Fundamentals and Control of Nitrification in Chloraminated Drinking Water Distribution Systems

MANUAL OF WATER SUPPLY PRACTICES **M56**

First Edition

American Water Works Association

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AWWA MANUAL M56

First Edition

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Preface

A group of volunteers from the Distribution Systems Water Quality Committee of the American Water Works Association prepared this manual of practice. The need for a manual on nitrification control results from the increased use of chloramine as a residual disinfectant in drinking water distribution systems and the ubiquitous presence of nitrifying bacteria in the environment. Consequently, all chloraminating systems need to consider nitrification control.

The manual is organized into two main parts: chapters 1 through 6 provide background information on the occurrence and microbiology of nitrification in various water environments. Chapters 7 through 10 are intended to provide current practical approaches to nitrification prevention and response. Each chapter can be read independently; therefore, there is some limited repetition between the chapters to provide necessary background of important concepts or reference to another chapter. Some distribution system maintenance techniques may also be used for multiple purposes. For example, breakpoint chlorination or flushing can be used both as nitrification prevention and response methods; therefore, they are discussed in multiple chapters. However, one subject is discussed in detail only in the most appropriate chapter and typically shorter discussion is provided elsewhere. The index can be helpful in finding information on a subject of interest presented in different context throughout the manual.

Several nitrification prevention methods are commonly used for regular distribution system maintenance. For example, cleaning, flushing, and reduction of water age have been thoroughly discussed in other AWWA and Awwa Research Foundation resources. Interested readers should refer to those references. These distribution system maintenance practices are discussed in this manual specifically from the nitrification point of view.

The materials included herein provide a compendium of the state-of-the-art knowledge as of the writing of this manual. Several new advances are being made, such as:

- Development of molecular methods for identification of nitrifying bacteria,
- Improvement of reservoir mixing techniques,
- Better understanding of the effects of booster chlorination and chloramination,
- Development of improved on-line free ammonia instrumentation,
- Investigation of chlorite as a nitrification prevention measure, and
- Installation of membrane filtration, which will result in better particulate, microbial, and organic substances removal.

These advances will have an impact on the application of chloramine and nitrification control. Therefore, the present manual will likely be updated in the future to reflect these advances and improved understanding of nitrification in drinking water distribution systems.

As this is the first edition of AWWA Manual M56, *Fundamentals and Control of Nitrification in Chloraminated Drinking Water Distribution Systems*, the Water Quality and Technology Division's Distribution System Water Quality Committee and AWWA welcome comments and suggestions for improving future editions of this manual. Please send an e-mail attachment to the AWWA Water Quality Engineer at eharring@awwa.org or a hard copy correspondence to 6666 W. Quincy Ave., Denver, CO 80235.

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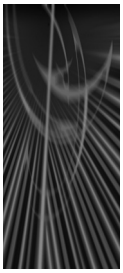

Chapter 1

Introduction to Nitrification in Drinking Water and Its Impact on Regulatory Compliance

Y. Koby Cohen
Melinda Friedman

INTRODUCTION

Nitrification is a microbiological process by which reduced nitrogen compounds (primarily ammonia) are sequentially oxidized to nitrite and nitrate (AWWA and EES, 2002). Nitrification can be problematic in potable water systems that use chloramines for residual (secondary, or distribution system) disinfection. The objectives of this manual of practice are to:

- summarize existing knowledge and provide updated information on the current practices of water suppliers and issues related to nitrification;
- provide water utilities with the latest information on nitrification in water distribution systems;
- provide information to help utilities maintain a chloramine residual in tap water; and
- help utilities effectively mitigate nitrification episodes that may occur in their systems.

There are many literature sources that discuss the various aspects of nitrification. Several American Water Works Association Research Foundation (AwwaRF) reports discuss nitrification in conjunction with other topics, primarily drinking water disinfection and chloramination. Over the last few years, several trends in chloramination and chloramine residual maintenance have emerged as a result of field experience and the progress made through research and pilot studies. For example, in the past, water utilities formed chloramine at a predominant weight ratio of 3:1 chlorine

to ammonia-nitrogen (Cl_2:NH_3-N); now, however, most utilities try to minimize free ammonia and therefore are forming chloramines at a 5:1 Cl_2:NH_3-N ratio. Another trend is the use and maintenance of a higher chloramine residual in the distribution system to provide more effective microbial or biofilm control. An emerging trend is the use of booster chloramine disinfection within the distribution system as opposed to maintaining a higher entry point chloramine residual.

There is a growing need for easy access to information related to nitrification occurrence, prevention, and control in drinking water distribution systems that use chloramine. This manual attempts to provide a balanced approach between theories developed during fundamental research and field practices applied by water utility personnel. To accomplish this balance, references to scientific papers are presented throughout the manual, and examples of water utility programs and practices are provided in every chapter. The final product is a manual that can be used by chloraminating utilities, as well as utilities considering chloramination, for use in their systems, as well as by consulting engineers and researchers trying to control or mitigate nitrification through operational practices, engineering improvements, a better understanding of the conditions that promote biological growth, and treatment options for the inactivation of nitrifying bacteria.

The following is a brief summary of each chapter:

- Chapter 1 provides background information on disinfection practices, nitrification, the impact of the use of chloramines, and the impact of nitrification on regulatory compliance.
- Chapter 2 provides an overview of the potential for nitrification to develop and occurrences in drinking water and wastewater treatment facilities.
- Chapter 3 summarizes information on nitrification occurrence and the mechanisms of nitrification in drinking water distribution systems.
- Chapter 4 provides an overview of water quality, operational, and design parameters that contribute to or cause nitrification in the distribution system.
- Chapter 5 presents information on the morphology, taxonomy, and growth of ammonia- and nitrite-oxidizing bacteria and the microbiology of nitrifying and denitrifying bacteria.
- Chapter 6 provides information on the options for inactivation of ammonia- and nitrite-oxidizing bacteria.
- Chapter 7 discuses water quality monitoring plans and programs to evaluate nitrification. This chapter also provides key monitoring parameters, monitoring locations, and monitoring frequencies for predicting nitrification.
- Chapter 8 summarizes nitrification prevention methods related to distribution system operation as an overview of current operational practices used by utilities to prevent nitrification and recommendations for best practices.
- Chapter 9 describes operational practices used by water utilities to assess and respond to nitrification episodes, to provide actions and operational practices to mitigate nitrification episodes and restore water quality in the distribution system.
- Chapter 10 discusses nitrification prevention and control methods that are related to engineering practices and capital improvements. The methods discussed in this chapter require more planning, time, and financial resources than the monitoring and operational prevention methods discussed in earlier chapters.

Each chapter begins with an introduction and summary of key points, which are designed to help the reader in reviewing the contents of the chapter. Table 1-1 presents the summary of key points derived from chapter 1.

Table 1-1 Key points from chapter 1

Background Information	• Free chlorine and chloramine are two disinfectants used in the distribution system, each has advantages and disadvantages. Free chlorine provides a strong disinfectant residual but reacts with organic matter to form disinfection by-products (DBPs). Chloramine has lower disinfection power than free chlorine but provides a more stable residual and halts the formation of trihalomethanes (THMs) and haloacetic acids.
	• The use of chloramine in the United States started in the early 1920s, but usage decreased due to ammonia shortages during WWII. Renewed interest in chloramination occurred after the introduction of the US Environmental Protection Agency (USEPA) Disinfectants/Disinfection By-Products (D/DBP) Rule, due to the potential reduction in THM and haloacetic acid formation possible with chloramines.
Nitrification Basics	• The nitrogen cycle as it occurs in nature consists of biological reversible transformations of nitrogen between ammonia, nitrite, nitrate, cellular organic nitrogen, and inorganic nitrogen gas.
	• Ammonia-nitrogen is converted to chloramine-nitrogen at the point of chloramine formation. The chloramine-nitrogen is converted back to ammonia-nitrogen as chloramines degrade in the distribution system.
	• The nitrogen cycle as it occurs in the distribution system mainly consists of ammonia being utilized by microorganisms as a food source and, in the process, nitrite and nitrate are produced.
Nitrification and Regulatory Compliance	• In the Safe Drinking Water Act, primary maximum contaminant levels (MCLs) for nitrite and nitrate at the entry to the distribution system are 1 mg/L and 10 mg/L as N, respectively. Currently there are no regulations or MCLs for nitrate or nitrite within the distribution system. If these MCLs were applied to locations in the distribution system, it is possible that the nitrite MCL could be exceeded during nitrification episodes.
	• Nitrification may lead to violation of the USEPA Surface Water Treatment Rule and Total Coliform Rule due to increased microbiological activity and the possibility of coliform growth. The requirement to maintain a detectable disinfectant residual may be impacted.
	• Nitrification may impact USEPA Lead and Copper Rule compliance due to reduction in pH and alkalinity, resulting in increased lead and copper solubility.

