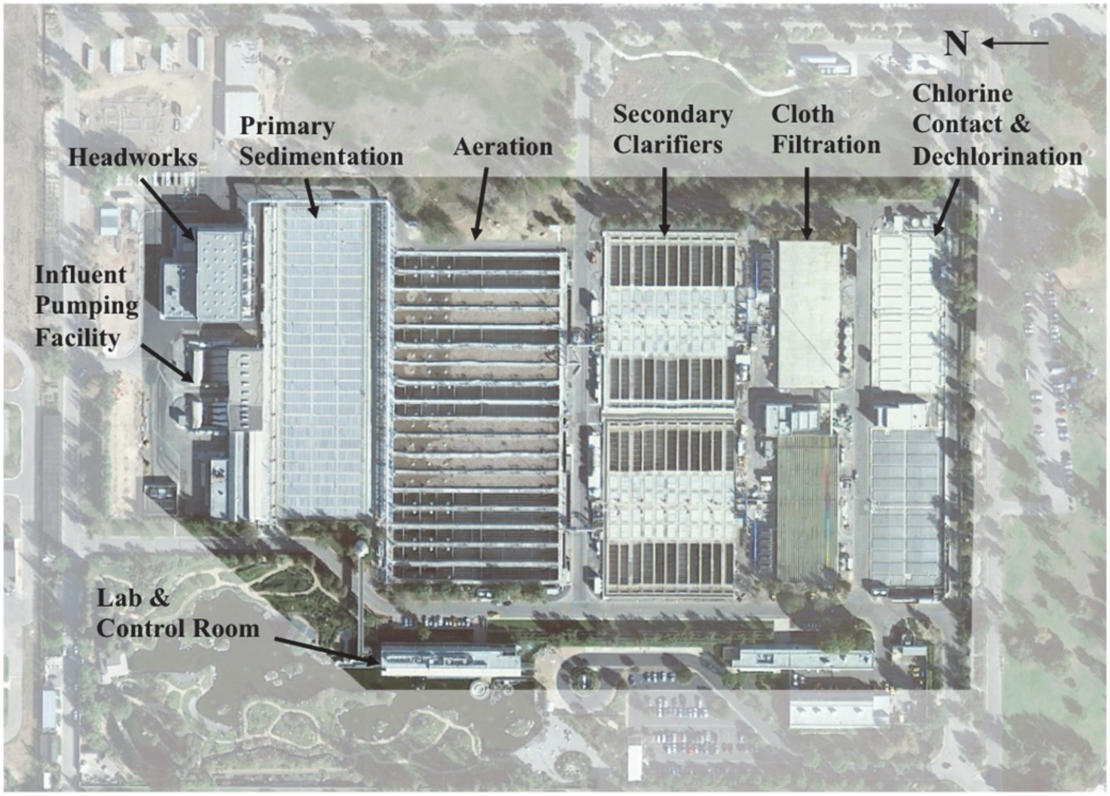

Figure 2.4. Aerial view of Tillman WRP.

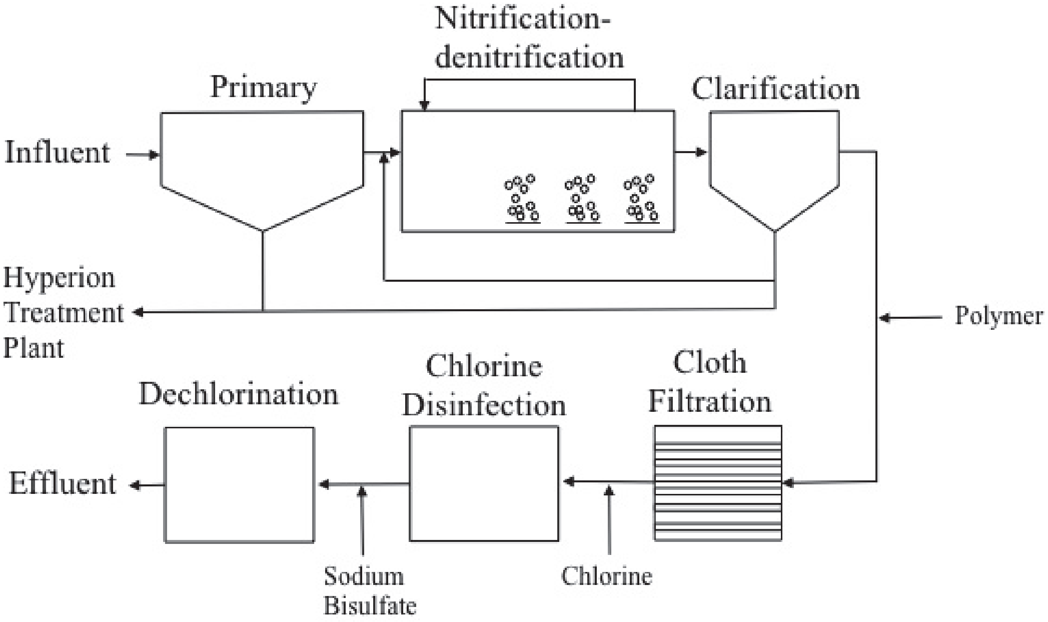

Figure 2.5. Tillman WRP treatment train process flow diagram.

The biological treatment at the Tillman WRP is CAS that has been modified to support the NDN process (Figure 1.4). Biochemical reactions in the basin lead to the degradation of organics and the transformation of reduced nitrogen (NH_3) to nitrate via nitrification as well as to the subsequent transformation of nitrate to N_2 gas via denitrification. The aeration tanks are followed by a secondary clarifier that separates the biomass in the effluent from the liquid stream as shown in Figure 2.5. A recycle system redirects a portion of the activated sludge back to the aeration tank to maintain biological equilibrium, while the remaining portion is discharged to the sewer, which flows to the Hyperion Treatment Plant.

2.2.2 Process Performance in Ammonia Removal

The results of the continuous online ammonia monitoring at the Tillman facility from September to December 2011 are presented in Figure 2.6. Data from the TresCon unit are not included because the instrument had not yet arrived from the manufacturer. Toward the end of the testing, the readings from the ATI instrument began to increase. The reasons for this increase were not determined; however, the fact that the instrument worked correctly at subsequent field-testing sites suggests that the cause of the increased concentrations may have been calibration issues, sensor fouling, or issues with the chemical reagents.

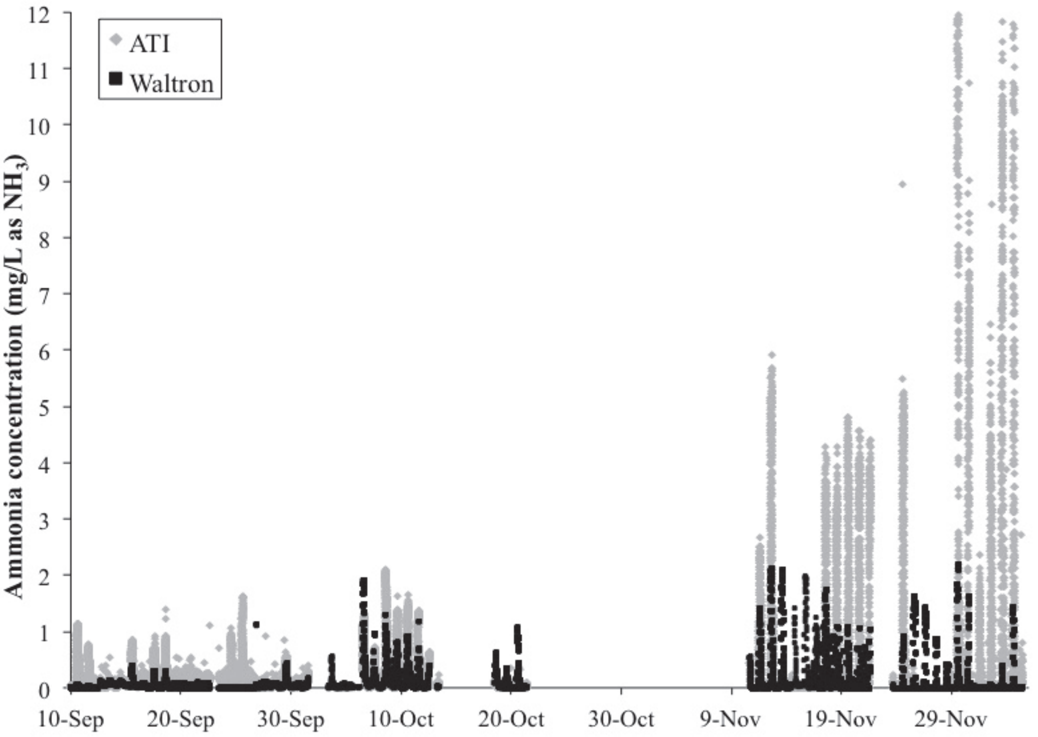

Figure 2.6. Online ammonia concentration data recorded at Tillman WRP from September through early December 2011.

With the exception of the inaccurately high levels from the ATI, the nitrification process at Tillman showed consistently low levels of ammonia in the effluent. One salient feature of the ammonia profiles from the two monitors was the daily bleed-through events. Figure 2.7 focuses on 1 week of the data to provide further detail on the diurnal fluctuations in ammonia levels. Both the Waltron and ATI instruments were able to consistently detect the ammonia bleed-through that occurred each afternoon as a result of peak ammonia mass loading. The ammonia concentrations during these bleed-through events were below 2 mg/L 95% of the time and below 0.5 mg/L 90% of the time. These levels of ammonia during bleed-through events are high but within the range of concentrations that might realistically be overcome by breakpoint chlorination. Although the historical data were not analyzed in this study, the testing at least provides short-term evidence that the nitrification process is both consistent and reliable.

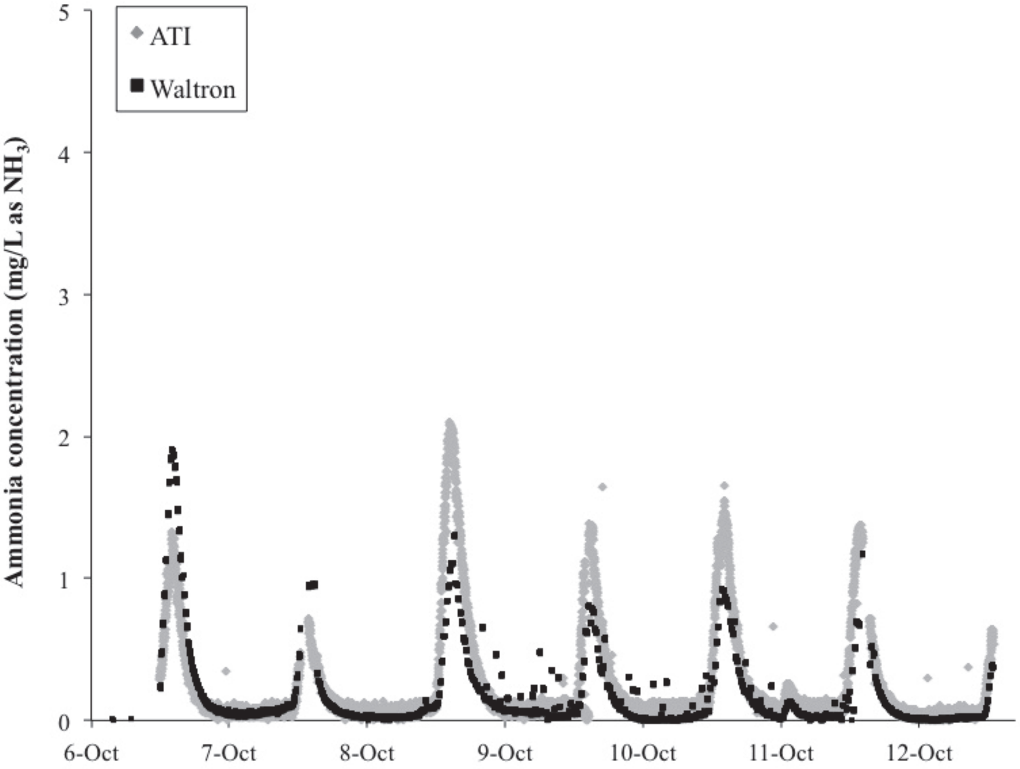

Figure 2.7. Online data recorded from Oct 6 through Oct 12, 2011 at Tillman WRP.

Figure 2.7 also provides evidence of the high level of monitoring reliability provided by the analyzers, particularly with regard to the congruity between the profiles—both ammonia peaks and low-ammonia effluents were similarly detected by both monitors. One question that remains is the cause of the ATI variability at the end of testing. These fluctuations with higher values were also observed at subsequent sites but to a lesser degree. Changes were made to the maintenance frequencies of the instruments between the second (Santa Paula) and third (San Diego) sites. Nonetheless, the ATI continued to read higher background concentrations (as compared with the other instruments), a fact that was unresolved and may have been a result of some interference with background ion concentrations.

2.3 Santa Paula Water Recycling Facility

2.3.1 Background

The Santa Paula Water Recycling Facility (WRF) is located north of Los Angeles in Ventura County, CA (Figure 2.8). In operation since 2010, the facility has the capacity to treat a design average dry weather flow of 4.2 MGD. The existing MBR process can treat 3.4 MGD, but additional membranes can be added to expand the rated capacity to 4.2 MGD.

Figure 2.8. Aerial view of the Santa Paula WRF.

The biological process at Santa Paula WRF includes nitrification and denitrification in an MBR that uses an ultrafiltration (UF) membrane for solids separation (Figure 2.9 and Figure 2.10). Nitrogen transformation occurs in two zones, an anoxic zone followed by an aerobic zone. The two zones are connected through internal recycling, which brings nitrates from the aerobic zone back to the anoxic zone, where denitrification occurs. After separation by UF, the waste activated sludge (WAS) is thickened and further treated by aerobic digestion, allowing for further nitrification of any remaining ammonia. The digesters are maintained in aerobic conditions by air diffusers that provide DO. The solids are dewatered, and return flows are sent to the MBR.

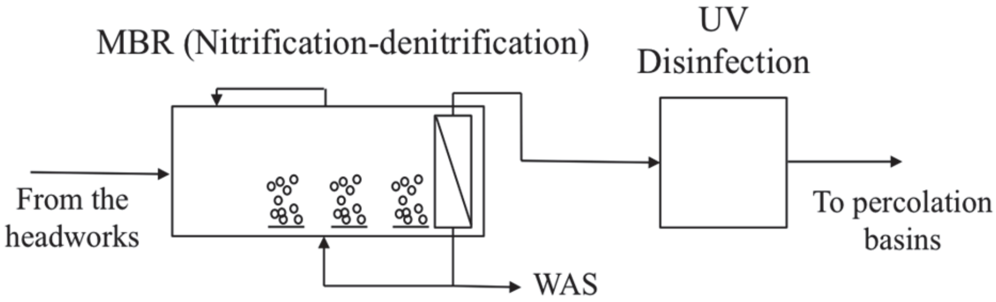

Figure 2.9. Santa Paula WRF treatment train process flow diagram.

Figure 2.10. Santa Paula WRF's membrane separation tanks.

2.3.2 Historical Review

The historical performance of the nitrification process is illustrated in Figure 2.11, which shows the ammonia concentrations of weekly grab samples over the period from April 2011 to January 2012. During this period, nitrification reliability was high with average ammonia concentrations of 0.50 mg/L. Furthermore, the facility achieved very consistent performance with 95% of the measurements below 1.2 mg/L and all but one measurement below 1.36 mg/L. The cause of the single high value (7.1 mg/L) in January 2012 is not known.

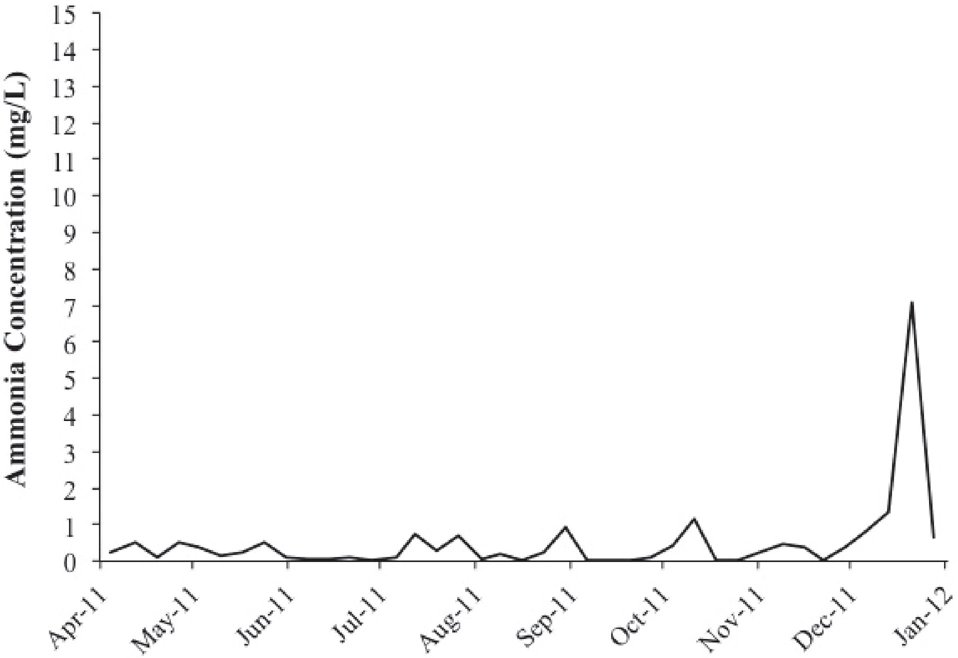

Figure 2.11. Effluent weekly grab samples from Santa Paula WRF from April 1, 2011 through Jan 31, 2012.

2.3.3 Process Performance in Ammonia Removal

The ammonia analyzer skid was installed at the Santa Paula WRF in early December 2011. Data recorded at Santa Paula WRF during the months from January through March 2012 are reported in Figure 2.12. Unfortunately, during this period one of the aerobic digesters experienced a diffuser failure in its aeration system. The failure of the diffuser allowed ammonia levels to build up within the digester. Consequently, the recycle streams from the solids handling greatly increased the ammonia loading to the MBR process. Although the microbiological population in the MBR was still nitrifying, the high loading from the digester return overloaded the system and allowed moderate levels of ammonia to pass through the tertiary process. These high loads occurred daily when the manual digester wasting was performed. The higher ammonia levels in the secondary effluent were therefore the result of a mechanical failure, not a biological upset. Repairs to the diffuser began during the testing period at Santa Paula and were ongoing throughout the study period.

The downside of this blower failure was that the nitrification reliability of the WRF could not be measured under typical conditions. Based on the historical data, however, the facility maintains a high level of control over the process. One benefit of testing during this period was that it provided an opportunity to evaluate the instruments during a period of elevated ammonia concentrations. Figure 2.12 shows that each instrument was responsive to the higher ammonia levels present. The concentrations that were measured varied from instrument to instrument, but all responded to the ammonia spikes present. Short-term ammonia bleed-through occurred on a near-daily basis in the late morning. Peak ammonia concentrations were about five times larger than average concentrations.

Daily ammonia concentrations were also tested periodically during the testing period using grab samples measured with a bench-top ammonia monitor (data not shown). The average ammonia concentrations observed through grab sampling were significantly less than the instantaneous peaks recorded by the online analyzers. This finding emphasizes the need for near-continuous ammonia monitoring to ensure nitrification reliability given that grab samples typically fail to capture transient peaks that would impact a free chlorine disinfection strategy.

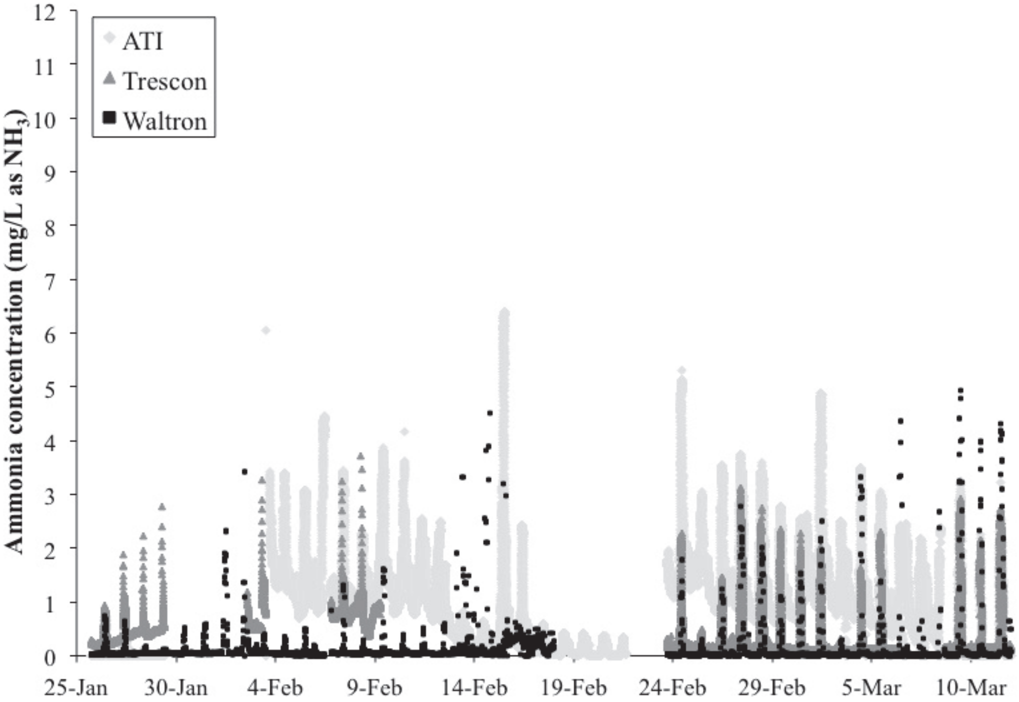

Figure 2.12. Online ammonia concentration data and operator-collected grab samples recorded at Santa Paula WRF from January through March 2012.

Figure 2.13 focuses on 1 week of the data to provide further detail on the diurnal fluctuations in ammonia levels. Although all three instruments provided simultaneous detection of ammonia bleed-through events, one important aspect is the difference in the background and peak ammonia levels detected between them, particularly the ATI. One possible explanation for this discrepancy is that at lower concentrations, there was background interference with other ions in the water. Alternatively, the high background levels reported by the ATI may have been related to calibration; the frequency of maintenance was increased after testing at the Santa Paula facility.

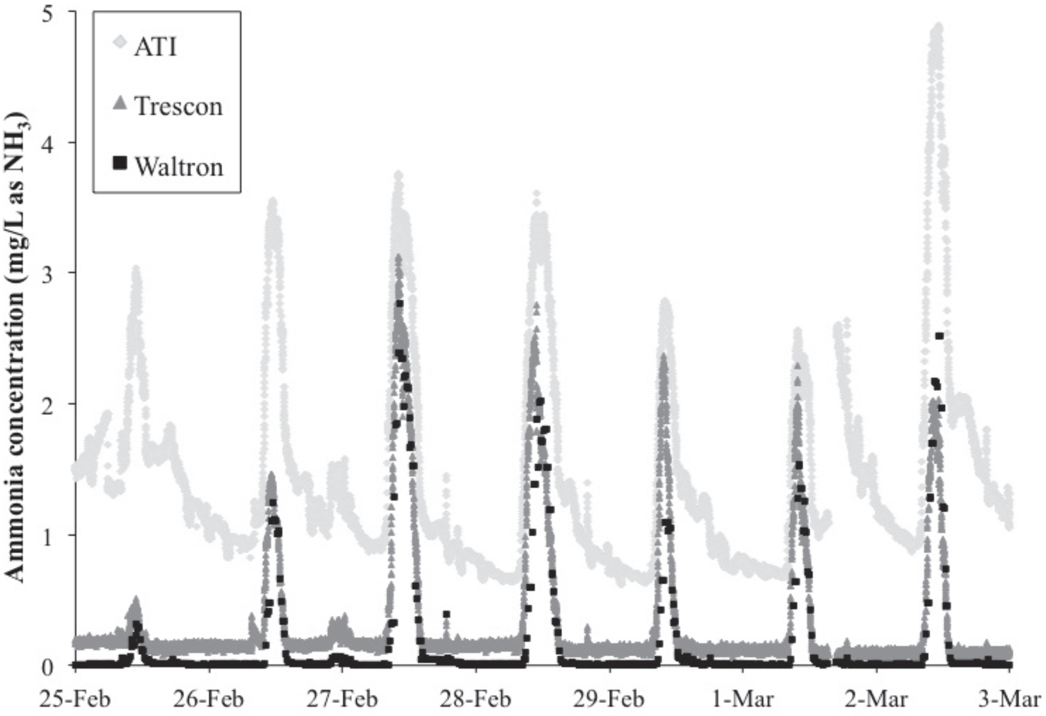

Figure 2.13. Online ammonia concentration data recorded at Santa Paula WRF from Feb 25 through March 2, 2012.

2.4 North City Water Reclamation Plant

2.4.1 Background

The North City WRP has been producing recycled water for communities in northern San Diego, CA since 1997. The 30 MGD facility is the first large-scale water recycling facility in San Diego. Recycled water uses include irrigation, landscaping, and industrial applications.

Figure 2.14. View of North City WRP's covered aeration basins.

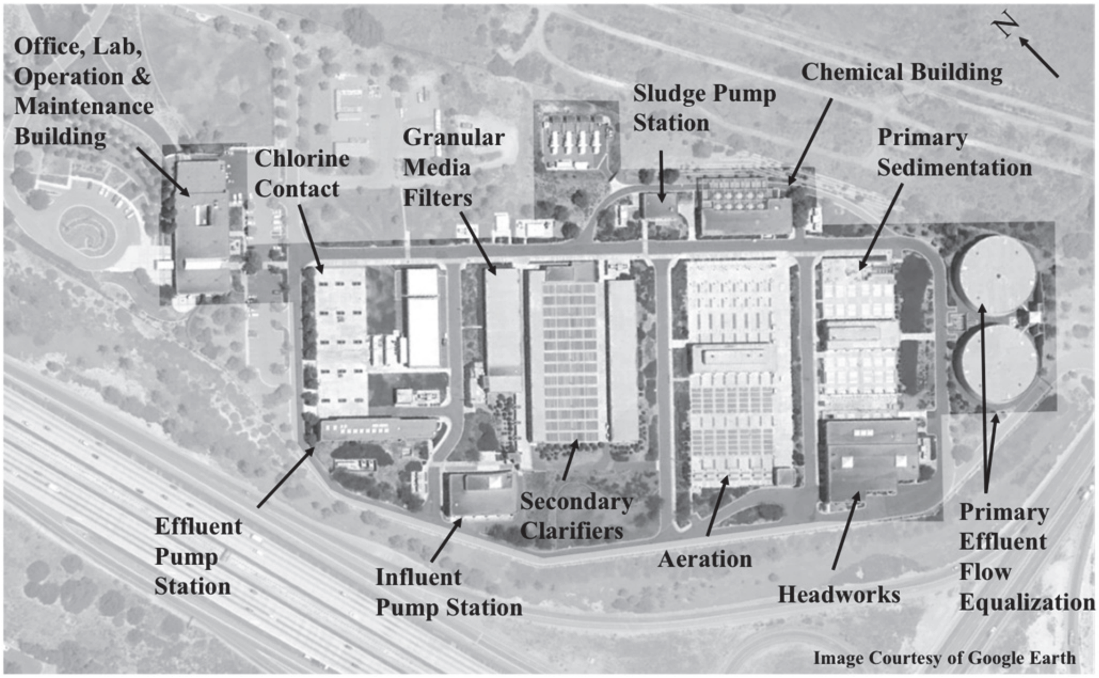

Figure 2.15. Aerial view of North City WRP.

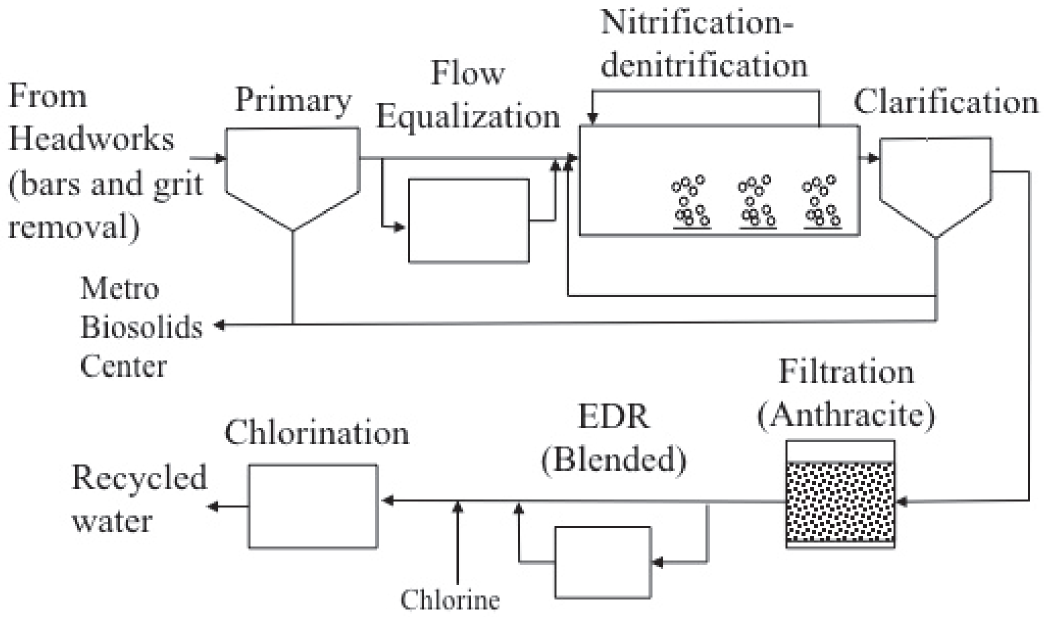

Figure 2.16. North City WRP treatment train process flow diagram.

Note: EDR = electrodialysis reversal.

The biological process at North City WRP is a modified Ludzack-Ettinger (MLE) process that incorporates an anoxic zone upstream of the CAS process to achieve partial denitrification. The MLE process is similar to the Santa Paula WRF biological processes; the main difference is that MLE has a return on mixed liquor to the anoxic zone. Anoxic selection is used to control the growth of filamentous organisms in the activated sludge.

2.4.2 Historical Review

The historical performance of the nitrification process at North City WRP from January 2010 to April 2011 is illustrated in Figure 2.17. During this period, the average ammonia concentration was 0.7 mg/L, though readings were not taken during the entirety of this 16 month period. Approximately six bleed-through events saw ammonia concentrations exceed 5 mg/L, with the maximum reaching up to 12 mg/L. Although elevated, these peak ammonia concentrations were typically short-lived (i.e., not lasting longer than a single sampling period).

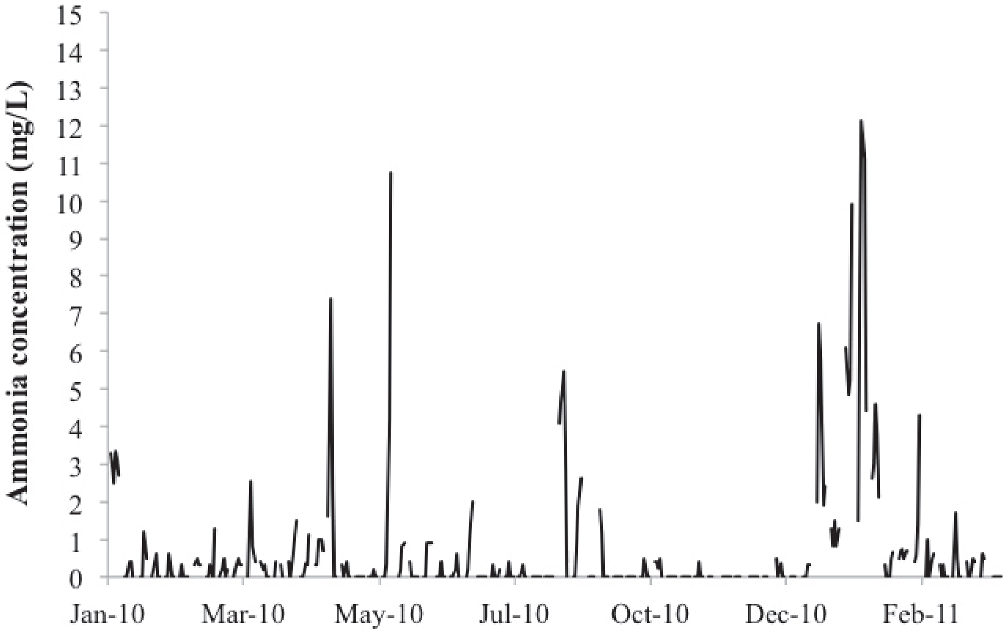

Figure 2.17. Secondary effluent grab samples from North City WRP from Jan 1, 2010 through April 1, 2011.

2.4.3 Process Performance in Ammonia Removal

Ammonia analyzers collected data at the North City WRP from the beginning of April to the middle of May 2012 (Figure 2.18). The analyzers were installed at the effluent of the granular media filters and upstream of chlorine addition. In the first 10 days of testing, there was an upset in the nitrification process that was due to low solid retention times (SRTs; data not shown). The low SRTs were the direct result of a high rate of wasting of the WAS. After recovering from this upset, the filtered ammonia concentrations were typically low (< 0.5 mg-NH_3/L) with near-daily ammonia bleed-through events lasting approximately an hour with average ammonia spikes of 1.2 mg/L. The daily fluctuations in ammonia concentration are shown in greater detail in Figure 2.19.

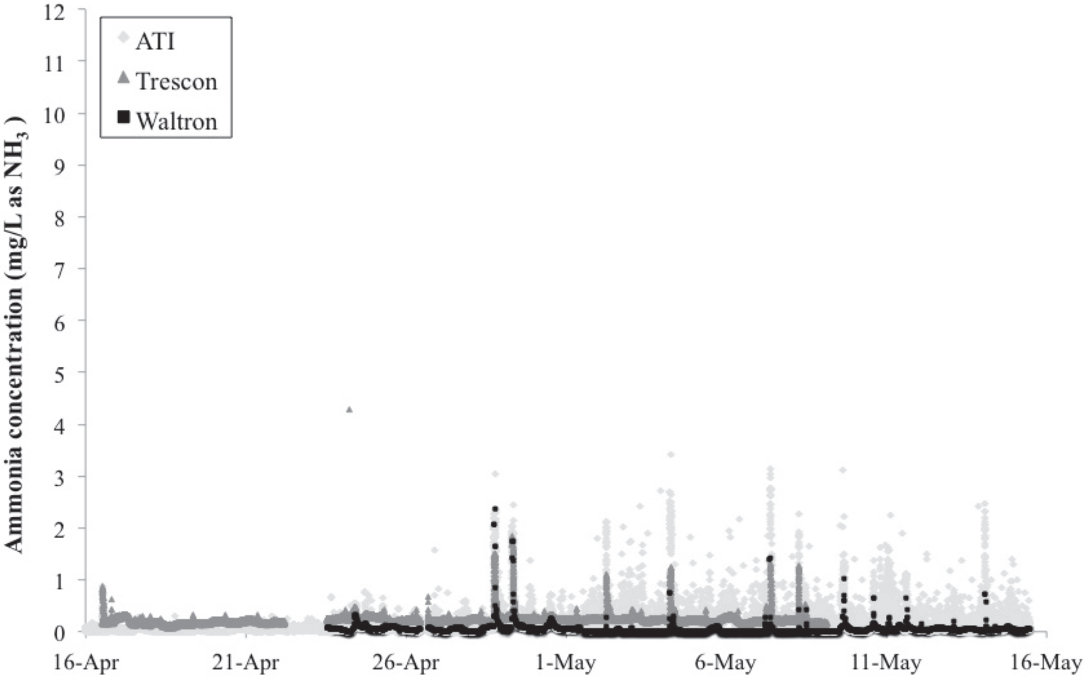

Figure 2.18. Online ammonia concentration data recorded at North City WRP from April through mid-May 2012.

As they had at previous field sites, all instruments showed similar trends during the largest ammonia peak events (greater than 1 mg/L); however, only the TreCon and Waltron instruments measured distinguishable peaks at lower ammonia levels. The ATI instrument had considerable noise at concentrations below 1 mg/L. The background concentrations reported by the ATI analyzer were more similar to those of the other analyzers at the North City facility than during testing at the other facilities; it is unclear whether this had to do with improved O&M (i.e., more frequent calibration and reagent changing) or if it was the result of a reduction in some sort of chemical interference. Because of various instrument issues, only 2 weeks of data were collected when all three instruments were in operation at the same time.