DISTRIBUTION SYSTEM DISINFECTION PRACTICES

The practice of disinfecting drinking water and carrying a disinfectant residual throughout the distribution system started in the early 1900s to control waterborne diseases such as typhoid fever, cholera, and dysentery. Disinfectants used for distribution system residuals in the United States are primarily free chlorine and chloramines. These disinfectants can be effective at destroying some pathogenic microorganisms and controlling the growth of microorganisms in the distribution system. Chlorine dioxide has been used to a lesser extent.

Secondary disinfection is used in water distribution systems for the following purposes:

- Control the growth of coliforms and opportunistic pathogens in the distribution system. Maintaining an adequate disinfectant residual in the distribution system, in addition to other measures, can help prevent or minimize the regrowth of coliforms and opportunistic pathogens such as *Legionella* spp.

- Reduce the impacts of system contamination that can occur through external sources. Bacteriological contamination of the distribution system may occur through a cross-connection with a contaminated water supply, during main breaks and main repairs, from intrusion due to leaking sewage lines located next to leaking water lines, from pressure transients that may allow contaminants to enter the distribution system when the pressure within the distribution system is lower than the pressure external to the distribution system, and from the microbial contamination of distribution system storage tanks and reservoirs.
- Limit biofilm growth. Disinfectant residuals help minimize biofilm growth on distribution system surfaces, especially in areas of water stagnation, at dead-ends of water mains, and in storage tanks, provided that the disinfectant residual can be maintained in these locations.
- Control the development of tastes and odors. Drinking water or tap water is expected to be of good taste and odor quality. By minimizing biological regrowth, the development of biologically formed tastes and odors is also controlled. Also, the oxidation of some taste and odor chemicals, such as hydrogen sulfide and ferrous iron, can mitigate problems.
- As a water quality indicator for water quality deterioration. A sudden or unusual reduction in the level of disinfectant residual may indicate that biological or other contaminants have entered the distribution system and consumed the disinfectant. Also, a loss in residual may indicate that unacceptably long water age exists and/or that active corrosion is occurring.

The ability of secondary disinfectants to meet each of these objectives is currently being researched and assessed by drinking water utilities and regulators alike.

HISTORY OF CHLORAMINATION IN THE UNITED STATES

As reported by Kirmeyer et al. (2004), in the early 1900s chloramines were found to be effective in destroying pathogenic organisms and were easy to use and cost effective. The Denver Union Water Company was using chloramine as early as 1917 to prevent bacteriological "re-growth" problems, and chloramine was first used in Ottawa, Canada, at a water treatment facility in 1918. Between 1920 and 1936 chloramines gained popularity in water treatment since they were more stable or longer lasting than free chlorine and caused fewer taste and odor problems compared to free chlorine. By the end of the 1930s, a survey of 2,541 water utilities in 36 states found that 16% used chloramines. However, due to an ammonia shortage during World War II in the 1940s, the use of chloramine dropped from 16% to 2.6%, as indicated in a survey of 11,500 municipal water suppliers in 1962. As a result of the introduction of the Total Trihalomethane Rule in 1979, more water utilities began using chloramines in an effort to reduce the production of trihalomethanes (THMs), a group of halogenated disinfection by-products (DBPs). THMs are suspected carcinogens that are formed when free chlorine reacts with natural organic matter (NOM) in source water. In the distribution system, the ongoing reaction of free chlorine with residual NOM produces additional THMs. By the 1990s, chloramines were being used in approximately 20% of the water treatment facilities in the United States, mainly for controlling DBP levels in the distribution system (Kirmeyer et al., 2004), with the application of free chlorine during water treatment for primary disinfection.

Recently, the use of chloramines has become more popular due to the US Environmental Protection Agency (USEPA) Stage 1 and recently published Stage 2 Disinfectants/Disinfection Byproducts (D/DBP) rules (USEPA, 2001b). The main goal of these rules is to reduce the levels of various DBPs in drinking water. A review of the

Information Collection Rule (ICR) database indicated that 33% of 353 treatment plants serving 100,000 people or more use chloramine (Federal Advisory Committee Act [FACA], 2000) for distribution system residuals.

The regulatory impact analysis for the Stage 2 D/DBP Rule predicted that the use of chloramines could increase to as much as 65% for surface water treatment systems (FACA, 2000). For non-ICR systems serving less than 10,000 people, it is estimated that approximately 50% of utilities will shift from free chlorine to chloramines as a distribution system residual to reduce DBP levels below the Stage 1 D/DBP Rule maximum contaminant levels (MCLs) (FACA, 2000).

Chloramine Formation

Chloramines used for drinking water disinfection are formed by a chemical reaction between chlorine and ammonia, ideally at a weight ratio of approximately 5:1 of Cl_2:NH_3-N to form the preferred monochloramine specie. Chlorine is introduced to the water either as a gas, as a sodium hypochlorite solution (in bulk liquid or generated on-site), or by dissolving calcium hypochlorite tablets. Ammonia is introduced as a solution of dry ammonium sulfate or liquid ammonium hydroxide or by dissolving anhydrous ammonia gas into solution.

The generalized inorganic chloramine formation reactions are shown below:

Monochloramine (NH_2Cl)*

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \quad (1\text{-}1)$$

Dichloramine ($NHCl_2$)

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad (1\text{-}2)$$

Trichloramine (NCl_3)

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad (1\text{-}3)$$

Monochloramine is the desired inorganic chloramine specie to form in drinking water treatment and to maintain in the distribution system. Monochloramine is preferred because it does not normally cause significant taste and odor problems, while dichloramine and trichloramine are known to produce detectable chlorinous tastes and odors at relatively low concentrations (Kirmeyer et al., 2004). For interested readers, a report by Kirmeyer et al. (2004) discusses the chloramination process in detail. As with free chlorine, after entering the distribution system, the chloramine residual starts to decay based on water quality conditions and water age, and in this process free ammonia is released into the water. Free ammonia may also enter the distribution system from the treatment plant due to an overdose of ammonia or incomplete reaction with free chlorine.

NITRIFICATION BASICS

The Nitrogen Cycle

All biological growth processes require nitrogen for the synthesis of cellular proteins and nucleic acids. Microorganisms can utilize a range of nitrogen compounds for these syntheses under a variety of conditions; in some cases, the oxidation state of nitrogen is changed while in others it is not. Nitrogen-containing compounds can be used as oxidizers to provide energy for synthetic reactions (Painter, 1970). The main biological

* It should be noted that the speciations of ammonium ion and hypochlorous acid are pH-dependent. For $7.5 < pH < 9.3$, NH_4^+ and OCl^- are the dominant species.

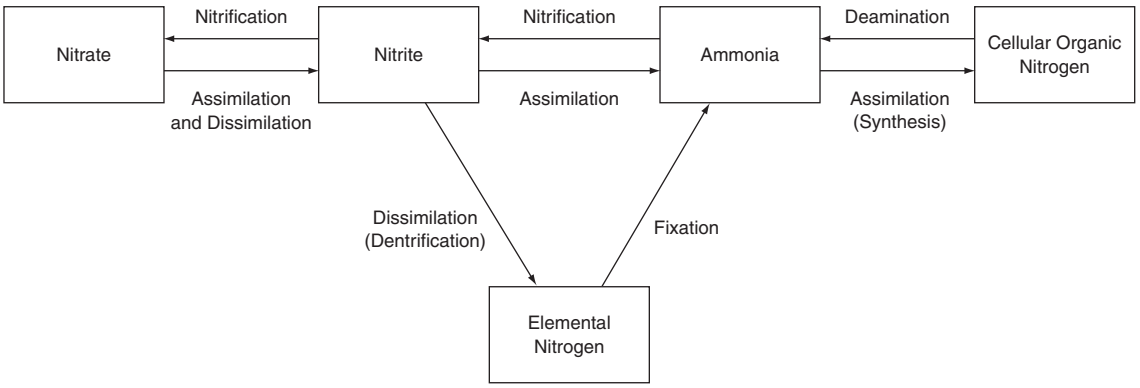

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Figure 1-1 Main biological processes involving nitrogen transformation

processes involving nitrogen transformation are shown in Figure 1-1. These reactions involving nitrogen, in addition to nitrification, may take place in drinking water distribution systems and may affect the water quality.

Nitrogen fixation involves the synthesis of cellular nitrogen compounds from elementary nitrogen; such reactions commonly occur in soils, surface waters, and, to a limited extent, in activated sludge wastewater processes. The microbiological conversion of ammonium and nitrite to dinitrogen gas (anaerobic ammonium oxidation or anammox conversion) is a very recent addition to the biological nitrogen cycle (Kuenen et al., 2001; Strous et al., 1999a). Discovered as late as 1986, so far it is the most unexplored part of the cycle. Nitrification is the oxidation of ammonia to nitrate via nitrite and is carried out by a limited number of autotrophic bacteria. Free ammonia is metabolized by species of nitrifying bacteria called ammonia-oxidizing bacteria (AOB), which are ubiquitous in the environment and chloraminated water distribution systems. The AOB metabolize the free ammonia and produce nitrite, which in turn is metabolized by nitrite-oxidizing bacteria (NOB) into nitrate. Nitrite can also act as a dechlorination agent due to chemical reaction with either free chlorine or chloramines. The microbiological process of converting free ammonia (NH_4^+) into nitrite (NO_2^-) and then nitrate (NO_3^-) is called nitrification. The following are approximate equations for nitrification reactions by the AOB *Nitrosomonas* and the NOB *Nitrobacter* (Morel and Hering, 1993):

Nitrosomonas reaction:

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^- \quad (1\text{-}4)$$

and

Nitrobacter reaction:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \quad (1\text{-}5)$$

More information on nitrification reactions by AOB and NOB is provided in chapter 5.

In general, distribution system nitrification leads to decreases in chloramine residual, alkalinity, and pH; elevated levels of nitrite and nitrate; and increased microbial counts. If left uncontrolled, it can lead to further water quality degradation. Both complete (to nitrate) and incomplete (to nitrite) nitrification has been frequently observed in chloraminated drinking water distribution systems. Nitrate metabolism can occur either through assimilation (conversion of nitrate to cellular, organic nitrogen via ammonia) or dissimilation (oxidation of carbon compounds at the expense of

nitrate, which acts as the alternative hydrogen acceptor to oxygen). Denitrification is a special case of dissimilation in which gaseous N_2 and/or N_2O are the end products. Denitrification is an important wastewater treatment process. Deamination and lysis of the cell wall occurs in the dying cells and ammonia is formed from organic nitrogen compounds by various deamination reactions (Painter, 1970). The growth of heterotrophic bacteria (as evidenced by high heterotrophic plate counts [HPCs] during nitrification) as well as AOB and NOB will result in eventual cell lysis and increased chloramine demand. A decrease in relative concentrations of inorganic chloramines and an increase in organic chloramines has been reported in storage reservoirs subject to long detention times; whether cell lysis could contribute to this transformation is currently poorly understood.

Nitrification in the Environment

Nitrifying bacteria are found in soils, compost piles, wastewater, fresh water, marine habitats, and in most other aerobic environments. Many environments with suboptimal conditions still support the growth of nitrifying bacteria. For example, nitrifying bacteria are strict aerobes, yet they can be isolated from wastewater aeration tanks that are extremely low in dissolved oxygen water (see chapter 6 for more information). The highest concentration of nitrifying bacteria is found in the upper 10-cm layer in soils, at the sediment–water interface in rivers and streams, and attached to the sides of the aeration tanks in wastewater treatment plants (Watson et al., 1981). Sustained high levels of ammonia in the water column of some lakes and deeper rivers would indicate that nitrification is a sediment-based process in these environments. Sediment resuspension might transport the nitrifiers into the water column and macrophytes may serve as surfaces for nitrifiers in the water column. Nitrifiers are localized in the oxic sediments of the lake and their activity is likely inhibited by anoxia during the period of summer stratification and by low temperatures in winter (Pauer and Auer, 2000). Considerable amounts of nitrifying bacteria (as well as ammonia and nitrate, and other nitrogen-based compounds) are brought into rivers through the discharge of treated and untreated urban wastewater. Seeding of the receiving water body with nitrifying bacteria was more pronounced with untreated sewage than for treated effluents. For example, nonnitrified secondary wastewater effluents result in high levels of ammonia that remain present for a longer time in the river environment (Brion and Billen, 2000). In the marine environment, nitrifiers are localized in the upper 200 m of the water column or at the sediment–water interface (Watson et al., 1981).

Ammonia, nitrate, and nitrite can typically be found in surface water supplies as a result of natural processes. The concentration of nitrite nitrogen in surface water and groundwater is normally far below 0.1 mg/L (Sawyer and McCarty, 1978). Other sources of nitrogen can include agricultural runoff from fertilization or livestock wastes or contamination from sewage. Ammonia also occurs naturally in some groundwater supplies, and groundwater can become contaminated with nitrogen as agricultural runoff percolates into aquifers.

Seasonal highs in surface water ammonia concentrations typically occur in winter when nitrification rates decline. Groundwater generally contains low concentrations of ammonia because of the cation exchange capacity of soil, unless there have been anthropogenic inputs (Bouwer and Crowe, 1988). No organism that has been identified is capable of fully oxidizing ammonia to nitrate. Consequently, the classification of nitrifying bacteria is based primarily upon oxidation of either ammonia or nitrite. Even though several species of heterotrophic bacteria are able to produce nitrates and nitrites, their contribution to total nitrification seems to be insignificant in comparison to autotrophic processes (Kihn et al., 2002).

NITRIFICATION AND REGULATORY COMPLIANCE

Nitrification and the Safe Drinking Water Act

Nitrification can lead to chemical and biological degradation of water quality and can potentially impact compliance with the following Safe Drinking Water Act (SDWA) requirements:

- Surface Water Treatment Rule (SWTR),
- Total Coliform Rule (TCR),
- Lead and Copper Rule (LCR),
- Stage 1 D/DBP Rule and recently published Stage 2 DBP Rule,
- primary MCL for nitrate and nitrite,
- Phase II Inorganic Contaminant Rule.

It should be noted that currently there are no case studies reported in the technical literature that link nitrification episodes to direct violation of any existing rules under the SDWA; however, nitrification is mentioned as a possible contributor among other parameters that caused a violation of an SDWA rule, specifically, the LCR. Also, nitrification may have an impact on compliance with new rules, such as the Stage 2 D/DBP Rule. It is unclear how nitrification may impact compliance with potential revisions to the TCR. Table 1-2 provides a summary of water quality and possible compliance issues as they relate to nitrification.

Another indirect impact of nitrification is that degradation in water quality can affect the aesthetic quality of the water and generate customer complaints due to taste, odor, and particles in the water.