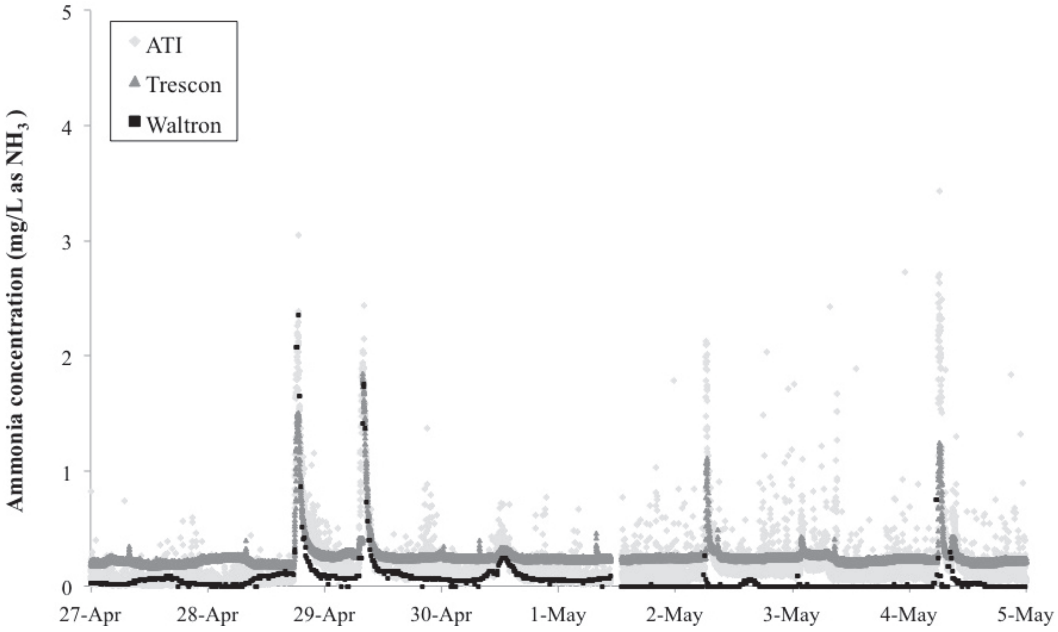

Figure 2.19. Online ammonia concentration data recorded at North City WRP from April 27, 2012 through May 4, 2012.

2.5 Padre Dam Water Recycling Facility

2.5.1 Background

Padre Dam's Ray Stoyer WRF in Santee, CA has the capacity to produce 2 MGD of tertiary disinfected recycled water. Approximately half of the recycled water is used for irrigation and commercial uses, whereas the remaining flow maintains the water levels in the Santee Lakes. The Padre Dam WRF is a satellite reuse facility: it only treats the flows needed for reuse and returns all of the solids to the sewer line. The wastewater flow not captured by the facility flows to the Point Loma Wastewater Treatment Plant in San Diego. As a result, the Padre Dam WRF flow does not experience diurnal flow variations, nor does it need to treat return flows from solids handling processes. The Padre Dam facility was upgraded in 1997 to expand the tertiary capacity and to achieve strict nutrient discharge limitations (approximately 1 and 0.1 mg/L for total nitrogen and total phosphorous, respectively, based on a 2 MGD flow).

An aerial layout and a process flow diagram of the Padre Dam WRF treatment processes are shown in Figure 2.20 and Figure 2.21. Treatment at Padre Dam includes primary treatment, secondary activated sludge, clarification, denitrifying tertiary filtration, and chlorine disinfection. The secondary treatment consists of a five-stage biological nutrient removal (BNR) activated sludge process (Bardenpho® process) followed by secondary clarification in rectangular secondary clarifiers. Settled secondary effluent undergoes further clarification which consists of coagulation (alum and polymer), flocculation, and sedimentation. Tertiary filtration with denitrifying sand filters is accomplished using methanol as a carbon source to support the denitrifying microbial populations. After chlorine disinfection, a fraction of the flow undergoes dechlorination with sulfur dioxide. Sludge and scum from the primary clarifier, WAS and scum from the secondary clarifier, and sludge from the sedimentation basins are discharged to the Metro sewer line for treatment at the Point Loma Wastewater Treatment Plant in San Diego.

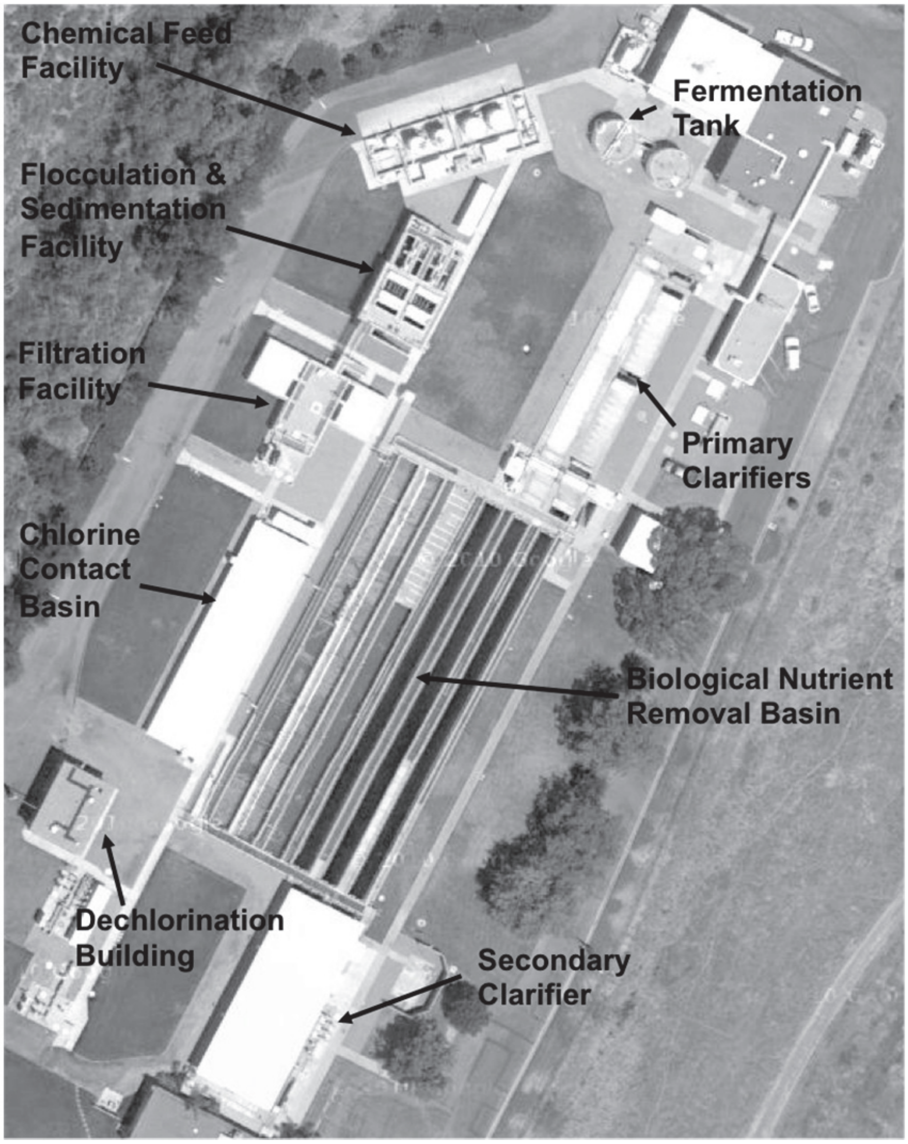

Figure 2.20. Aerial view of Padre Dam WRF.

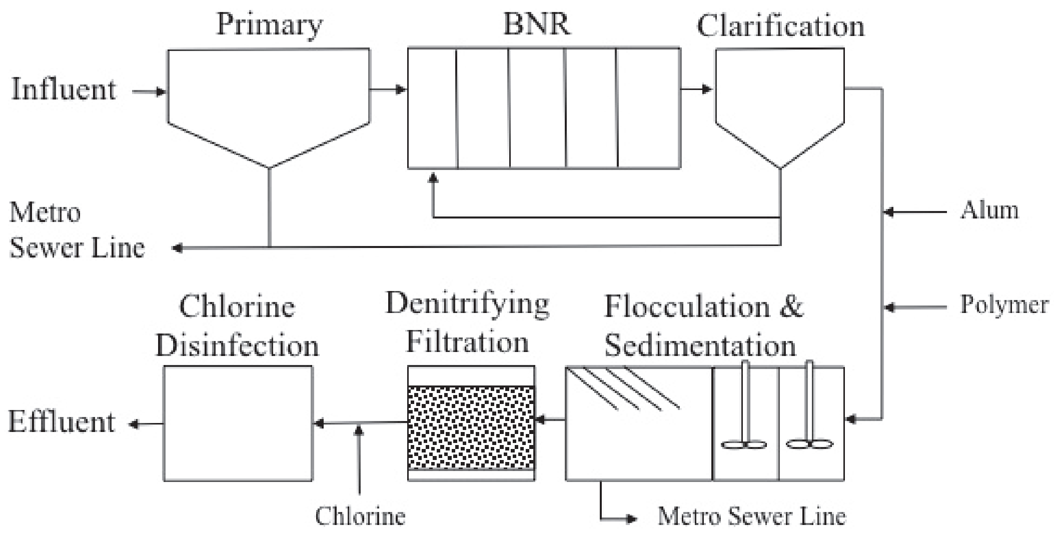

Figure 2.21. Padre Dam WRF treatment train process flow diagram with BNR.

The modified Bardenpho® process (five-stage) is a BNR process that removes nitrogen, phosphorous, and carbon (schematic in Figure 2.22; photo in Figure 2.23). The five stages are designated as anaerobic, first anoxic, first aerobic, second anoxic, and second aerobic. In the anaerobic stage, primary effluent is mixed with return activated sludge from the secondary clarifier. In the first anoxic stage, nitrified flow from the first aerobic stage (containing nitrate) is mixed with the flow from the anaerobic stage, allowing denitrification to occur. In the first aerobic stage, the addition of air promotes the process of nitrification and allows phosphorous-accumulating organisms to remove dissolved phosphorous from the water. In the second anoxic stage, additional denitrification occurs. In the second aerobic stage, air is added to reoxygenate the water, strip residual nitrogen gas, and allow for additional phosphorous uptake.

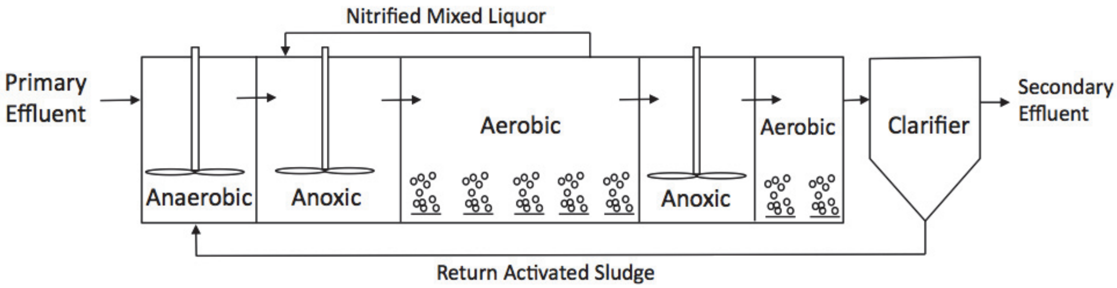

Figure 2.22. Bardenpho® BNR process diagram.

Figure 2.23. Padre Dam WRF's secondary treatment aeration basin (first aerobic stage).

2.5.2 Historical Review

Effluent ammonia data have been collected by the operations staff since 1997 when the upgraded BNR process went online. Data from 1997 to 2011 are plotted in Figure 2.24. As seen in the figure, ammonia levels below 5 mg/L were achieved throughout nearly the entire time period. Initially, a few notable ammonia events occurred as a result of several factors including significant increases in flow rate, low mean cell residence times, and low DO levels. Later transient ammonia peaks were related to planned plant shutdowns for maintenance activities. As nitrifying populations are reestablished in the secondary process after these shutdowns, brief periods of high ammonia levels are expected. This longer-term historical record therefore provides valuable information regarding the impact of different operational parameters and underscores the need to control these parameters to ensure the reliability of the nitrification process.

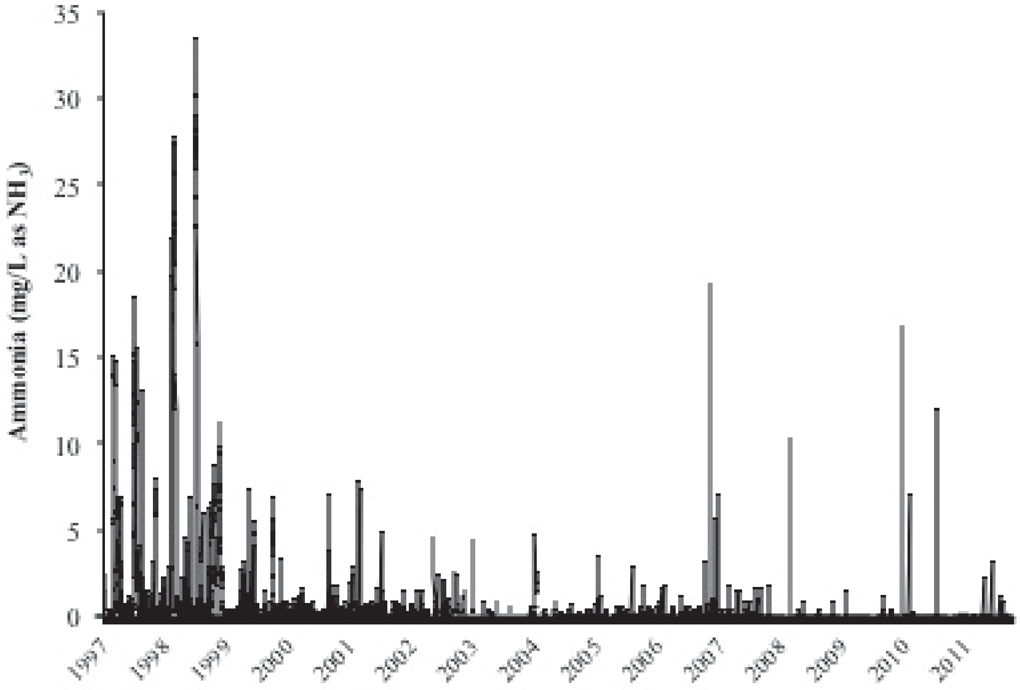

Figure 2.24. Ammonia grab samples (daily) at Padre Dam WRF from March 1997 through December 2011.

2.5.3 Process Performance in Ammonia Removal

The ammonia analyzers collected data at Padre Dam WRF from the middle of May until late June 2012. The testing skid, located downstream of the tertiary filters, was fed tertiary effluent prior to chlorination. The ammonia analyzer data collected at the Padre Dam WRF are shown in Figure 2.25. During this period, there were approximately 3 weeks when all three instruments collected concurrent data. In general, low ammonia concentrations were observed for the entire testing period, providing evidence of the high degree of nitrification reliability. A 1-week subset of the Padre Dam data is shown in Figure 2.26 to better illustrate ammonia fluctuations throughout a day. Ammonia concentrations were always below 1 mg-NH_3/L and exceeded 0.2 mg-NH_3/L less than 2% of the time. Ammonia concentrations were below the limit of detection of the ATI instrument the majority of the time; however, this analyzer also reported the highest peak concentrations. Both the TresCon and Waltron instruments reported similar results, with the TresCon displaying a slight diurnal variation in concentration that was related to its daily internal calibration process. Atypical readings were also observed immediately following a manual calibration for both the TresCon and the Waltron units. The high ammonia levels that immediately followed were determined to be artifacts of the calibration and were consequently omitted from the analysis.

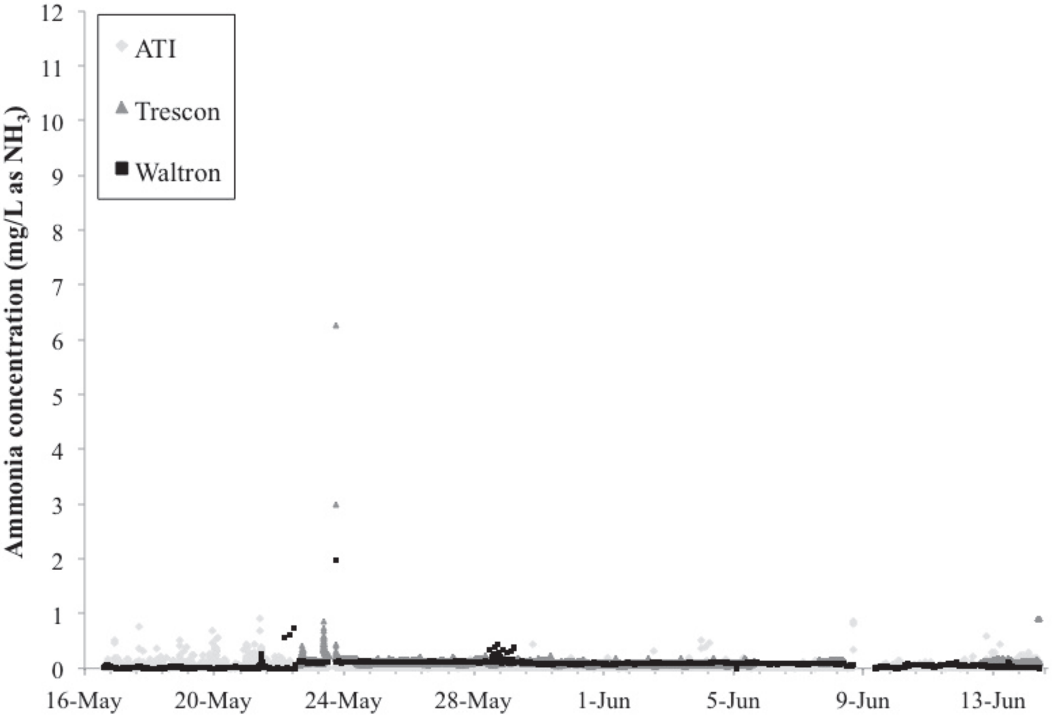

Figure 2.25. **Online ammonia concentration data recorded at Padre Dam WRF from May through June 2012.**

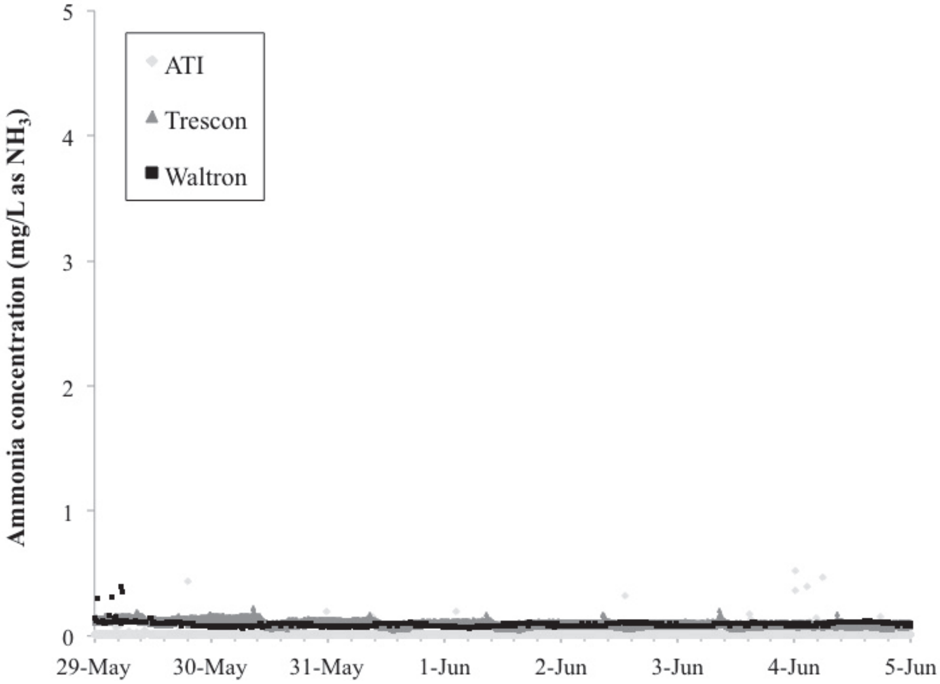

Figure 2.26. **Online ammonia concentration data recorded at Padre Dam WRF from May 29, 2012 through June 4, 2012.**

2.6 Conclusions

The field studies provide evidence that nitrification reliability can currently be achieved in terms of both process reliability and monitoring reliability. Process reliability was evaluated by monitoring ammonia concentrations in the field at four nitrification facilities. All four sites demonstrated a high degree of control over their nitrification processes. Differences were seen in the performance of the nitrification process at the four facilities tested, but all of them demonstrated that ammonia levels could be reliably controlled at low levels if a goal of continuous ammonia control were in place. Figure 2.27 provides a probability plot of the ammonia concentrations at the four facilities tested during the field trials. Numerical metrics to define what constitutes nitrification reliability have not yet been established by the industry and will likely evolve as the goals of nitrification evolve. One option is to use 1 mg/L as the nitrification goal, as this value could be reasonably overcome with breakpoint chlorination. Based on the probability plots from the field testing, all four sites achieved this goal at least 95% of the time, and three of the four achieved this level at least 99% of the time.