Table 1-2 Water quality and compliance issues caused by nitrification

Water Quality Issues		Compliance Issues
Chemical	Disinfectant depletion	Surface Water Treatment Rule, Total Coliform Rule
	Nitrite/nitrate formation	MCL violation*
	Dissolved oxygen depletion	Total Coliform Rule, Lead and Copper Rule
	Reduction in pH and alkalinity	Lead and Copper Rule
	DBP formation due to mitigation techniques	Stages I and II Disinfectants/Disinfection By-products Rule
Biological	HPC increase	Surface Water Treatment Rule, Total Coliform Rule
	Coliform occurrences	Surface Water Treatment Rule, Total Coliform Rule
	Increase in AOB and NOB	Surface Water Treatment Rule, Total Coliform Rule, primary nitrate and nitrite MCLs*

NOTE: AOB, ammonia-oxidizing bacteria; HPC, heterotrophic plate count; MCL, maximum contaminant level; NOB, nitrite-oxidizing bacteria.

* Compliance with nitrate and nitrite MCLs is required at the point of entry to the distribution system, not within the distribution system.

Surface Water Treatment Rule

Disinfectant depletion and HPC count increases are examples of water quality impacts associated with nitrification that are addressed under provisions of the SDWA. The loss of a disinfectant residual does not necessarily pose a direct public health threat; however, disinfectant decay can allow microbiological growth of organisms within the bulk water or accumulated sediments.

The Surface Water Treatment Rule establishes maximum contaminant level goals (MCLGs) for viruses, *Legionella*, HPC, and *Giardia duodenalis* (formerly *G. lamblia*). It also includes treatment technique requirements for filtered and unfiltered systems that are specifically designed to protect against the adverse health effects of exposure to these microbial pathogens. The SWTR requires that a "detectable" disinfectant residual be maintained in at least 95% of samples collected throughout the distribution system on a monthly basis (or HPC measurements not exceeding 500 cfu/mL). In general, the minimum detectable residual may be considered the detection limit of the field test analysis employed. This is assumed to be 0.01 mg/L for chlorine and chloramines (APHA et al., latest edition). A system that fails to comply with this requirement for any two consecutive months is in violation of the treatment technique requirement. Public water systems must monitor for the presence of a disinfectant residual (or HPC levels) at the same frequency and locations as total coliform measurements taken pursuant to the TCR. The growth of HPC bacteria can interfere with the detection of coliform bacteria and falsely indicate the safety of a water supply.

Lead and Copper Rule

Nitrification may have an indirect effect on LCR compliance. For example, reductions in pH and alkalinity due to hydrogen ion formation as a symptom of nitrification may, in turn, affect lead leaching and lead scale. Although reductions in pH and alkalinity may not pose a direct public health threat, such reductions could theoretically result in enough elevated lead samples to contribute to an exceedance of the LCR action level (USEPA, 1991) as well as failure to maintain optimal water quality parameters such as pH.

In 1997, the City of Willmar, Minnesota, conducted a study to determine the causes of copper corrosion within household plumbing systems. Preliminary indications were that both nitrification and copper corrosion proceeded simultaneously during water distribution in the customer plumbing system, so that there might be a causal relationship between the two phenomena within specific households (Murphy et al., 1997). System-wide LCR violations due to nitrification have not yet been cited in the literature.

Nitrite and Nitrate Primary MCLs and Phase II Inorganic Contaminants

Under the SDWA, primary MCLs have been established for nitrite, nitrate, and the sum of nitrite plus nitrate. The MCLs are 1 mg/L for nitrite (as N), 10 mg/L for nitrate (as N), and 10 mg/L for total nitrate/nitrite (as N). The USEPA Phase II Inorganic Contaminant regulations require water systems to sample for nitrite and nitrate at each entry point to the distribution system at least annually. Additional monitoring is required on a quarterly basis for at least 1 year following any one routine sample in which the measured concentration is greater than 50% of the MCL (USEPA, 2001a). It should be noted that the nitrite and nitrate MCLs apply at the point of entry to the distribution system, and therefore, elevated nitrite/nitrate levels measured as a result of nitrification within the distribution system are not currently regulated. However, in

Table 1-3 Overview of nitrification and chloramine reactions

Reaction Description	Overall Reaction
1. Ammonia and nitrite utilization	$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$
	$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$
2. Release of ammonia through chloramine decay (autodecomposition)	$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+$
3. Release of ammonia through oxidation of organic matter by chloramine	$1/10C_5H_7O_2N + NH_2Cl + 9/10H_2O \rightarrow 4/10CO_2 + 1/10HCO_3^- + 11/10NH_4^+ + Cl^-$
4. Release of ammonia through reaction of chloramine with corrosion products at pipe surfaces*	$1/2NH_2Cl + H^+ + Fe^{2+} \rightarrow Fe^{3+} + 1/2NH_4^+ + 1/2Cl^-$
5. Release of ammonia through catalysis reactions of chloramine at pipe surfaces	$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+$
6. Release of ammonia through oxidation of nitrite by chloramine*	$NH_2Cl + NO_2^- + H_2O \rightarrow NH_3 + NO_3^- + HCl$

Adapted from Woolschlager et al. 2001.

* These equations may not be significant in distribution systems, especially in situations of biologically accelerated chloramine decay.

some states if any drinking water sample is analyzed using certified methods and a regulated contaminant is found above its MCL, then the result must be reported to the regulator/state, even though it might not be reported as part of the official regulatory compliance program.

Ammonia can be released from chloramine through a series of complex reactions, as shown in Table 1-3. Reactions 2 through 6 describe five mechanisms of ammonia release presented by Woolschlager et al. (2001). According to Valentine et al. (1998), the overall net stoichiometries can be used to examine the relationship between chloramine decay and ammonia production. According to Table 1-3, reactions 1 and 2, for every mol of ammonia-N produced by chloramine decay, a 1-mol equivalent of nitrite-N is produced by subsequent utilization of the ammonia-N by AOB. Subsequently, for every mol of nitrite-N produced by AOB, a 1-mol equivalent of nitrate-N is produced by NOB.

Nitrite and nitrate are produced during nitrification through ammonia utilization by nitrifying bacteria. The results in Table 1-4 show that by using reaction 3 in Table 1-3, which is the most conservative chloramine decay reaction in terms of quantity of ammonia produced, the nitrite-N MCL of 1 mg/L could theoretically be exceeded if the chloramine dose is at 3 or 4 mg/L (as total chlorine) and the Cl_2:NH_3-N ratio is less than 5:1. As the chlorine to ammonia-N ratio decreases, more ammonia becomes available for the nitrification process. In a pilot-scale distribution system, Harrington et al. (2002) measured nitrite concentrations equal to 1 mg/L as N with an average total chlorine concentration of 4.6 mg/L and a Cl_2:NH_3-N ratio of 3.9:1. The pilot train represented conventionally coagulated Lake Mendota (Madison, Wisconsin) water at a pH of 9.

Valentine et al. (1998) conducted a series of mass and redox balances on solutions of varying pH, NOM concentration, and initial chloramine concentration. For all conditions that were studied, the amount of nitrate formed as a percentage of monochloramine decay was less than 15%, and for all but three cases the amount was less than 10%. The authors concluded that although nitrate is an important decomposition product of monochloramine decay, it is not the major nitrogen-containing species of decomposition.

Table 1-4 Theoretical nitrite/nitrate production based on chloramine decay stoichiometry (using reaction 3 in Table 1-3)

Chlorine to Ammonia-N Ratio	Total Chlorine Dose (mg/L)	Ammonia-N Dose (mg/L)	Nitrite/Nitrate-N Produced* (mg/L)
5:1	4	0.8	0.9
4:1	4	1.0	1.1
3:1	4	1.3	1.5
5:1	3	0.6	0.7
4:1	3	0.8	0.8
3:1	3	1.0	1.1
5:1	2	0.4	0.4
4:1	2	0.5	0.6
3:1	2	0.7	0.7
5:1	1	0.2	0.2
4:1	1	0.3	0.3
3:1	1	0.3	0.4

From AWWA and EES, 2002.

*Assumes: (1) 100% of chloramine decay according to reaction: $^1/_{10}C_5H_7O_2N + NH_2Cl + {}^9/_{10}H_2O \rightarrow {}^4/_{10}CO_2 + {}^1/_{10}HCO_3^- + {}^{11}/_{10}NH_4^+ + Cl^-$; (2) 100% conversion of ammonia to nitrite/nitrate.

Using data from a survey of 40 utilities that use chloramine as a disinfectant and an earlier survey by Hack (1984), Wilczak et al. (1996) indicate that nitrite-N and nitrate-N levels may increase by 0.05 to 0.5 mg/L, although increases of greater than 1 mg/L are possible. The authors concluded that changes in nitrite and nitrate levels in drinking water usually caused by nitrification are not substantial enough to exceed regulatory requirements as long as source-related levels are not near the regulatory MCLs. Nitrite levels during nitrification episodes have been reported ranging from 0.005 to 0.5 mg/L as NO_2^--N, with levels more frequently ranging from 0.015 to 0.1 mg/L (Wolfe and Lieu, 2001). Figure 1-2 is an example of ammonia and nitrite levels found in one utility distribution system during a nitrification event (Cohen, unpublished data). Figure 1-3 compares treatment plant effluent and distribution system nitrite concentrations in nine chloraminating utilities (Wilczak et al., 1996). The figures show that nitrite levels during nitrification events can vary from as little as 0.005 mg/L to as much as 1 mg/L.

CONCLUSIONS

Nitrification is a microbiological process by which reduced nitrogen compounds (primarily ammonia) are sequentially oxidized to nitrite and nitrate. The use of chloramine as a secondary disinfectant and the passage of nitrifying bacteria into the distribution system are the main causes of nitrification in water distribution systems. Since nitrifying bacteria are ubiquitous in the environment and the distribution system, nitrification will occur if the physical and chemical conditions that support the growth of these organisms exist and sufficient levels of free ammonia are present in the water.

Ammonia is present in drinking water through naturally occurring processes, through ammonia addition during secondary disinfection to form chloramines, and

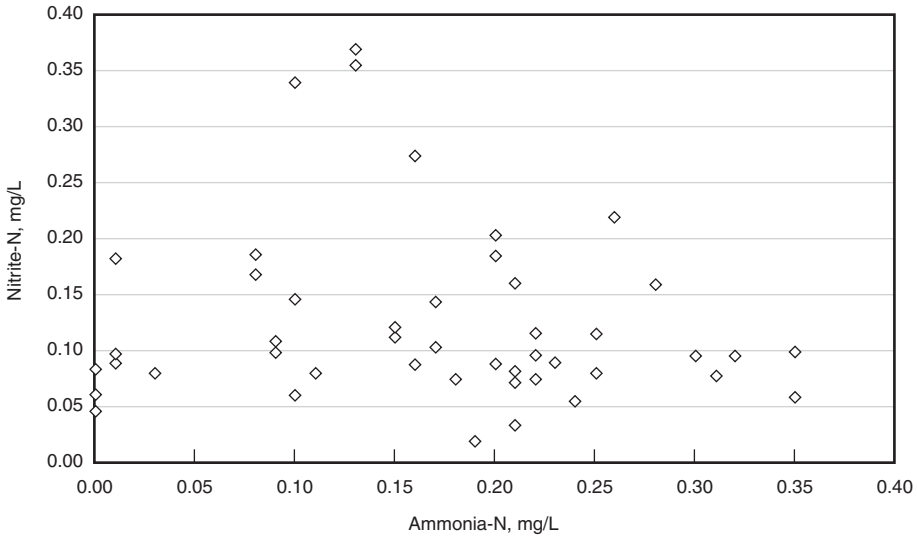
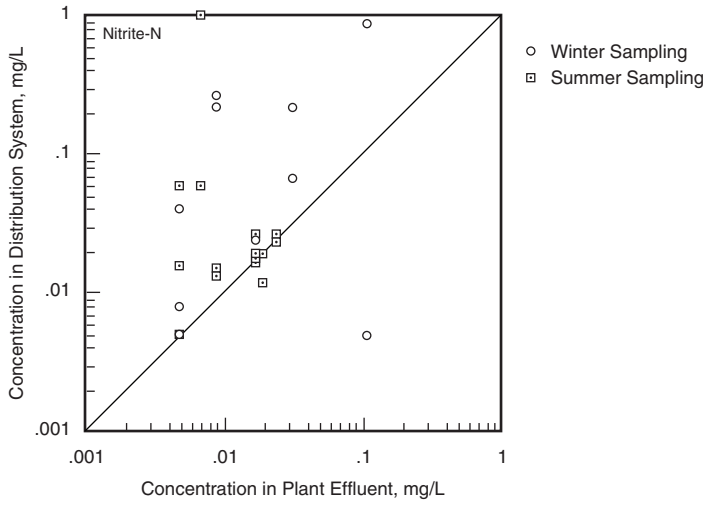


Figure 1-2 Ammonia and nitrite levels at one utility



Source: Kirmeyer et al., 1995.

Figure 1-3 Comparison between plant effluent and distribution system concentrations of nitrite

when it is released into the water due to chloramine degradation. Since the use of chloramine is expected to increase in the near future as a response to more stringent DBP MCLs associated with the Stage 1 and Stage 2 D/DBP Rules, the occurrence and impacts of nitrification are expected to increase.

There are several symptoms of nitrification that can impact distribution system water quality. Of the water quality issues identified in the literature and summarized in Table 1-2, only the formation of nitrite and nitrate within the distribution system poses a potential direct public health threat and is not addressed through

current provisions of the SDWA. However, a nitrite or nitrate MCL violation within the distribution system is unlikely, unless treated water nitrite and nitrate levels are already near their respective MCLs due to poor source water quality. As to the impact of nitrification on the LCR, ongoing research and more information should be available in the future. Although current regulations do not seem to be impacted directly by nitrification, it is a good practice to minimize the adverse effects of nitrification in the distribution system, especially the loss of a disinfectant residual, the growth of HPC bacteria, the formation of nitrite and nitrate, and any decrease in pH and alkalinity.

The causes of nitrification, its prevention, and mitigation are discussed in detail in the following chapters. Prevention of nitrification should be considered a good water quality maintenance practice since it helps to provide a more stable chloramine residual in the distribution system and water that is biologically stable in terms of limiting AOB and NOB growth as well as the growth of HPC bacteria prevalent during nitrification episodes. Maintenance of a disinfectant residual and the biological integrity of the distribution system also appear to be important from a customer perception point of view as well as from a distribution system security point of view, since a disinfectant residual is commonly used as one "indicator" of distribution system integrity.

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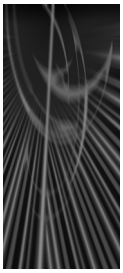


Chapter 2

Nitrification in Water and Wastewater Treatment

Andrzej Wilczak

INTRODUCTION

This chapter discusses available information on the occurrence of nitrification in water treatment plants and its potential impact on distribution system water quality. Nitrification as part of the water treatment process can occur whenever ammonia is present in or added to the source water, and water is not initially free chlorinated to achieve breakpoint. Nitrification can be either controlled or uncontrolled. Controlled nitrification may be conducted, for example, when the concentrations of source water ammonia are high and the desire is to remove it partially or completely. Nitrification has been used and modeled extensively in wastewater treatment, and it is useful to understand the lessons learned there and draw certain comparisons and parallels that may improve our understanding of nitrification in water treatment and distribution. The key findings of this review are summarized in Table 2-1.