One important note is that nitrifying facilities do not currently operate to achieve continuous, low ammonia concentrations; the main goal is typically to achieve monthly or daily nutrient discharge limits, which are more resistant to brief periods of ammonia bleed-through. This topic is covered in greater detail in the following chapter.

The reasons that ammonia bleed-through occurred at the facilities could not be definitively identified in this study. As described in Section 1.3, a number of factors impact nitrification efficiency including the nitrification configuration (e.g., NDN), DO concentrations, SRT, flow peaks, organic loading, and ammonia concentrations. To ascertain which of these variables was primarily responsible for bleed-through, a testing campaign would be needed to provide continuous monitoring of these variables throughout the day. For example, to determine the impact of ammonia loading at a wastewater treatment plant would require the monitoring of ammonia levels both in the raw wastewater influent and in the secondary effluent. The scope of the current project did not extend beyond the testing of ammonia in the secondary effluents, and so these investigations remain outstanding. Identifying the main causes of breakthrough would provide important information for the design of nitrifying facilities in which continuous low levels of effluent ammonia are required (see Chapter 3).

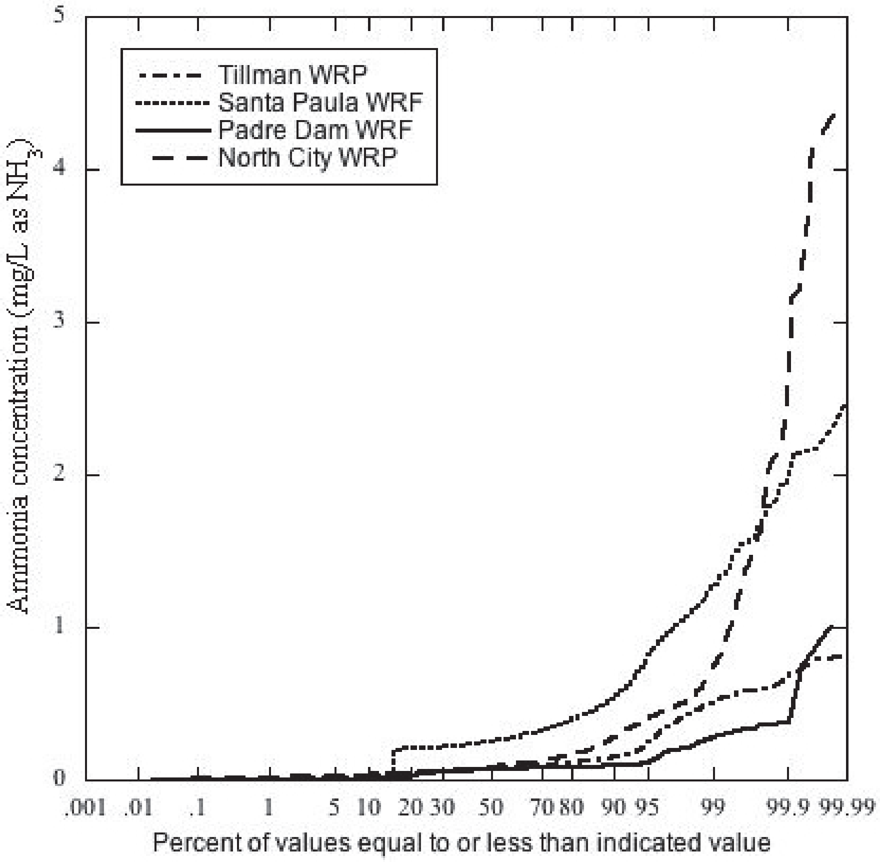

Figure 2.27. Probability distributions of the secondary effluent ammonia concentrations at the four field-test sites.

Note: Distribution functions are based on the average ammonia concentrations detected by the three online analyzers.

The ammonia data does provide some insights into potential causes of breakthrough. For example, the periodicity of the breakthrough events can be analyzed to determine the frequency and time of day at which the events occurred. Although there was no consistent pattern of the time of day *across* plants in this study, the pattern was typically consistent for a given plant. Tillman WRP showed ammonia peaks every 24 hours at roughly 2–3 p.m. The cause of these events was not determined, but the fact that they occur regularly (i.e., daily at the same time of day) should make it easier to root out the underlying cause. Future analyses should begin by looking for other water quality or flow changes that occur with the same periodicity. Similarly, the Santa Paula WRF saw regular, diurnal peaks that occurred earlier in the day, around 10 a.m. to 12 p.m. The cause of these events was likely tied to the recycling of aerobic digester streams to the secondary process. During field testing, the failure of a blower in the aerobic digester led to high levels of ammonia in the recycle streams; the presence of higher ammonia loads was likely the cause of these bleed-through events. Future studies could determine the degree to which such events occur when all blowers in the digester are functioning. The last facility with bleed-through events—North City WRP—also showed evidence of daily bleed-through, though it did not show the same consistent pattern with regard to the time of day.

Another important conclusion from the field testing is that the use of single daily or weekly sampling events would not be sufficient in a free chlorine disinfection system. Most facilities showed evidence of diurnal bleed-through events, though the magnitude of these events varied between facilities. The fact that ammonia levels tend to fluctuate throughout the day, even at well-run nitrifying facilities, means that constant ammonia monitoring will be necessary to provide proper process control. The online monitors tested in this study provide sufficient temporal resolution and sensitivity to allow continuous or near-continuous verification of the nitrification process. With continuous ammonia monitoring in place, the causes of diurnal breakthrough can be better understood and, eventually, eliminated.

The second main goal of the testing period was to evaluate monitoring reliability. To gain insight into this question, three online ammonia analyzers were evaluated through a series of tests including a laboratory verification study, a series of four field studies, and field challenge tests. The minimum requirements for the analyzers were that they provide a high level of accuracy and detection frequency. The TresCon and Waltron instruments best met these criteria for this application. A number of other factors should also be considered when selecting an analyzer, including response time, detection range, operability, O&M requirements, costs for parts and reagents, durability of design, and integration into SCADA. The four tested monitors offered advantages and disadvantages in terms of the other requirements; Table 2.2 can be consulted to determine which analyzer best suits the needs of a specific plant and its operation.

Chapter 3

Design of Free Chlorine Disinfection Systems for Nitrifying Facilities

The main conclusion of the testing at the water recycling facilities is that it is possible to achieve the type of highly reliable nitrification process necessary to pursue free chlorine disinfection. The testing also provided insight into additional design and operational considerations that are necessary in creating a free chlorine disinfection system. In this chapter we describe several of the elements of this system including

- Operational requirements
- Design considerations
- Monitoring and control considerations
- Failure response systems

3.1 Operational Paradigm Shift

We begin with the discussion of operations, instead of design, because it is possible that many nitrifying facilities could pursue free chlorine disinfection credit without significant upgrades or modifications. The discussion of operations begins by looking back at the types of failures commonly experienced by nitrifying facilities and the impact of these failures under current operational paradigms. Figure 3.1 shows the two main types of failure: short-term ammonia bleed-through events and longer-term events often related to biological upsets. Both types of failure were observed at the water reclamation facilities presented in Chapter 2.

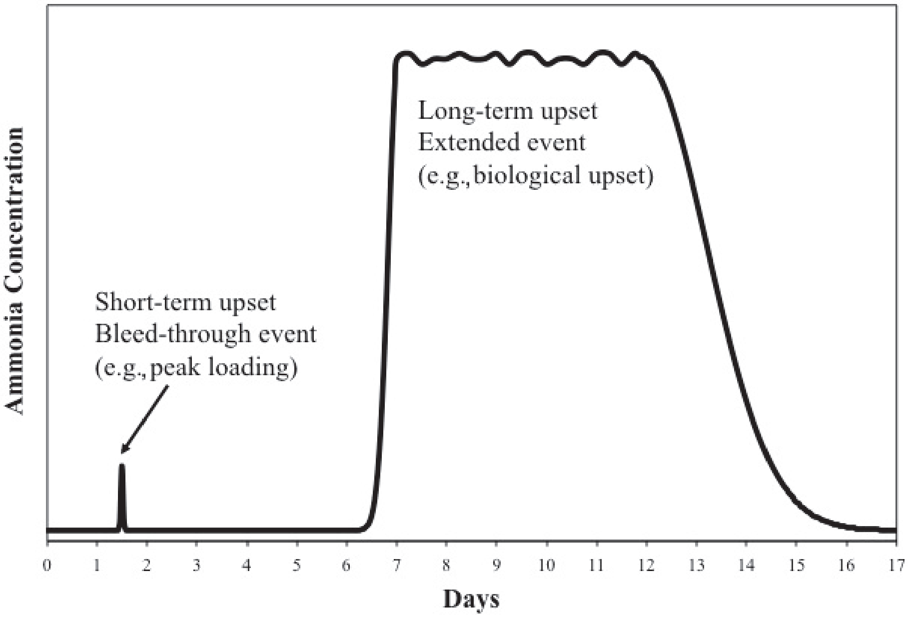

Figure 3.1. Typical types of nitrification upsets including short-term bleed-through events and long-term biological failures.

Most facilities that practice nitrification do so to meet their discharge requirements for nutrients. Because these permits are typically based on monthly or daily nutrient loads (e.g., pounds of ammonia discharged per month), the systems can tolerate short ammonia events (such as diurnal bleed-through) as long as the averages stay within specified discharge limits. Consequently, most nitrifying facilities are operated with the goal of meeting these longer-term (e.g., monthly) targets. The impact of small bleed-through events is minimized, assuming nitrification occurs reliably throughout the rest of the day. Reliability in its current context is therefore premised on achieving the permit limits.

Long-term failures, such as loss of the nitrifying microbiological populations or mechanical failures, result in extended periods of high nutrient levels in the effluent. During such times, discharge limits are difficult or impossible to achieve, and therefore a facility requires either additional ammonia control strategies or other assurances that this high-nitrogen water would not be discharged (e.g., discharge to emergency storage or reprocessing).

For nitrifying facilities seeking to obtain free chlorine disinfection credit, a new operational paradigm will be required. The focus of the operational strategy must switch from meeting discharge permit requirements to achieving consistent and constant low levels of ammonia throughout the day and from one day to the next. Stated otherwise, operations must shift to minimize not only long-term failures, but also the transient ammonia peaks associated with bleed-through events. This is necessary to ensure that free chlorine conditions can exist at all times in the contact basins. The definition of reliability must also be modified to address the new focus of achieving instantaneous low ammonia levels. The following sections discuss operational changes that will promote reliable nitrification for free chlorine disinfection.

3.1.1 Avoid Low DO Levels

The process of nitrification requires the action of aerobic, that is, oxygen-respiring, bacteria. As a result, DO concentration is a major driver of effective nitrification, and higher DO concentrations enable faster reaction rates. In general, an optimum DO concentration of at least 2 mg/L is used to maintain a proper aerobic environment to ensure adequate oxygen for the nitrifying populations to transform ammonia to nitrate (a minimum DO of 0.5 mg/L is required). Lower DO levels will result in slower reaction rates and, depending on other conditions, may result in some ammonia bleed-through. Thus, a common operational strategy to aid in ensuring proper nitrification is to monitor and maintain DO levels above specific set points. One configuration strategy is to install DO probes in the aeration basins to provide automated feedback that regulates airflow to the biological basin to respond to increased loads or additional DO needs. The implementation of this type of control scheme will increase blower output during peak load events to help maintain consistent DO concentrations.

3.1.2 Provide Flow Equalization

One of the main causes of ammonia bleed-through is diurnal peak flows—in which the organic load, nitrogen load, and flow all increase—that can exceed the nitrification capacity of the system. These diurnal events were witnessed (to varying degrees) at nearly all of the facilities described in Chapter 2. Flow equalization strategies are an excellent tool to attenuate these peak loads and provide a consistent load to the biological process to enable a more reliable ammonia removal performance. By leveling the nutrient load, this strategy can help decrease the frequency and severity of bleed-through events.

3.1.3 Ensure Sufficient SRT at the Wastewater Temperature

Maintaining stable populations of nitrifying bacteria requires that SRTs are maintained at sufficiently long times at the given wastewater temperature. Monitoring SRTs is therefore a key element of process control to ensure reliable ammonia removal. Operational modifications that ensure that some safety factor is maintained to prevent the system from approaching the minimum SRT will consequently help in preventing bleed-through events.

A larger aeration basin will provide additional aeration time. This will provide improvements to nitrification reliability by ensuring reactor capacity and by ensuring that DO concentrations are maintained through peak load events. Of course, a larger reactor requires a more significant capital investment, and higher DO concentrations will increase the operational costs of the biological ammonia removal process.

In some cases, anoxic or anaerobic selectors can be used to improve sludge settleability and to increase the SRT that an existing facility can support.

3.1.4 Use Breakpoint Chlorination

Whereas the previous strategies have focused on preventing ammonia bleed-through, breakpoint chlorination offers a way to respond to a bleed-through event such that free chlorine disinfection may still occur at many existing facilities with more challenging conditions. This strategy—a response versus a prevention step—is discussed further in the design and failure response sections.

3.1.5 Allow for Conservative Operation

One final option to prevent ammonia bleed-through is to rerate existing nitrification facilities to allow for a more conservative operational approach. As discussed at the beginning of this section, facilities that have been designed to achieve their nutrient discharge load limits may not have the capacity to achieve the new operational goal of consistent, instantaneous low ammonia concentrations. Rerating the facilities for lower capacities would provide less stress on the existing infrastructure—for example, flow peaking, blower capacity, residence time—and allow a more consistent performance. Rerating is not practical at all locations but could be feasible at satellite facilities or could alternatively be achieved through the addition of flow equalization. Reducing maximum flows will provide fewer challenges to existing systems, allowing better control over the nitrification process.

3.2 Design Considerations

The construction of new or upgraded facilities provides an opportunity to incorporate design components to facilitate higher nitrification reliability in free chlorine disinfection. This section discusses a number of components that should be considered in design, including dosing strategies, basin and mixing criteria, and the impact of water quality.

3.2.1 Chlorine Dose

Three principal components contribute to the required chlorine dose: the dose must (1) achieve breakpoint residual ammonia, (2) satisfy any additional non-ammonia chlorine demand, and (3) provide the desired free chlorine residual. The breakpoint dose is a function of the chlorine-to-ammonia demand ratio. On a weight-by-weight basis, 7.6 mg/L of free chlorine is needed for every 1 mg/L of ammonia (7.6:1). In practice, however, ratios of 8:1 to 10:1 are more common and ratios as high as 15:1 may be needed (American Water Works Association, 2011). A maximum ratio of 20:1 represents oxidation to nitrate, as shown in Equation 3.3.

Chlorine demand is due to the presence of reduced constituents in the water that consume chlorine during the oxidation process. Constituents that exert chlorine demand may be organic or inorganic—including Fe(II), manganese, and components of BOD—and result in the creation of more oxidized species such as organochloramines and Fe(III). Chlorine demand is also impacted by the type of oxidant used, with stronger oxidants exerting higher chlorine demand. For example, free chlorine produces higher chlorine demand than chloramines because of its higher oxidative strength. Organic nitrogen and constituents that impart color are also oxidized by free chlorine but are not oxidized by combined chlorine. After satisfying the chlorine demands of ammonia and other constituents, any further chlorine added to the system remains free chlorine, resulting in the free chlorine residual.

Eventually, demonstration testing may be necessary to determine the precise operating conditions needed to meet the disinfection requirements. These operating conditions may include requirements for a number of factors including minimum free chlorine residual (in mg/L), minimum free chlorine modal contact times (in minutes), and free chlorine CTs (in mg-min/L). Safety factors have been used in the development of chlorine dosing requirements in drinking water regulations (United States Environmental Protection Agency, 1991) and may be required for recycled water as well. Failure to meet the required dosing should trigger appropriate action to ensure that the discharged water meets requirements.

3.2.2 Chlorine Feed Rate and Storage

All three elements discussed previously need to be considered in the design and selection of chlorine feed rates and storage. Given that the occurrence of ammonia bleed-through is both common (it occurred at each of the facilities) and frequent (data showed the diurnal pattern nearly every day at some facilities), free chlorine systems should be designed with these issues in mind. Clearly, breakpoint chlorination is a feasible strategy under certain conditions. Given the 10:1 chlorine-to-ammonia dosing requirement, however, there are upper limits to the chlorine dosing achievable with breakpoint strategies. For example, to breakpoint 5 mg/L of ammonia requires a chlorine dose of 50 mg/L—a level greatly exceeding typical dosing systems (see the discussion of disinfection by-product (DBP) formation in Section 3.2.8).

At least three scenarios may be used in the design of chlorine feed and storage for breakpoint: (1) typical conditions, during which background ammonia levels are present, (2) ammonia bleed-through events, taking into account both the extent and duration, and (3) extreme events. The first scenario represents the average conditions at the facility, when nitrification is reliably occurring and low levels of ammonia are present in the secondary effluent. This scenario can serve as a starting point for dosing systems, allowing chlorine dosing and storage to be calculated based on the breakpoint with the typical background ammonia levels. Dosing systems should also incorporate the second type of scenario, typical bleed-through events. As seen in Figure 2.19, North City WRP experiences small, daily bleed-through events that could be easily treated with breakpoint chlorination. The ammonia load that passes through during these events can be calculated based on the duration and profile of the ammonia concentrations. Appropriate chlorine dosing can then be determined based on these numbers. By incorporating both the typical background levels and the typical bleed-through events, breakpoint dosing schemes can be appropriately calculated.