NITRIFICATION IN DRINKING WATER TREATMENT PROCESSES AND IMPACT ON THE DISTRIBUTION SYSTEM

Nitrification may be promoted within the treatment plant as a strategy to manage ammonia present in the source water and avoid its carryover to the distribution systems. When free chlorine is the desired residual disinfectant in the distribution system, the removal of ammonia naturally occurring in the raw water is beneficial to reduce chlorine demand and avoid chloramine formation. Such treatment is more common in countries where chloramination is not practiced, e.g., France and Germany. Both physicochemical and biochemical processes can be applied for ammonia removal. The physicochemical processes (ion exchange and chemical oxidation) have certain disadvantages. There is no selective cation exchanger for ammonium ion and, therefore, the sorption capacity of the cation exchanger is also exhausted by cations other than ammonium ion. Breakpoint chlorination may require high chlorine doses and possibly more advanced treatment, such as granular activated carbon (GAC) adsorption to remove resulting taste and odor compounds as well as chlorination byproducts. In the United States, breakpoint chlorination has been the most prevalent

Table 2-1 Key points from chapter 2

Nitrification in Water Treatment	• Nitrification as part of the water treatment process can occur whenever ammonia is present in or added to the source water and water is not initially free chlorinated to achieve breakpoint. • Controlled and complete nitrification (to nitrate) can be accomplished in various types of filter beds. • Uncontrolled and incomplete nitrification (to nitrite) in filter beds is not desirable because it increases chlorine demand and can lead to serious nitrification in the distribution system. • Temperature is one of the major factors impacting nitrification in a filter bed. Low loading rates, long solids retention times, and steady-state operation are needed to achieve a high degree of nitrification in a filter bed. Nitrification can occur even in very cold waters at 1°C (34°F) if long detention time and appropriate nutrient concentrations are available. • More porous filter media are better for achieving nitrification in a filter bed, especially in cold water, in order of decreasing effectiveness: macroporous carbon > microporous carbon > anthracite > sand. • Preammoniation or passing chloramines through a GAC bed can lead to colonization of the treatment train and distribution system by the nitrifying bacteria and severe nitrification in the distribution system. • A final barrier should be placed at the effluent of the treatment train utilizing nitrification or biological organic carbon removal: postdisinfection, nonbiological granular media, or membrane filtration to ensure that neither undesirable organisms nor growth products pass into the distribution water.
Nitrification in Wastewater Treatment Versus That Occurring in Drinking Water Treatment and Distribution Systems	• The growth rate of AOB in the wastewater treatment process is mostly independent of ammonia concentration and is an "all-or-none" phenomenon; it either proceeds at 100% ammonia removal or near zero when bacteria grow too slowly and are washed out. Nitrification in wastewater treatment is typically modeled as Monod, or dual Monod kinetics for low DO systems, which is independent of ammonia at NH_3 concentrations somewhat higher than the half-saturation constant, *K*, estimated at 1 mg/L N. • Although the nitrification rate may be zero order (independent of substrate concentration, i.e., ammonia) at the head of a plug-flow system, e.g., attached growth reactor, this is not the case near the outlet where the substrate concentrations decrease substantially. • The growth rate of AOB in drinking water systems may also depend on free ammonia concentration, except that *Nitrosomonas oligotropha* requires very little substrate and its growth rate may become substrate-limited only at very low NH_3 concentrations below 0.1 mg/L N or even less. This is still an issue of scientific debate because very few studies have been done so far on *Nm. oligotropha*. Nevertheless, keeping free ammonia low in the distribution system should be considered key to nitrification control. • Nitrification in drinking water distribution systems can occur over a wider range of temperature, pH, and DO than in wastewater given very long residence times for the nitrifying bacteria in drinking water distribution systems and low levels of ammonia. This may also be due to the difference in microbes between the two systems. The drinking water systems have *N. oligotropha* while the wastewater systems have different species. • Based on experience gained from water and wastewater treatment practices, optimal nitrification control in drinking water storage facilities should occur in completely mixed, clean reservoirs with minimal deposits, having high water turnover to surpass AOB growth rate and cause their washout. A completely mixed tank will provide the highest possible chloramine concentration and lowest possible free ammonia concentration (it also provides more uniform concentrations throughout the tank).

NOTE: AOB, ammonia-oxidizing bacteria; DO, dissolved oxygen; GAC, granular activated carbon.

method for removing source water ammonia. Based on average raw water ammonia concentrations less than 0.2 mg/L N, as reported in chapter 1, a 1.5-mg/L dose of chlorine will achieve breakpoint and free chlorine residual. Currently, the practice of raw water chlorination is becoming less popular and the first chlorine addition point may be relocated further downstream, e.g., after the filters. In that case, biological nitrification may develop in the holding or sedimentation basins or within the filter beds.

Biological nitrification consisting of water aeration and subsequent (or simultaneous) biological step has been generally recommended in Europe as preferable to chemical methods (Janda and Rudovsky, 1994). Filter media (sand, anthracite, or GAC) have been used as a support for the growth of nitrifying bacteria. Sand covered with manganese dioxide has also been reported to be an effective support for attachment of nitrifying bacteria (Janda and Rudovsky, 1994). Kimura et al. (2001) described operation of an experimental rotating biofilm membrane (polysulfone, 750,000 Dalton molecular weight cut-off) pilot reactor treating coagulated and settled river water for ammonia removal.

Impact of Filter Media and Filtration Conditions

Laurent et al. (1997) stated that temperature was one of the major factors impacting nitrification in a filter bed with the optimum between 25 and 30°C. When temperature dropped below 7°C, nitrification in biological activated carbon (BAC)/sand filters was more effective than in the sand filters. Filter media porosity, the filtration rate, and the empty bed contact time (EBCT) are the key parameters for the removal of biodegradable organic matter (BOM) and ammonia at filtration rates varying from 5 to 16 m/h. More porous filter media are better for achieving nitrification in the filter bed, especially in cold water:

macroporous carbon > microporous carbon > anthracite > sand

Macroporous carbon was colonized much faster by the nitrifiers than microporous carbon (Laurent et al., 1997).

Rittmann and Snoeyink (1984) described four types of nitrification process units and conditions for filtration: biological filters (flooded or trickling), fluidized bed filters, rapid sand filters, and GAC beds. Low loading rates, long solids retention times, and steady-state operation are needed to achieve effluent ammonia concentration less than 0.1 mg/L N. Gravel filters treated Thames River water at rates of 0.8 to 2.8 m/h with a raw water ammonia concentration of 2 to 3 mg/L N. Despite reduced efficiency, the biological filter maintained about 50% efficiency at 5°C and a loading rate of 2.4 m/h and maintained good nitrification even at 3°C. In a fluidized filter reactor, nearly 100% removal was achieved at temperatures from 4 to 21°C, as long as the fluidized solids concentration was at least 30% by volume. About 50% removal of 1.3 mg/L ammonia nitrogen occurred during rapid sand filtration of Illinois groundwater at 4.9 m/h. Activated carbon columns loaded at 4.84 m/h (9 min EBCT) removed 78% of ammonia across the bed. No information was given if nitrification was complete (to nitrate) or incomplete (to nitrite) in any of these cases (Rittmann and Snoeyink, 1984). Filters filled with GAC provided better nitrification than sand or anthracite filters, especially when external conditions were unfavorable (low ammonia concentration, low temperature). On a volumetric basis, GAC appeared to be three times more effective than sand (Kihn et al., 2002).

A period of colonization is required following startup of biological filters before constant ammonia removal is reached. During this period, ammonia breakthrough and nitrite formation can alter the quality of filtered water. The GAC filters at 20°C showed that nitrification occurred 2 weeks after the filters were in service (Kihn et al., 2002).

Cases of Incomplete Nitrification

Seasonal variations in temperature lead to periods of process instability and incomplete removal of ammonia or increased nitrite production, both of which are undesirable from a process control and water quality point of view. Other potential issues with the application of biological processes as part of the treatment process include biomass shedding and generation of microbial growth by-products, which may lead to an increased disinfectant demand.