One final scenario to consider is the level of safety or conservatism that is desired in the dosing strategy. Clearly, the effectiveness of the system against the third scenario, larger ammonia events, will be determined by the dosing system's maximum capabilities in terms of both pumping capacity and storage volume. The benefits of higher pumping and storage are that the system is resistant to higher ammonia excursions and therefore less likely to need to divert or waste water that has not reached the breakpoint. These benefits come at a higher capital cost for large pumps and storage as well as having increased footprint demands. O&M costs may also be substantially larger, given both the energy requirements of large pumps and the limitations on chlorine storage. Chlorine cannot be stored indefinitely because of auto-degradation that occurs over time. To maintain the efficacy of chlorine stock, the proper technique should be followed when storing large volumes of chlorine, including a maximum chlorine storage turnover rate of about a month to avoid significant degradation. A balance is clearly needed that maximizes both protection from breakthrough events and cost-effectiveness.

3.2.3 Breakpoint Reaction Time

The reactions occurring during breakpoint chlorination do not happen instantaneously. Thus, free chlorine added to an ammonia-containing water will start off at elevated levels and will decrease over time until the breakpoint reactions have been completed. Any chlorine remaining after this point will be present as free chlorine. Note that a free chlorine residual is present throughout the entire breakpoint chlorination reaction, assuming that chlorine has been added in excess of the levels required for breakpoint (Saunier and Selleck, 1979). Free chlorine disinfection, therefore, is not affected by the breakpoint reactions if a sufficient dose has been added. The free chlorine residual measurement at the end of the contact basin therefore serves as a conservative measurement of the residual within the contact basin.

The breakpoint reaction itself proceeds in overlapping stages with each stage requiring a different amount of time for completion. The difference in rates is a function of the reaction kinetics, which vary for the different reactions taking place. Monochloramine formation occurs most rapidly (typically complete in less than 10 s), whereas the oxidation of monochloramine and dichloramine may take as little as 4 min or as long as 160 min, depending on the concentration of ammonia present, the pH, and the mixing rate immediately after the chlorine is added. Reactions increase in rapidity with increasing ammonia concentration and are most rapid in the pH range of 7 to 9 (Saunier and Selleck, 1979; White and Black & Veatch, Inc., 2010). Lower temperatures and higher levels of organics, particularly organic nitrogen, slow the reaction. Although knowledge of these reactions is critical to understanding the shape of the free chlorine residual curve, the addition of a sufficient dose of chlorine will ensure that a free chlorine residual is present both during and after the breakpoint reactions.

3.2.4 Contact Basin Size

The size of the contact basin is calculated based on the required contact time and the process flow rate. A 90 min modal contact time is required for chloramination under California's Title 22 Recycled Water Guidelines, but significantly shorter contact times will be required for free chlorine disinfection. This is due to the stronger oxidative capacity of free chlorine compared with that of combined chlorine. Studies have shown that equivalent levels of disinfection can be obtained with both disinfectants, although doses of free chlorine are typically approximately two orders of magnitude lower than doses of combined chlorine. In cases in which pathogen shielding is an important factor, inactivation of coliform bacteria may be better achieved through chloramines (because of their lower reactivity, they have a greater ability to diffuse through a biofilm), and compliance with total coliform requirements should be considered. In the design scenario that follows, a contact time of 5 min is assumed for free chlorine disinfection.

3.2.5 Mixing

Under ideal conditions, chlorine should be rapidly mixed with the secondary effluent to ensure that the breakpoint reaction proceeds via the steps described in Section 1.1.2. Insufficient mixing may allow the creation of unwanted chemical species, including nitrate (which exerts higher chlorine demand) and nitrogen trichloride (which causes odor issues). "Pockets" of unmixed chlorine may result in high chlorine-to-ammonia ratios that favor the production of such unwanted species. To avoid such conditions, an initial rapid mixing process can be added at the chlorine dosing location.

3.2.6 Water Quality Implications

pH and Alkalinity

Chlorination typically uses one of two main forms of chlorine—chlorine gas [$Cl_2(g)$] or sodium hypochlorite [$NaOCl(s)$]. During breakpoint chlorination, both compounds undergo reactions that affect pH and alkalinity. Chlorine gas undergoes a disproportionation reaction when mixed with water, creating one mole of hypochlorous acid (HOCl) and one mole of chloride for every mole of added gas, along with the consumption of one mole of alkalinity. Hypochlorous acid subsequently undergoes a number of reactions, some rapid, some reversible, and some consecutive and poorly reversible. One reaction pathway is the reversible dissociation to the hypochlorite ion, a pathway that is pH dependent and consumes one mole of alkalinity per mole of chlorine dissociated. Both acid and base species can consume chlorine demand by oxidizing reduced constituents or through substitution. A common rule of thumb is that one mole of alkalinity is consumed for every mole of chlorine demand consumed (White and Black & Veatch, Inc., 2010). The last major reaction pathway is the breakpoint reaction, a series of reactions described in greater detail in Section 1.1.2.

The breakpoint reaction is an irreversible reaction that occurs when chlorine is in the presence of ammonia and certain organic nitrogen compounds. Breakpoint involves the oxidation of ammonia to inorganic chloramines, which in turn are oxidized to nitrogen gas and, to a lesser degree, nitrate (Section 1.1.2). Some organic nitrogen is also oxidized to organochloramines in a parallel reaction. The overall reaction of chlorine gas oxidizing ammonia to nitrogen gas, which are the dominant reactant and product, respectively, is shown in Equation 3.1. The overall reaction using sodium hypochlorite is shown in Equation 3.2.

$$3Cl_2 + 2NH_4^+ \rightarrow N_2 + 6Cl^- + 8H^+ \qquad (3.1)$$

$$3NaOCl + 2NH_4^+ \rightarrow N_2 + 3Na^+ + 3Cl^- + 3H_2O + 2H^+ \qquad (3.2)$$

Four moles of alkalinity are consumed per mole of ammonia oxidized by gaseous chlorine, and one mole of alkalinity is consumed per mole of ammonia oxidized by sodium hypochlorite. In practice, 1.05 moles of alkalinity per mole of ammonia oxidized by gaseous chlorine is observed (Metcalf & Eddy, Inc., et al., 2003). Note that Equation 3.1 includes the alkalinity consumption from both the disproportionation of gaseous chlorine and the breakpoint reaction. Estimating alkalinity using Equations 3.1 and 3.2 assumes a chlorine-to-ammonia ratio of 7.6, which represents the stoichiometric, or lower limit, required for breakpoint.

The overall oxidation of ammonia to nitrate by hypochlorous acid is shown in Equation 3.3. The conversion of ammonia to nitrate requires a higher chlorine-to-ammonia ratio than the conversion to nitrogen gas, and it also consumes more alkalinity.

$$NH_4^+ + 4HOCl \Leftrightarrow NO_3^- + 4Cl^- + 6H^+ + H_2O \tag{3.3}$$

Gaseous chlorine will lead to an overall reduction in alkalinity, with reductions occurring both from the disproportionation reaction and the breakpoint reaction. Sodium hypochlorite produces a net increase in alkalinity, with a large, rapid increase occurring initially upon addition, followed by a gradual consumption of alkalinity through the breakpoint reactions.

Consequently, systems that use gaseous chlorine may need additional alkalinity added to control the pH. Acid addition may be necessary to maintain pH control when using sodium hypochlorite.

Total Dissolved Solids

The addition of chemicals for breakpoint chlorination (and subsequent neutralization) increases the total dissolved solids (TDS) of the treated water, as shown in Table 3.1.

Table 3.1. Effects of Chemical Addition on TDS in Breakpoint Chlorination

Chemical Addition	Increase in TDS Per Unit of NH_4^+-N Consumed
Breakpoint with chlorine gas	6.2
Breakpoint with sodium hypochlorite	7.1
Breakpoint with chlorine gas - neutralization of all acidity with lime (CaO)	12.2
Breakpoint with chlorine gas - neutralization of all acidity with sodium hydroxide (NaOH)	14.8

Source: From Metcalf & Eddy et al., 2003

Nitrogen Loading

Although the role of ammonia nitrogen in breakpoint chlorination has been discussed, organic nitrogen also impacts the process. Organic nitrogen impacts chlorine residual measurements, residual stability, breakpoint reaction speed, and chlorine demand. Organic nitrogen reacts with free chlorine to form organochloramines at a rate faster than free chlorine reacts with ammonia (White and Black & Veatch, Inc., 2010) and thus constitutes part of the chlorine demand. Organic nitrogen is typically present at the level of 1 to 2 mg/L, with higher concentrations found in agricultural or industrial wastewaters.

3.2.7 Cost

The capital and chemical costs of free chlorine and chloramine disinfections differ for a number of reasons. The main capital requirements of free chlorine disinfection are the contact basin and the chlorine feed and storage system; these requirements include site excavation and site work, equipment, concrete and steel, labor, valves and piping, housing, electrical equipment and installation, architectural considerations, special site work, contractor overhead and profit, land, interest during construction, yard piping, and engineering, legal, and administrative costs. Chemical prices are affected by freight fees and material and labor costs. Typical chlorine costs range from $0.50 to $1.50 per pound; capital costs can be estimated using a cost-estimating manual (McGivney and Kawamura, 2008).

The capital costs of free chlorine disinfection are significantly lower than those of chloramine disinfection because shorter contact times allow the use of significantly smaller chlorine contact basins (CCBs). As discussed in Section 1.1.3, free chlorine has the potential to decrease the disinfection CTs specified in the California Water Recycling Criteria from 450 to 10 mg-min/L, that is, a 45-fold reduction in CTs. This benefit stems from the fact that free chlorine is a significantly more potent disinfectant. Free chlorine CCBs still require significant capital costs, however, even at low volumes. For example, a CCB that is 1/45 of the size of another does not necessarily scale linearly in terms of capital costs; the CCB will be less expensive, but might only be 1/10 of the cost of the larger basin. Factors that increase capital costs (e.g., high cost of land) favor free chlorine disinfection.

The chemical costs of free chlorine disinfection are slightly higher at low ammonia levels but become significantly higher at higher ammonia levels. Free chlorine disinfection requires breakpoint chlorination of ammonia, necessitating larger chlorine doses with increasing concentrations of ammonia. Chloramine disinfection requires ammonia addition at low ammonia levels to avoid breakpoint, but chlorine addition is not a function of the ammonia concentration. Further, because free chlorine is a more powerful oxidant than chloramines, the chlorine demand for free chlorine is higher.

3.2.8 Additional Considerations

Nitrogen Trichloride

Nitrogen trichloride (trichloramine) is an odorous compound that is an undesirable by-product of breakpoint chlorination. Nitrogen trichloride increasingly forms at higher chlorine-to-ammonia ratios and with higher levels of organic nitrogen. It begins to form at a chlorine-to-ammonia ratio of 12:1 and forms at significant levels at a ratio of 14:1 up to pH levels of 9 (White and Black & Veatch, Inc., 2010). Nitrogen trichloride is highly volatile and acts as an eye irritant that causes watering or tearing of the eyes at low concentrations.

Disinfection By-Products (DBPs)

In general, allowing for free chlorine CTs will reduce DBP formation, as it will allow for both lower chlorine residuals (and thus lower doses) and shorter contact times; many recycled water facilities are currently providing significantly greater CTs than are actually needed to achieve a 5-log virus inactivation (e.g., 450 mg-min/L). During periods of time when breakpoint chlorination is needed to address bleed-through, chlorinated DBP formation is expected to increase; but assuming these time periods are brief, the overall DBP formation is expected to be lower under this new approach. N-nitrosodimethylamine (NDMA) formation is expected to decrease significantly at well-nitrified facilities that intentionally add ammonia to form chloramines, as many of the free chlorine molecules will oxidize many of the NDMA molecules. Breakpoint chlorination would form less NDMA but more trihalomethane (THM) compared with chloramination (Huitric et al., 2006).

Residual Stability

The free chlorine residual during the breakpoint reaction is less stable in the presence of organic nitrogen and may rise and fall as organochloramines decompose and as new inorganic chloramines are formed and oxidized. pH has been shown to impact organochloramine reactivity, with lower pH levels allowing for greater oxidation of organochloramines (Saunier and Selleck, 1979).

Sequential breakpoint and residual management. One alternative dosing strategy is sequential breakpoint and residual management. In this practice, sufficient chlorine is added to achieve breakpoint chlorination in an initial step, which is then followed by a second round of dosing to provide a free chlorine residual. This practice can reduce the overall chlorine requirements; one study showed that this practice can save up to 1 mg/L-Cl_2 compared to a strategy that doses chlorine in a single step (based on a residual of 5 mg/L-Cl_2; Saunier and Selleck, 1979). Sequential dosing also reduces nitrogen trichloride formation.

Trace Organics

Free chlorine provides an additional, ancillary benefit relative to chloramines in that it can readily oxidize a number of trace organic compounds in reclaimed waters (Tang et al., 2011).

3.3 Monitoring and Control

The data from the online monitoring study demonstrate that ammonia concentrations tend to fluctuate throughout the day. Consequently, single daily ammonia measurements are not sufficient to provide proper control over free chlorine disinfection systems. Online ammonia analyzers providing continuous or near-continuous monitoring are therefore a critical element in monitoring nitrification reliability and controlling free chlorine dosing.

One option for implementing an ammonia monitoring and free chlorine control system is presented in Figure 3.2. Equipment needs include two online ammonia monitors and two online free chlorine monitors. The first ammonia monitor is positioned to measure ammonia concentrations in the secondary effluent prior to the free chlorine dosing point. This monitor serves a number of roles, including (1) providing constant monitoring of nitrification reliability, (2) showing trends that might signal ammonia upsets prior to the levels exceeding their threshold value, (3) signaling alarms for ammonia concentrations above the thresholds, and (4) providing feed-forward information for use by the chlorine dosing control system. Monitors may also be linked to the failure response systems, for example, automatically triggering wasting of secondary effluent during large-scale or catastrophic nitrification failures.

The use of redundant monitors may help to ensure monitoring reliability by providing continuous ammonia measurement even during the maintenance or failure of one of the units. Based on the findings in Chapter 2, the O&M requirements of the ammonia monitors are more intensive than those of other online monitors. Given the demands for oversight, maintenance, and repair, a redundant monitoring scheme would likely prove to be a more reliable long-term operating strategy.

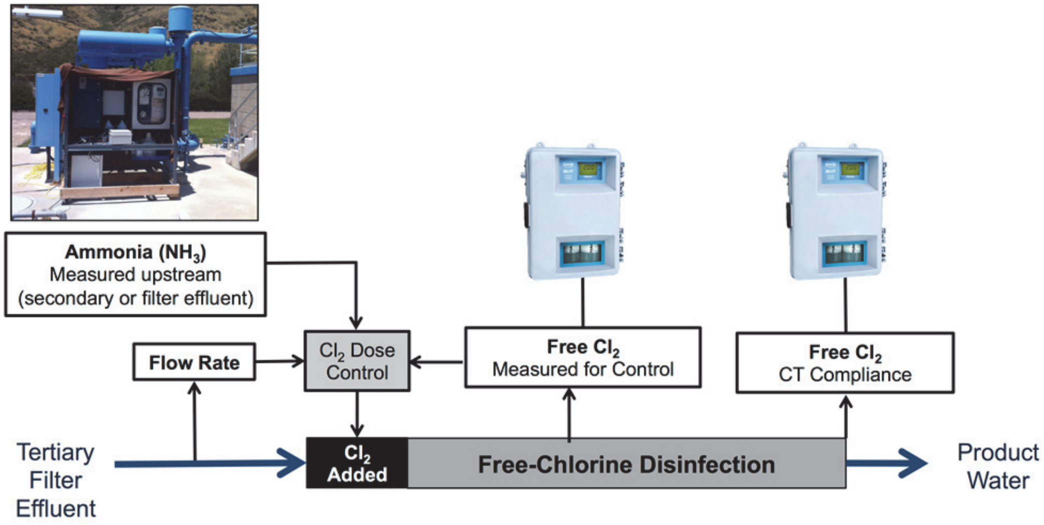

Figure 3.2. Possible configuration of ammonia monitoring and control system for free chlorine disinfection.

The proposed chlorine dosing control system has both feed-forward and feedback components. Feed-forward variables include both flow rate and influent ammonia concentrations, which provide information to the control system to predict an initial target dosing value. Additional chlorine demand (non-ammonia) will also be present within the secondary effluent, and the control logic should incorporate this component into the calculation of the initial target dose.

To ensure that an adequate free chlorine residual is present within the CCB, two chlorine monitors are used, one at an upstream location and one at the compliance point at the end of the CCB. Compliance is measured at the second free chlorine monitor location, but the initial monitor provides a rapid indication of a dosing failure. It also increases monitoring reliability by providing redundant measurements. The free chlorine levels determined by the monitors provide feedback to the chlorine dosing control loop, refining the predictive dosing (feed-forward calculation) with the chlorine residuals actually achieved (feedback). By providing a near-continuous monitoring of free chlorine residuals, the analyzers also provide operators with data to spot trends that may signal issues with the disinfection system prior to the development of a large-scale failure. Failures that do occur are monitored by the analyzers, which could be configured to automatically sound alarms and/or to waste water that does not meet specifications.

3.4 Rapid Response

The final component of the free chlorine system design is a response system that reacts to both types of ammonia event—both transient and catastrophic failures—and ensures the protection of public health.

3.4.1 Transient Failures

In the context of free chlorine disinfection, ammonia bleed-through events will be the most common upsets in nitrification systems. Systems should be designed to detect and respond to these events (Section 3.3; e.g., through breakpoint chlorination) or configured to ensure that high nitrogen water will not be discharged (e.g., discharge to emergency storage or reprocessing). One option might be to discharge the off-spec water to applications with less stringent recycled water requirements, for example, toward applications with restricted access use.

3.4.2 Catastrophic Failures

In some cases, ammonia concentrations may reach levels that preclude the use of breakpoint chlorination. This may occur, for example, if the nitrifying populations are accidentally killed or washed out of the basin or if mechanical failures cause a complete failure in the nitrification process. Under such scenarios, breakpoint chlorination is likely not possible. Alternatives would be necessary either to further treat the water to remove ammonia prior to chlorination or to discharge the water to non-reuse receiving waters.

The technologies of ammonia removal fall broadly into two categories based on the nature of the removal process: biological and physical-chemical (Page et al., 2012). Biological processes require a steady input of food and nutrients, as discussed previously, and are not suited to intermittent use compared with physical-chemical ammonia-removal technologies. One major benefit of the physical-chemical processes is that they can be more easily brought online and offline as needed and can also operate on an intermittent basis (Section 1.3). Other methods to decrease ammonia concentrations include flow diversion (the rerouting or wasting of waters with high ammonia concentrations) and blending.