Andersson et al. (2001) reported 45 to 90% ammonia removal in full-scale filters at temperatures between 4 and 10°C, while this removal efficiency decreased to below 30% in cold water below 4°C. Uhl and Gimbel (2000) discussed the periodic inadequacy of the treatment process (ozonation, clarification, ozonation, dual-media filtration, GAC adsorption, groundwater infiltration) in Germany treating ammonia in river water. Ammonia concentration in the river water varied between 0.05 mg/L in summer and up to 4.2 mg/L in winter. During most of the year, effective ammonia removal by the treatment train was achieved. At temperatures above 20°C, up to 1 mg/L of ammonia was already removed during the clarification step. When water temperature dropped below 5°C, ammonia concentrations in the raw water increased very fast, and the removal capacity of nitrifying bacteria in the filters was not sufficient to treat these high concentrations.

Kors et al. (1998) discussed a case of incomplete nitrification in the Netherlands under extreme cold-water conditions below 4°C. Typically, the treatment plant (coagulation/sedimentation, holding reservoir with 100 days detention, rapid sand filtration, ozonation, softening, BAC filtration, slow sand filtration) can efficiently remove between 1.5 and 3.0 mg/L of the raw water ammonia. The holding reservoir typically accounts for 50 to 90% of ammonia oxidation to nitrate and the remaining ammonia (between 0.3 and 1.2 mg/L) is nitrified during passage through the rapid sand filters. Nitrite is typically not present in either reservoir or sand filter effluents. The temperature decreased in winter 1995–1996 to below 2.5°C for 100 days and was less than 1°C for 35 days. The water production was reduced by 20%, the backwash frequency of the filters was reduced, and low-ammonia raw water was blended to help maintain nitrification. These steps improved the removal, but the rapid sand filter effluent ammonia concentration increased to 0.8 mg/L. A phosphate salt solution was dosed ahead of the rapid sand filters at 0.1 to 0.15 mg/L PO_4^{3-} and resulted in an improvement of nitrification efficiency after 7 to 10 days lag time. Positive results in restoring nitrification by phosphate were known from the literature and other utilities' experiences. The authors indicated that a full restoration of nitrification was possible at 1°C with phosphate addition and other treatment changes discussed above.

Need for Posttreatment Following Nitrifying or Biological Filters

As early as 1935, Feben observed that a filter bed receiving ammoniated water was a near ideal environment for growth and multiplication of nitrifying bacteria and that the cells tended to clump into zoogleal masses. The sand grains become coated with aluminum hydroxide coagulant, in which ammonia-oxidizing bacteria (AOB) become imbedded. Organic matter, if present, is highly diluted and the bacteria receive an uninterrupted supply of nutrients as the waste products are washed away. The filter effluent contains these organisms and, if they survive postchlorination, they will enter the distribution system. Feben (1935) discussed nitrification in the filter beds and argued against preammoniation prior to the filters and chlorination after: "Sand filtration after ammoniation promotes their growth to a point where the chloramine process defeats its own purpose and becomes costly due to wasting of both ammonia to feed the

bacteria and chlorine to oxidize their products." He also demonstrated the relative difficulty in disinfecting nitrifying bacteria with chlorine.

Bacterial aggregates from biological processes or bacteria attached to sand or GAC particles are more resistant to disinfection than individual bacterial cells. Thus, a higher chlorine dosage and a longer contact time may be necessary following a biological process to effectively disinfect the product water (Bouwer and Crowe, 1988).

Skadsen (1993) and Tokuno (1999, 1997) reported cases of detrimental impacts of GAC filtration on distribution system chloramine stability and nitrification. In both instances, raw water was chloraminated and high doses of free ammonia were applied to fresh GAC filters. Skadsen (1993) reported the first incident of chloramine loss and nitrification in the distribution system to coincide with the change from sand to GAC filter medium. Predisinfection with monochloramine and 1.3 mg/L excess ammonia applied to the GAC filters was thought to be responsible for seeding the system with nitrifying bacteria growing in the filter bed. Possible release of GAC fines was also implicated in increased heterotrophic plate counts (HPCs) in the system. Tokuno (1997) compared operation of the newly installed GAC filter to anthracite/sand filters fed with 4 mg/L total chlorine and >0.5 mg/L free ammonia. Nitrification in the GAC filter was evidenced within 2 months of installation with complete removal of total chlorine and ammonia, pH drop of 0.4 units, 3 mg/L nitrite-N, and loss of residual in the distribution system.

Rittmann and Snoeyink (1984) stated that a single barrier (i.e., postdisinfection) between a process in which microbiological growth is encouraged and the consumer may be considered insufficient in the event undesirable organisms are produced by the process. A good alternative is to use a biological process, such as a fluidized filter bed, as the first process in the treatment train and to follow it with a conventional treatment sequence. Wilczak et al. (2003) observed that a free chlorine contact time of 1 hour or more was necessary after ozone/BAC filtration to avoid severe nitrification in the distribution system. Some modern applications of nitrifying anthracite filters in France are followed by membrane filtration, which ensures that neither undesirable organisms nor growth by-products pass into the product water (pers. commun., A. Wilczak, 2004). The impact of treatment processes on chloramine stability and subsequent nitrification is discussed in detail in chapter 4.

NITRIFICATION IN WASTEWATER TREATMENT PROCESSES

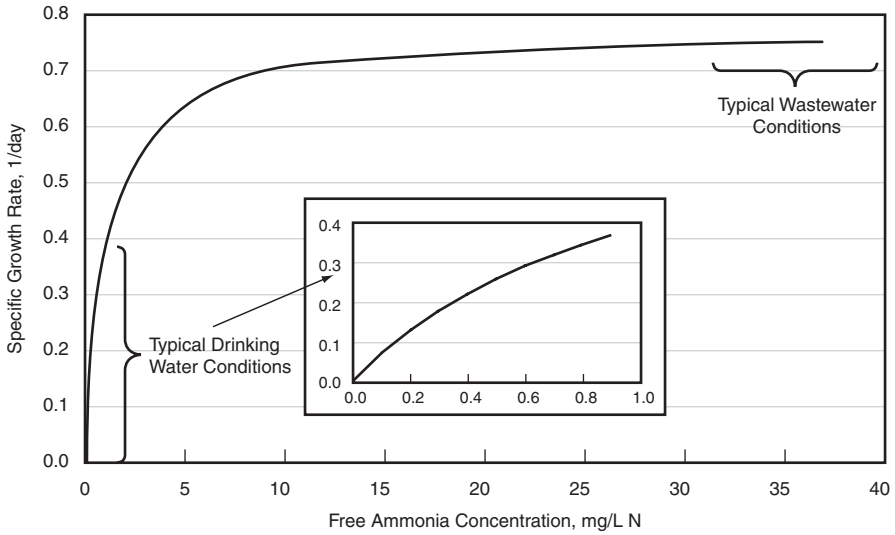
Controlled nitrification in wastewater treatment has been used successfully to reduce the load of ammonia on receiving waters (especially in-land waterways) and to reduce chlorine demand for final disinfection of treated wastewater discharges. Nitrification in wastewater has been well understood and modeled as a flow-through process at a wastewater treatment plant at ammonia concentrations (30 to 40 mg/L NH_3-N) and bacterial biomass levels orders of magnitude greater than in drinking water (<1 mg/L NH_3-N) and at both water and biomass retention times much shorter than in drinking water. Information about nitrification in wastewater is discussed briefly here to provide background for the reader and to present comparisons important for the understanding of the processes occurring in drinking water distribution systems. Interested readers may refer to Grady et al. (1999) and to Metcalf & Eddy (2003) for an in-depth discussion of nitrification in various wastewater unit processes.