3.5 Free Chlorine Design Calculations

Calculations for select design parameters are shown in the following. Determining pH is beyond the scope of this report, and the reader is referred to an introductory water chemistry textbook.

The required chlorine dose ($C_{Chlorine}$) can be calculated by

$$C_{Chlorine} = \varphi_{Cl:N} C_N \tag{3.4}$$

in which

$\varphi_{Cl:N}$ = chlorine-to-ammonia ratio needed to breakpoint
C_N = nitrogen concentration

The chlorine feed rate ($Q_{Chlorine,\,\max}$) can be calculated by

$$Q_{Chlorine,\,\max} = \frac{C_{Chlorine,\,\max} Q_f}{\eta_{Chlorine}} \tag{3.5}$$

in which

Q_f = process flow
$\eta_{Chlorine}$ = chlorine stock purity
$C_{Chlorine,\,\max}$ = maximum chlorine dose

The chlorine storage ($V_{Chlorine}$) can be calculated by

$$V_{Chlorine} = Q_{Chlorine,\ avg} t_{Chlorine} \tag{3.6}$$

in which

$t_{Chlorine}$ = chlorine storage time
$Q_{Chlorine,\ avg}$ = average chlorine flow rate

The contact basin size (V_{Contact}) is needed to estimate capital costs and can be calculated by

$$V_{\text{Contact}} = Q_{\text{Process}} t_{\text{Disinfection}} \tag{3.7}$$

in which

Q_{Process} = process flow

$t_{\text{Disinfection}}$ = time required for disinfection with free chlorine

Upon stipulating a contact basin size and a chlorine feed rate, the capital costs can be estimated using a cost-estimating manual as stated earlier. Alkalinity and TDS can be estimated using the stoichiometric ratios stated earlier.

3.6 Design Scenarios

To compare the free chlorine- and chloramine-based disinfection strategies, a number of design scenarios were developed. The following two sections provide both the findings and a comparative analysis.

3.6.1 Free Chlorine and Chloramine Design Scenarios

Evaluations of the two systems—free chlorine and chloramine—were developed based on average ammonia concentrations of 0.1, 0.5, 1.0, and 5.0 mg/L. Both the design criteria and the impacts on water quality are estimated based on assumed influent flow rates and water quality. The resulting values were calculated using the design equations from Section 3.5, standard engineering "rule of thumb" calculations, and water chemistry relationships. The influent flow and water quality assumptions are presented in Table 3.2, and the design criteria and water quality impacts are presented in Table 3.3.

Table 3.2. Assumed Water Qualities of Free Chlorine Disinfection Ammonia Scenarios

Parameter	Chemical Form	Value	Unit
Chlorine-to-Ammonia Ratio		10	w/w
Stock Purity	Cl_2 NaOCl	100% 12.5%	%
Flow		15	MGD
Storage Time		7	day
Chlorine Residual		5	mg/L-Cl_2
Chlorine Demand		8	mg/L-Cl_2
Temperature		20	°C
TDS		260	mg/L
pH		7	~
Alkalinity		90	mg/L-$CaCO_3$

Table 3.3. Design Criteria and Water Quality Parameters of Free Chlorine Disinfection Ammonia Scenarios

Parameter	Chemical Form	Value				Unit
Ammonia Scenario		Low	Medium	High	Maximum	~
Ammonia		0.1	0.5	1.0	5.0	mg/L
Chlorine Dose		14	18	23	63	mg/L
Chlorine Feed Rate[a]	Cl_2	9	11	14	39	gph
	NaOCl	70	90	115	315	
Chlorine Storage	Cl_2	1.5	1.9	2.0	7.0	MG
	NaOCl	12	15	19	53	
Alkalinity Consumption[b]	Cl_2	13	18	25	81	mg/L-$CaCO_3$
	NaOCl	-4	-5	-7	-21	
TDS Production[c]	Cl_2	1	6	12	61	mg/L
	NaOCl	1	3	6	31	
pH[d]	Cl_2	6.7	6.6	6.5	6.1	~
	NaOCl	7.1	7.1	7.2	8.0	

Notes: [a] Feed rates are based on average dose required; sizing should use peak dose

[b] Alkalinity consumption based on Cl_2:N (w/w) of 7.6 stoichiometry; assumes complete dissociation

[c] TDS using Cl_2 includes neutralization with lime; NaOCl does not include neutralization

[d] pH assumes no neutralization; only carbonate species contributions to alkalinity

gph = gallons per hour, MG = million gallons

Costs of both free chlorine and chloramine disinfection at different ammonia levels were calculated using cost equations. The flow and water quality assumptions for this comparison are listed in Table 3.4, and the cost estimates are listed in Table 3.5.

Table 3.4. Cost Model Parameters

Parameters	Values	Units
Cl_2:N to breakpoint	10	w/w
Cl_2:N to chloraminate	5	w/w
Chlorine demand	6	mg/L-Cl_2
Chlorine residual	5	mg/L-Cl_2
Increased free chlorine demand	2	mg/L-Cl_2
CCB baffling efficacy	75	%
Flow	15	MGD
Interest rate	6	%
Lifespan	20	years
Ratio of combined chlorine CT to free chlorine CT	45	~
Anhydrous ammonia	1	$/lb
Aqua stock purity	29	%
Aqua ammonia	2.50	$/gal

Notes: Engineering News Record (ENR) construction cost index (CCI), indexed to Los Angeles, CA, September 2012, i = 6%, n = 20; costs do not include architectural flourishes, special site work, general contractor overhead and profit, land, or interest during construction.

Table 3.5. Costs of Ammonia Scenarios

Ammonia Scenario	Ammonia (mg/L)	Free Chlorine Total Cost	Combined Chlorine Total Cost
Low	0.1	$734,789	$1,122,872
Medium	0.5	$926,470	$1,103,980
High	1.0	$1,163,820	$1,074,818
Maximum	5.0	$3,012,091	$1,074,818

Note: Under the conditions described in Table 3.4 with $100/ft^2 land development cost, a chlorine cost of $1/lb, and soil that is not easily excavated.

Figure 3.3 compares the costs of free chlorine and chloramine disinfections at additional ammonia concentrations.

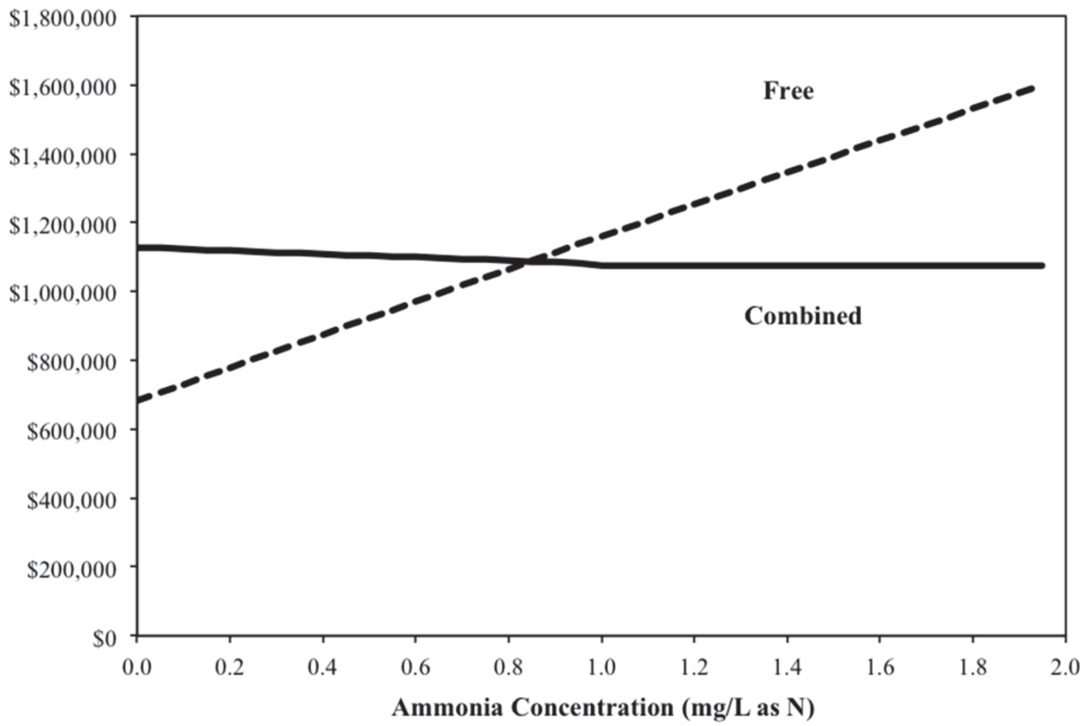

Figure 3.3. The cost of free chlorine disinfection versus that of chloramine disinfection at various ammonia concentrations under the conditions assumed in Table 3.4.

3.6.2 Review of Free Chlorine and Combined Chlorine Analysis

In a comparison involving cost alone, free chlorine disinfection is more economical than chloramine disinfection at low ammonia levels. Although free chlorine dosing strategies require higher chemical consumption (Section 3.2.7), the reduced capital costs outweigh this impact at low ammonia concentrations. The ammonia concentration at which the two strategies break even on cost is approximately 0.8 mg/L of ammonia. Above this concentration, the high chemical costs associated with breakpoint chlorination push the total costs of free chlorine disinfection above that of combined chlorine disinfection. The exact ammonia concentration that defines the break-even point depends on a number of elements including site conditions, flow, and other factors.

One additional consideration is the impact of these two strategies on factors beyond cost. Because free chlorine is a much more potent oxidant, it can provide demonstrable inactivation of a range of pathogen types including bacteria, viruses, and protozoa (e.g., *Giardia*). Chloramines also provide protection against bacteria but are less effective against viruses, even at longer CTs. They also provide limited to no protection against protozoa such as *Giardia* and *Cryptosporidium*. Pathogen control strategies that use free chlorine disinfection are therefore capable of providing protection against a broader set of contaminants of public health concern. As noted in Section 3.2.8, free chlorine also provides better protection against the other main contaminant group of concern, the trace organic compounds.

3.7 Conclusions

On the basis of the results of the field study, the nitrification process can be operated, monitored, and verified with sufficient reliability to pursue a free chlorine disinfection strategy. Ensuring consistent free chlorine residuals, however, will require a significant operational shift from the current paradigm. In this new context, reliability is no longer framed in terms of nutrient loading but in achieving consistent, low ammonia levels at all times. Ammonia peaks—both transient and long-term—offer challenges to the free chlorine strategy; therefore, both preventive and responsive strategies need to be incorporated into operations.

A number of design and operational modifications could be included to improve nitrification reliability and to allow recycling facilities to achieve free chlorine disinfection. These modifications range from increased monitoring (e.g., monitoring of DO, SRT, ammonia, and chlorine) to modified operations (e.g., flow equalization and chlorine dosing) and design (e.g., basin sizing, chemical feed systems, and storage). Although these practices prevent ammonia from entering the chlorine disinfection system, systems must also respond to failures by either removing residual ammonia (e.g., breakpoint chlorination, backup/redundant treatment systems) or rerouting off-spec flows.

One big-picture issue that still needs to be resolved is the appropriate level of redundancy needed in free chlorine systems. Ultimately what is sought is a system with a high level of reliability in achieving consistent, low ammonia levels at all times. Redundancy can aid in this goal by ensuring that failures of one process do not cause failures of the whole system. As witnessed in the field testing, the failure of a single process (in that case, the aeration system of the aerobic digesters) caused downstream failure of the nitrification system because of the excessive nitrogen loading. This example demonstrates the interconnectedness of the system and emphasizes the need to view the whole process in terms of what can be done to augment reliability. Redundancy will be an important concept in achieving this goal.

The system modifications detailed in Chapter 3 entail additional effort and/or costs. Based on the economic analysis, however, these modifications still provide a net savings as long as residual ammonia levels are relatively low. The main factor driving the lower cost of free chlorine is the capital cost savings resulting from the use of smaller CCBs. Free chlorine systems will have higher chemical costs, however, mainly because of the need to breakpoint chlorinate any residual ammonia. As effluent ammonia concentrations increase, the cost of additional chemical use begins to outweigh the capital savings, pushing the economic balance in favor of combined chlorine.

The advantages of free chlorine disinfection, however, extend beyond the economic considerations. Water quality improvements include lower DBP formation as well as higher pathogen and chemical removal rates. Facilities that currently provide consistent, reliable nitrification do not currently receive free chlorine credit and so provide free chlorine CTs of at least 450 mg-min/L to meet recycled water requirements. Granting permits to such facilities to perform free chlorine disinfection would mean significant reductions in their CT requirements (up to 45 times lower, assuming a 10 mg-min/L CT of free chlorine). Reducing free chlorine contact times would provide significant relief from DBP formation. At the same time, free chlorine has been proven to provide better and broader protection than chloramines against both pathogens and chemical contaminants.

Finally, obtaining free chlorine credit provides a way to optimize existing infrastructure and site limitations. By reducing the CTs needed for disinfection, free chlorine credit can allow facilities to increase the capacity of their existing CCBs. As previously discussed, the increased capacity is primarily tied to the increased oxidative strength of free chlorine compared with chloramines. Because free chlorine is significantly more potent, chlorine contact tanks can be rerated for increased capacities compared with their existing ratings. Reliable nitrifying facilities that want to increase their capacity may not need to expand their existing CCBs during upgrades, assuming they can receive free chlorine disinfection credit.

Similar benefits apply at new recycling facilities as well. New CCBs that are granted permits for free chlorine disinfection can be built at significantly smaller sizes than equivalent chloramine contact tanks, saving substantial capital investment. Furthermore, the smaller CCBs provide greater flexibility at new facilities with limited available footprints. In site-constrained scenarios, chlorine disinfection may not be possible based on the large CCBs needed to achieve 450 mg-min/L; however, chlorine disinfection may be possible if free chlorine CTs (e.g., in the range of 8–16 mg-min/L) are acceptable.

Chapter 4

Conclusions and Future Directions

4.1 Conclusions

In the context of free chlorine disinfection, nitrification reliability is no longer framed in its historical terms of controlling nutrient discharge loads. In this new context, nitrification reliability means providing consistently low ammonia concentrations on a continuous basis. The historical goal of avoiding long-term nitrification upsets is not eliminated, but it is subsumed by the more stringent goal of disinfection, which seeks to avoid even short-term upsets. By providing such consistent ammonia removal, reliable nitrification systems open the door to the feasible implementation of free chlorine disinfection of recycled water. Free chlorine disinfection systems offer important and diverse benefits including enhanced removal of pathogens and chemicals, more efficient site utilization, and lower overall cost. In many cases, these drivers can justify the additional efforts needed to achieve the stricter reliability requirements.

The last few decades have seen great improvements in our understanding and control of the biological nitrification process. Important factors impacting the process have been identified and exploited, and nitrifying facilities have used this knowledge to reliably meet their nutrient discharge goals. Much of the same knowledge can also be applied to the new reliability paradigm. By applying these principals more stringently, higher levels of reliability can be achieved. In Chapter 3, a nitrification reliability framework was proposed that provided recommendations for all aspects of the system, including design, operations, and failure response. Arguably, the most important change is the shift in operational strategies that reframes the water quality goals in the stricter terms of instantaneous compliance rather than long-term (e.g., monthly) targets.

The field studies and the historical operations data from the four water recycling facilities demonstrated that the new reliability requirements are an achievable goal. It is important to repeat that most nitrifying facilities are not currently operated with the goal of achieving the high level of reliability needed for free chlorine disinfection. Consequently, many of the facilities did not achieve the consistent performance needed to implement a free chlorine strategy. The fact that they are not *currently* meeting these requirements should not, however, be construed to mean that they do not have the capability to meet them in the future. Chapter 3 provides a framework for creating reliable nitrification systems and highlights a number of modifications that could be used to augment existing facilities.

In addition to needing the development of reliable treatment processes, nitrification systems also need a reliability metric that can be continuously monitored to ensure compliance. The reliability metric that was tested in this study was the use of online ammonia analyzers. Ideal characteristics of this reliability metric include (1) near-continuous or continuous measurement of ammonia levels in secondary effluents, (2) a high level of accuracy, and (3) acceptable O&M requirements. To test their ability to meet the criteria, the analyzers were subjected to a battery of tests including an initial laboratory verification of performance, a nine month field deployment at four recycling facilities, and a series of field challenge tests.

Through this study, it was concluded that all of the analyzers have the potential to monitor and verify nitrification reliability. Each analyzer demonstrated sufficient sensitivity to detect appropriately low levels of ammonia with monitoring frequencies capable of providing near-continuous resolution of effluent ammonia concentrations. One potential shortcoming of the existing monitors was the need to deal with frequent O&M issues. Although the O&M requirements were not trivial, the monitors provide valuable data for assessing nitrification reliability. Improvements that reduce the labor requirements for operation, cleaning, and maintenance will increase the robustness of the monitors (and by extension, the entire nitrification system) and should be sought. In the meantime, these monitors provide us with the capacity to demonstrate compliance with the new nitrification requirements.

4.2 Future Directions

Through this study, a number of knowledge and technical gaps were identified that should be addressed in future efforts. One of the most important next steps is to engage the relevant regulatory agencies on the issue of free chlorine disinfection credit for recycled water. These discussions should include defining the operating conditions needed to obtain free chlorine disinfection credit. One likely outcome of these discussions is the need to demonstrate the operation of a free chlorine system using a pilot- or full-scale demonstration system. One possible setup of such a system was presented in Chapter 3.

Two of the main goals of such a demonstration project include (1) verifying the chlorine control system and (2) demonstrating adequate inactivation of microbial contaminants of public health concern. The chlorine control system not only needs to provide appropriate dosing control to measure and respond to short-term ammonia bleed-through events but must also demonstrate appropriate responses to major failures. One of the clearest differentiators between free and combined chlorine is the higher disinfectant strength of the former; therefore, demonstration studies that document pathogen inactivation (e.g., virus inactivation) can provide powerful evidence of the reliability of the free chlorine disinfection system. The performance of the free chlorine system should look at the impact of various water quality parameters (including ammonia levels, pH, turbidity, and temperature) and account for reactor hydraulics. The ranges of values looked at should be representative of conditions experienced at the facility, including seasonal variations. Both aspects—chlorine control and pathogen control—will be principal components to verify in the demonstration testing.

Throughout the discussion with regulators, it is likely that other barriers will be identified that need to be addressed to obtain regulatory permission for the process. Identifying these additional barriers early in the process is recommended so that demonstration/pilot testing can concurrently address as many of these issues as possible at the same time.

Although all the ammonia monitors utilized in this study showed the potential to be used as continuous metrics of nitrification reliability, advancements that increase the operability and costs of the monitors would be beneficial. As the technology advances, some elements that could be addressed include minimizing the cost and replacement frequency of parts and reagents, automating as many process steps as possible (e.g., calibration and cleaning), and minimizing the time and frequency of calibration. One important finding from this study is that the monitors need to be calibrated frequently to maintain a high level of accuracy. Given this requirement, inexpensive ammonia standards with long shelf-lives should be sought. Finally, features that interrupt ammonia monitoring—such as an automatic shutdown after the triggering of an alarm—should be modified so that data is provided even during an upset in the process or monitoring systems.

Water recycling facilities that obtain credit for free chlorine disinfection receive a number of benefits from lower overall costs, smaller system footprints, and enhanced pathogen and chemical removal. Although free chlorine disinfection will have the widest applicability at facilities producing non-potable recycled water, the benefits will be equally or more important for potable reuse as well. For example, the California Department of Public Health's draft groundwater recharge regulations specify high levels of pathogen removal to ensure public health: 12-, 10-, and 10-log removals of virus, *Cryptosporidium* oocysts, and *Giardia* cysts, respectively. Virus removal is an important challenge because many physical removal processes (e.g., granular media filtration and microfiltration) are only partially effective at removing particles in the size range of most viruses. Reverse osmosis membranes do separate viruses from product streams, but this process needs to be supplemented by additional disinfection strategies to meet the high removal requirements. Taking advantage of the chlorine disinfection systems that currently exist at many recycling facilities provides an obvious economic advantage over the addition of a new disinfection process, such as UV or ozone. Furthermore, free chlorine disinfection of viruses is a proven disinfection control strategy that has been well studied and documented. This knowledge base should prove helpful in developing appropriate dosing strategies for regulatory approval.

Many of the existing indirect potable reuse facilities in California take advantage of the environmental buffer to provide additional levels of virus removal. Currently, a 1-log credit is given for every month that the water spends within an aquifer. As the country moves toward direct potable reuse (which eliminates the environmental buffer), the removal credits currently obtained in the aquifer will need to be replaced by engineered solutions. Free chlorine disinfection therefore has the potential to play an important role in meeting pathogen goals for potable reuse, both direct and indirect.

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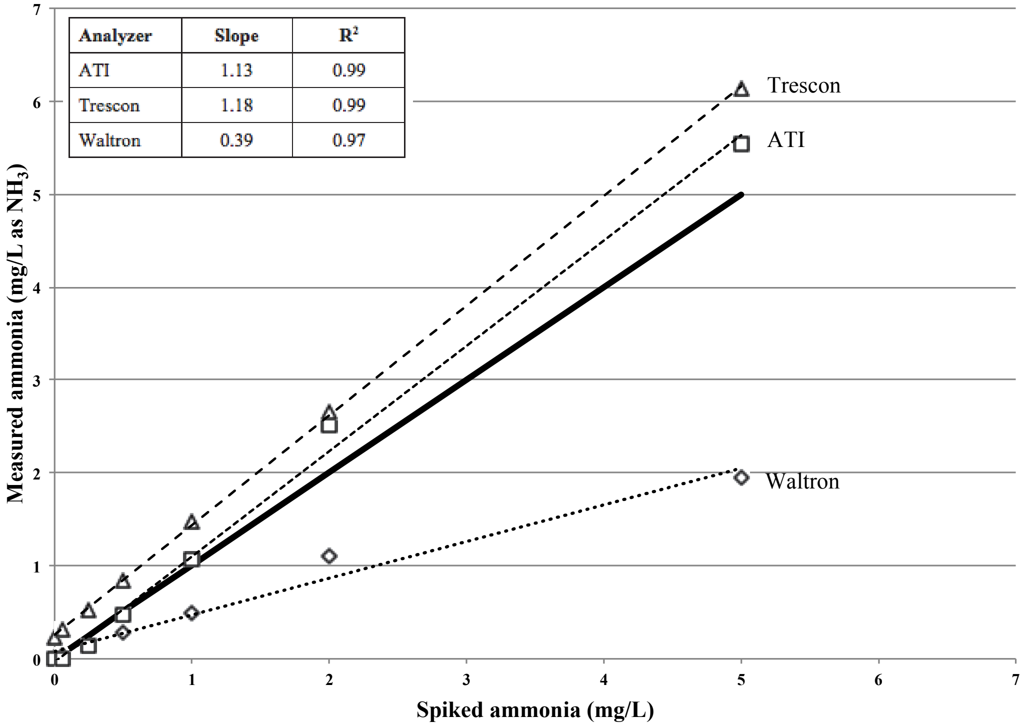
Appendix A

Laboratory Testing of Ammonia Analyzers

Additional ammonia analyzer laboratory testing, using the procedures described in the report, was performed on June 26 and 27, 2012. The results are shown in Figure A.1 and A.2.



Analyzer	Slope	R^2
ATI	1.13	0.99
Trescon	1.18	0.99
Waltron	0.39	0.97

Figure A.1. Results of laboratory testing of the ammonia analyzers on June 26, 2012.

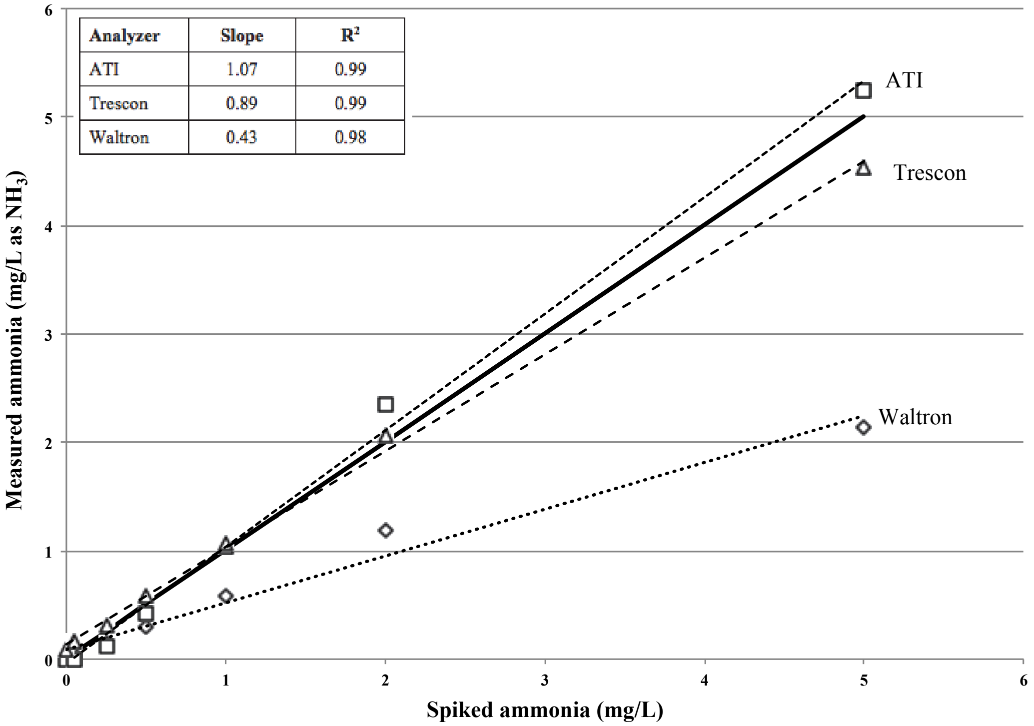

Analyzer	Slope	R^2
ATI	1.07	0.99
Trescon	0.89	0.99
Waltron	0.43	0.98

Figure A.2. Results of laboratory testing of the ammonia analyzers on June 27, 2012.

Appendix B

Ammonia Analyzer Data

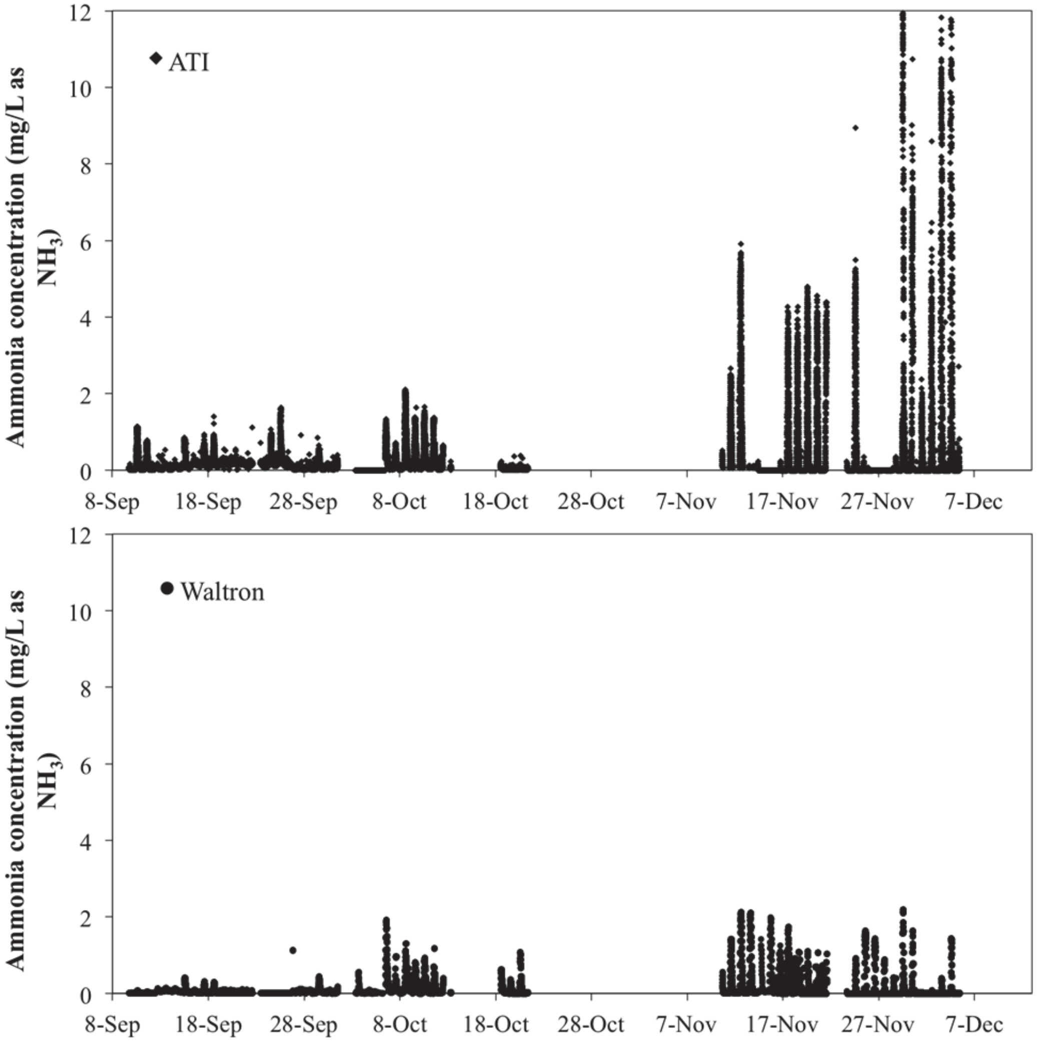


Figure B.1. Online ammonia concentration data recorded at Tillman WRP from September through early December 2011.

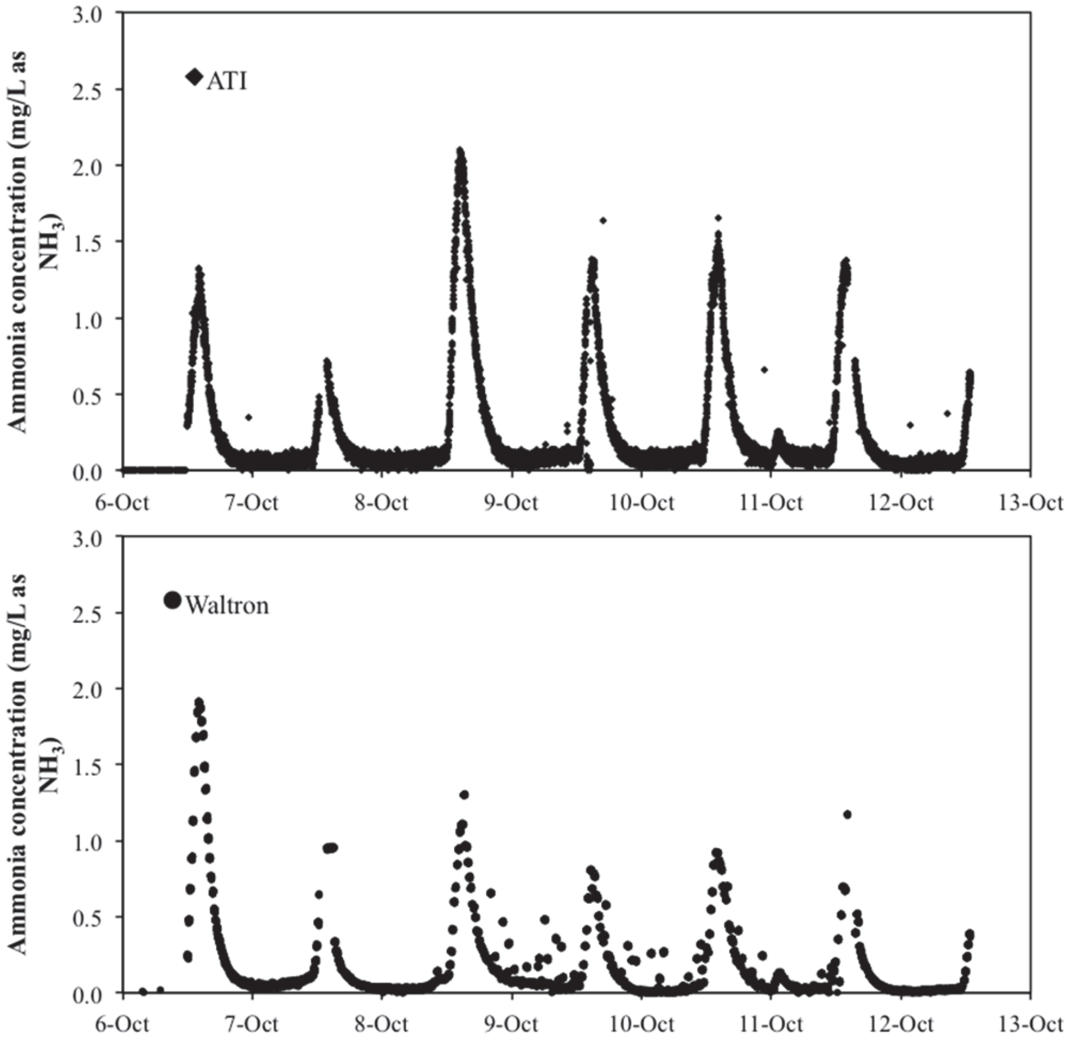


Figure B.2. Online data recorded from Oct 6 through Oct 12, 2011 at Tillman WRP.

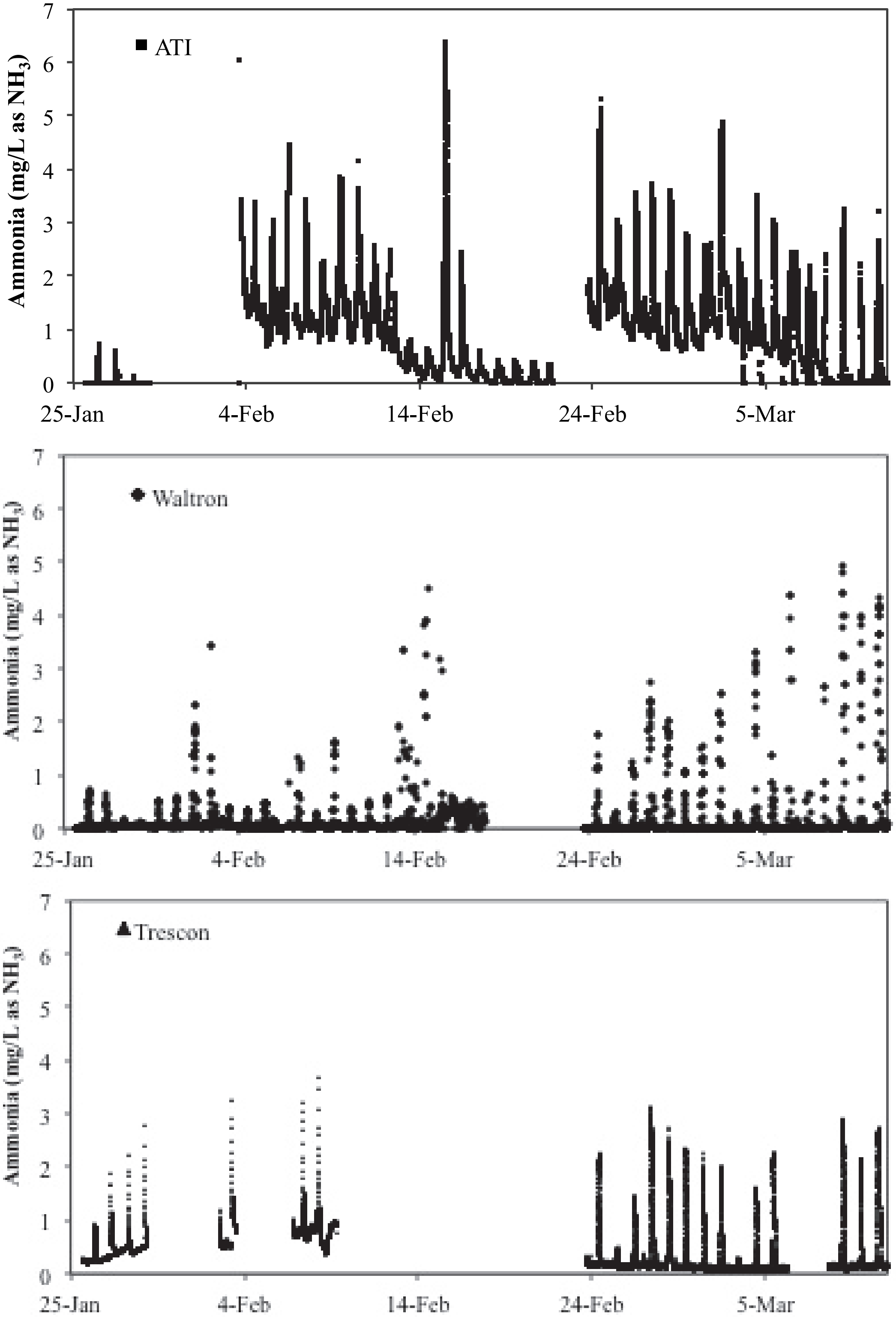


Figure B.3. Online data recorded from January through March 2012 at Santa Paula WRF.

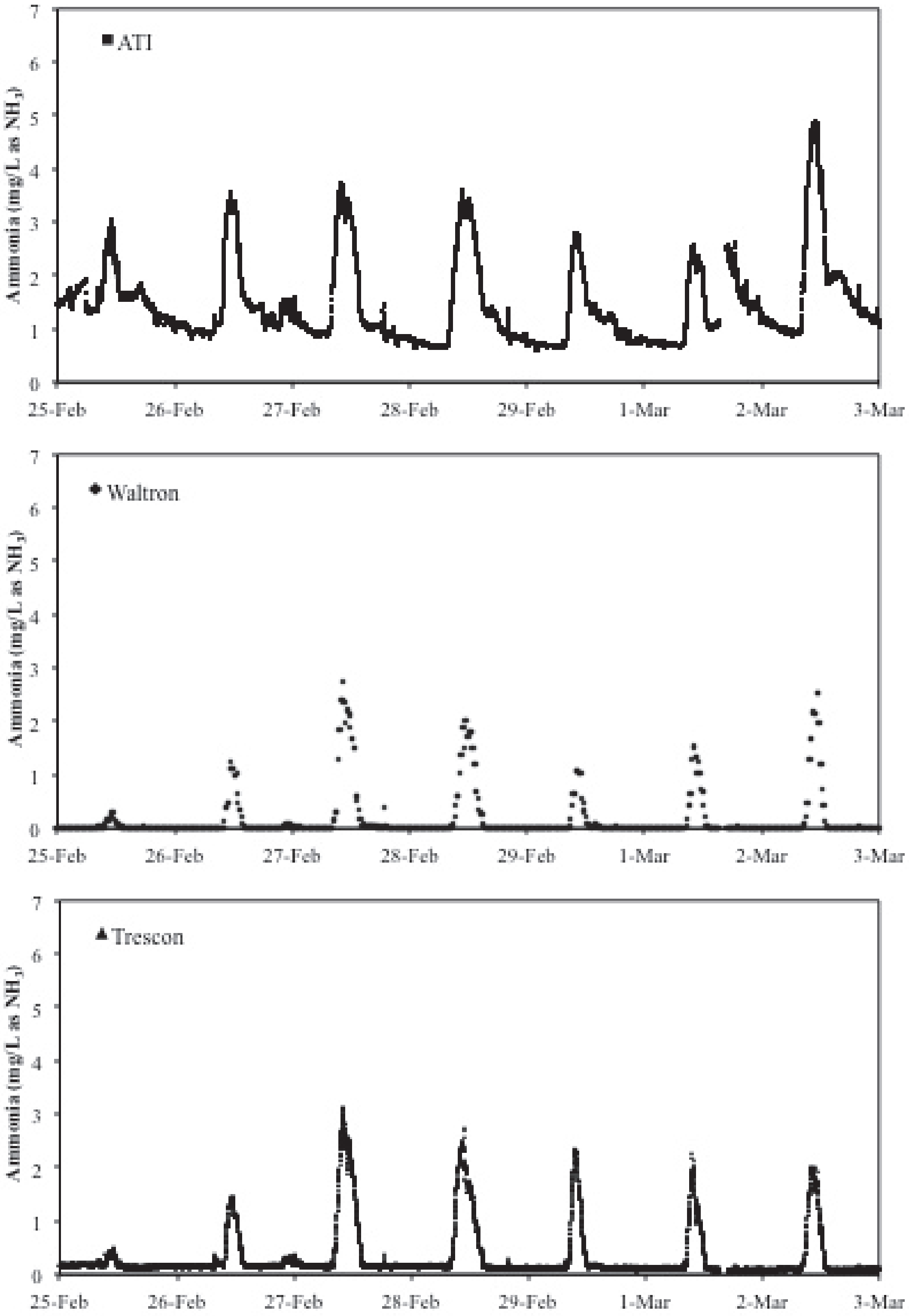


Figure B.4. Online data recorded from February 25 through March 3, 2012 at Santa Paula WRF.

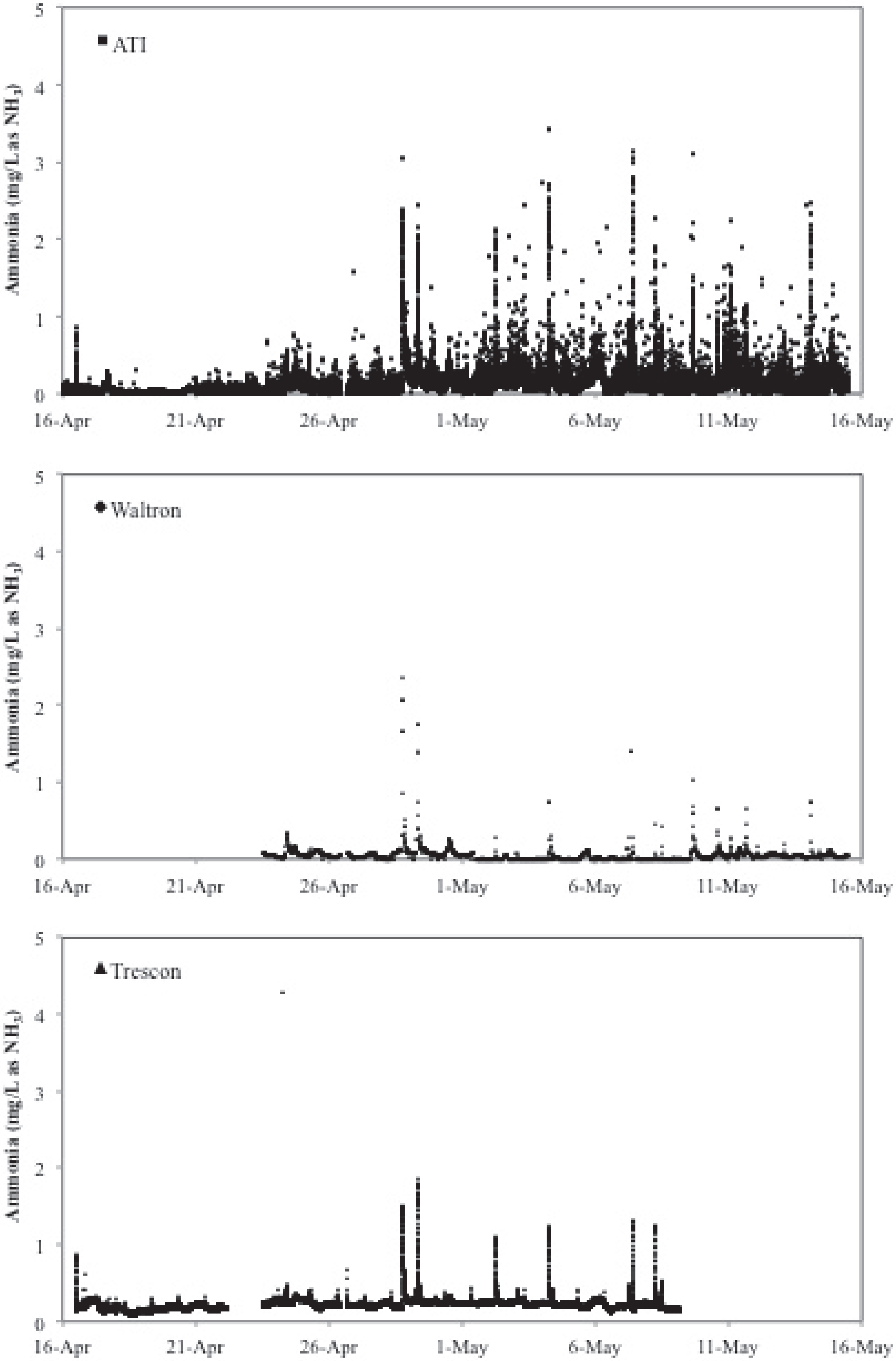


Figure B.5. Online data recorded from April through May, 2012 at North City WRP.

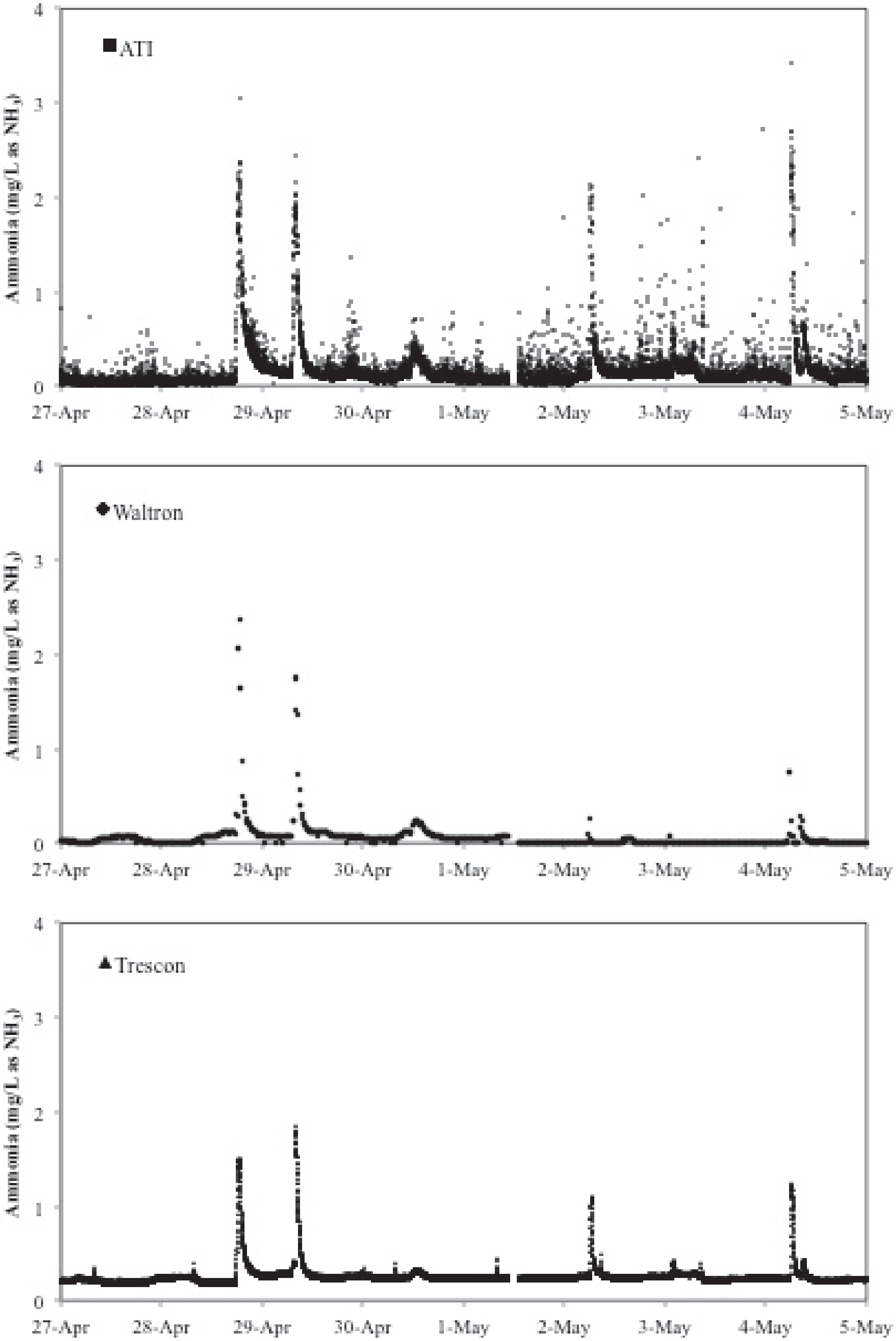


Figure B.6. Online data recorded from April 27 through May 5, 2012 at North City WRP.

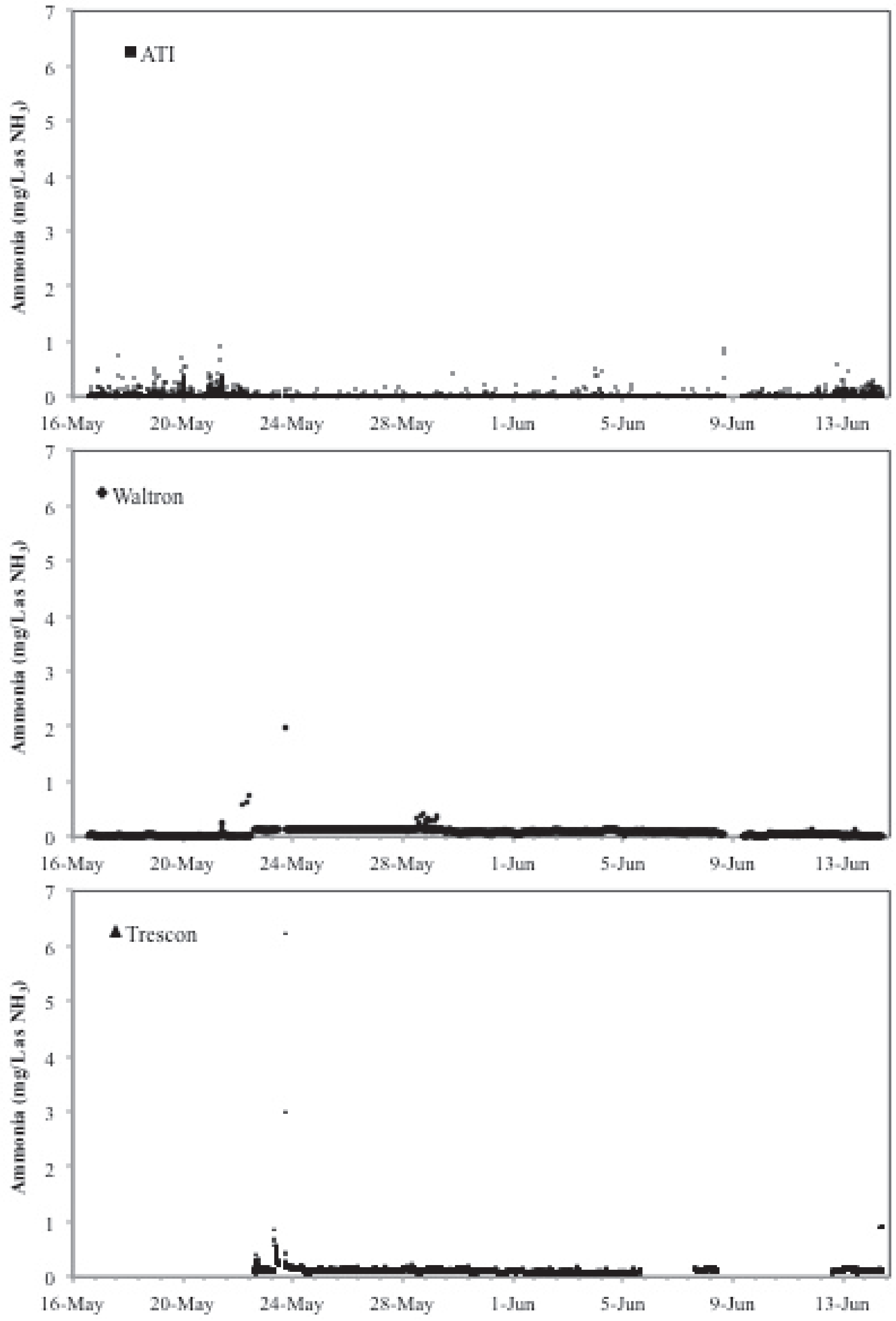


Figure B.7. Online data recorded from May through June at Padre Dam WRF.

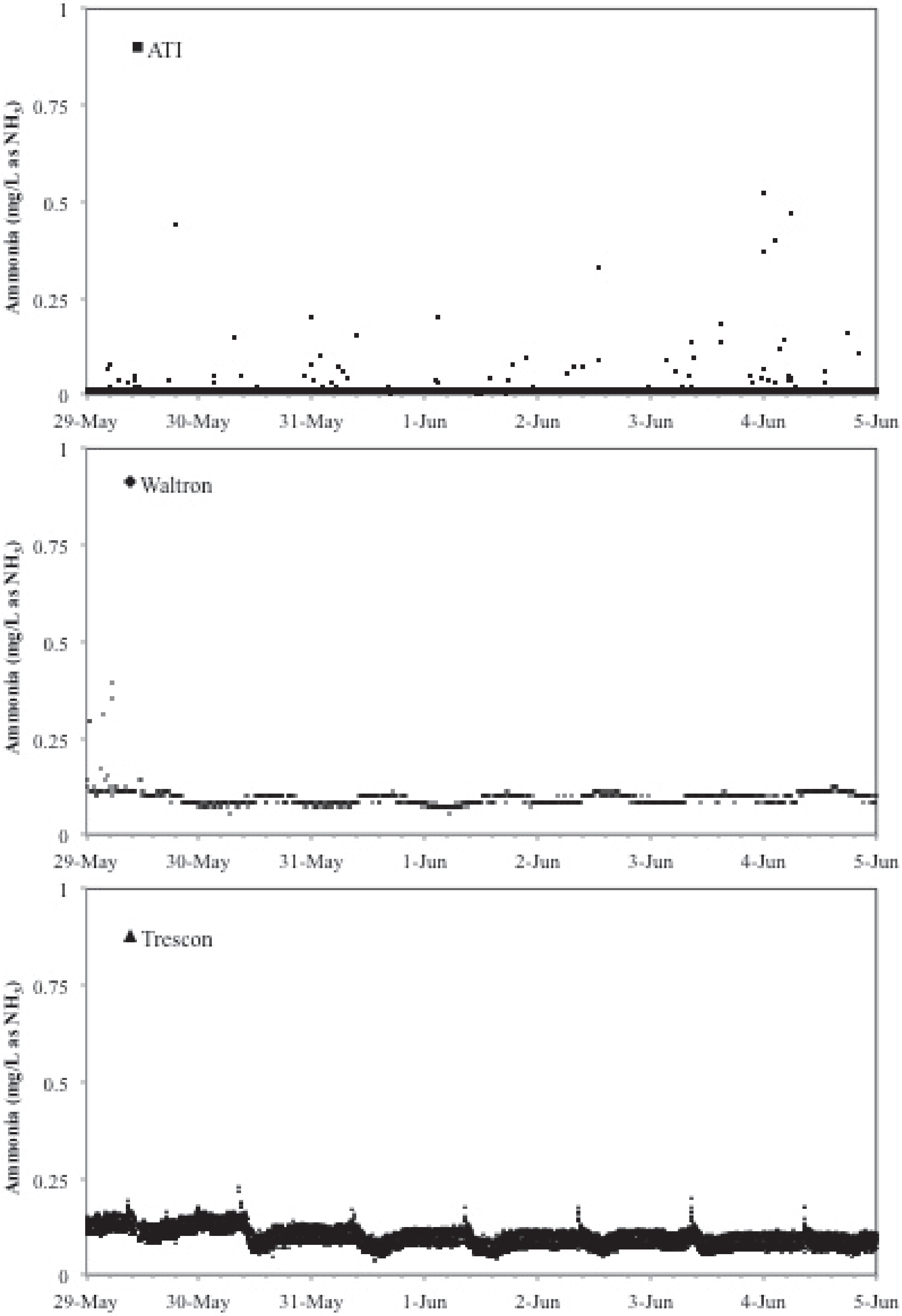


Figure B.8. Online data recorded from May 29 through June 5, 2012 at Padre Dam WRF.

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