Brion and Billen (2000) conducted a survey of wastewater systems for nitrifying bacteria. Nitrifying biomass in untreated wastewater generally exceeded that found in treated wastewater, including nitrified effluents evaluated at the wastewater treatment plants. Neither domestic nor industrial wastewater originally carries nitrifying bacteria, and the anoxic conditions thought to be associated with the raw wastewater should not be suitable for the growth of nitrifying bacteria in the sewer system. It is possible that nitrifying organisms grow where oxygenated conditions exist within the

sewer at the beginnings and at small waterfalls throughout the collection system. Secondary treatment of wastewater by an activated sludge process resulted in a reduction of the nitrifying biomass. This is probably related to the fact that nitrifying bacteria are associated with particulate matter removed during secondary sedimentation. Tertiary treatment in different nitrification systems did not necessarily result in an increase of the nitrifying biomass in treated wastewater. Indeed, the nitrifying biofilter effluents showed a reduction in the biomass probably because of the mechanical filtering effect and the active bacterial grazing occurring in these filters.

Nitrification in Suspended Growth Reactors

Nitrifying bacteria are the most important aerobic autotrophs found in wastewater, and for the nitrogen levels normally found in domestic wastewater the kinetics of their growth can be adequately represented by the Monod equation (Figure 2-1, Eq. 6-1). The Monod equation shows that the rate of growth sharply increases with the amount of free ammonia available and above 5 mg/L N or so that increase in growth rate is more gradual, eventually becoming flat and independent of ammonia concentration at very high ammonia levels. The growth of AOB is generally thought to be rate controlling. During the initiation of nitrification, nitrite concentrations will initially accumulate, as the growth of nitrite-oxidizing bacteria (NOB) cannot occur until the AOB generate nitrite (Metcalf & Eddy, 2003). The maximum specific growth rate coefficient for autotrophic bacteria is almost an order of magnitude lower than that for heterotrophic bacteria, around 0.8/day for both *Nitrosomonas* and *Nitrobacter* (NOB) at 20°C, suggesting that the sludge retention time (SRT) for nitrifying bacteria needs to be almost an order of magnitude longer than for heterotrophic bacteria. As a consequence, nitrifying bacteria can be lost from bioreactors under conditions that allow heterotrophic bacteria to grow freely.



Adapted from Grady et al., 1999, for *Nm. europea* in wastewater applications.

Figure 2-1 Typical *Nitrosomonas* specific growth rate versus ammonia concentration (Monod equation) at 20°C

Another characteristic of nitrifying bacteria is that their half-saturation coefficient K (substrate concentration allowing bacteria to grow at half of their maximum rate) is low; the typical value is 1.0 mg/L as N. Because of this relatively low half-saturation coefficient for AOB, the nitrification rate in wastewater applications is typically oxygen-limited and independent of ammonia concentration. As a consequence, nitrification in wastewater treatment often proceeds as an all-or-none phenomenon. In other words, since ammonia concentration entering municipal wastewater treatment systems is on the order of 30 to 40 mg/L, the percent nitrification approaches 100% whenever the SRT is long enough to give stable growth and rapidly falls to zero as washout of nitrifying bacteria occurs. The washout and rapid drop in nitrification (increase in effluent ammonia concentration) occurred between 2 and 5 days SRT in completely mixed wastewater reactors at temperatures above 20°C (Grady et al., 1999).

The growth of nitrifying bacteria in suspended-growth wastewater reactors is particularly sensitive to pH, temperature, and dissolved oxygen (DO) levels. The growth rate of *Nitrosomonas* reaches its maximum at a pH of about 8 and declines sharply for lower pH levels (Grady et al., 1999). The temperature has a profound impact on the SRT in completely mixed wastewater reactors. The minimum SRT required for nitrification was about 1 day at 25°C, about 2.5 days at 15°C, and about 4.5 days at 10°C (Grady et al., 1999). The typical design SRT values were listed by Metcalf & Eddy (2003) as 4 to 7 days at 20°C and 10 to 20 days at 10°C.

Nitrification in Attached-Growth Reactors

The presence of biofilm prevents washout of a continuous stirred tank reactor. As a result, reactors containing biofilms are capable of removing substrate at hydraulic residence times (HRTs) well below those that cause washout in a mixed reactor without a biofilm (Grady et al., 1999). In attached-growth systems used for nitrification in wastewater, most of the organic substrate must be removed before nitrifying organisms can be established. The heterotrophic bacteria have a higher biomass yield and thus can dominate the surface area of fixed-film systems over nitrifying bacteria. The nitrification rate decreases further down in the packing within a trickling filter as ammonia concentration decreases (Metcalf & Eddy, 2003). Hydraulic application rates for tertiary nitrification (after biological oxygen demand [BOD] has been removed) in trickling filters may range from 0.4 to 1.0 L/m^2-s. Surface nitrification rates range from 1.0 to 3.0 g/m^2-d, with about a 20 to 50% decline in the observed rate as the temperature decreases from 20 to 10°C. Some investigators have observed minimal temperature effects for tertiary nitrification, which may indicate that the impact of temperature on nitrifying bacteria in attached biofilm is less pronounced than on bacteria growing in suspension. Several submerged attached-growth reactor designs are available for nitrification and denitrification with HRTs as low as 1 to 1.5 hours (Metcalf & Eddy, 2003).

COMPARISONS BETWEEN NITRIFICATION IN WATER AND WASTEWATER

Nitrification is utilized during wastewater treatment because sewage often contains 40 mg/L N of ammonia (more specifically, total Kjeldahl nitrogen, which hydrolyzes to ammonia). An important phenomenon associated with nitrification in wastewater applications is washout when the bacterial biomass grows too slowly to sustain the process. Washout is to be avoided in wastewater treatment, and attached-growth reactors accomplish that.

Nitrifying bacteria are slower growing in drinking water distribution systems than in wastewater applications given that the levels of free ammonia are below the

half-saturation constant of 1 mg/L N. For example, assuming Monod kinetics and parameter estimates for *Nm. europea* (see Figure 2-1), with 0.5 mg/L free ammonia substrate, they would grow at 33% of the typical maximum specific growth rate of 0.77/day (see Figure 2-1), with 0.25 mg/L free ammonia at about 20% maximum growth rate, and with 0.1 mg/L free ammonia at only 10% of the maximum growth rate. These may not be absolute numbers representative of actual growth rates in drinking water distribution systems but they suggest that minimizing the concentration of free ammonia will slow down nitrifiers' growth rate. This is an important concept and key to nitrification control in drinking water distribution systems. It suggests that combining free ammonia with booster chlorination, a practice beginning to be used by water utilities and discussed in chapter 10, could be very effective for nitrification control. The presence of chloramine residuals, for example, during the fill cycle of a reservoir, would provide some inhibitory action and could further reduce the nitrifiers' growth rate.

Recent research by Regan and Harrington (unpublished data) indicates that *Nitrosomonas oligotropha* (the prevalent AOB in chloraminated systems) may have a significantly lower half-saturation constant (K), around 0.1 mg/L N or less, giving it a competitive advantage over other AOBs in these systems. If that is the case, *Nm. oligotropha* may not be as impacted by the levels of ammonia as other nitrifiers and the dependence between ammonia concentrations and the growth rate could occur only at very low ammonia concentrations near 0.01 mg/L N. Future research will elucidate it, but even if the half-saturation constant is lower than previously thought, the recommendation of boosting chlorine and combining free ammonia provides a good way of maintaining a more uniform disinfectant residual throughout the distribution system.

The drinking water nitrification process would be equivalent to that of a tertiary submerged attached-growth reactor since relatively little organic carbon is present and bacteria predominantly grow in the filter media, sediments, or wall deposits. Nitrification in drinking water occurs over a wider range of pH, temperature, and DO than in wastewater given the very long residence times for the nitrifying bacteria.

The impact of pH and DO in drinking water should not be as pronounced as in wastewater. Within the pH range between 7 and 9, the growth rate may drop to 80% of the maximum at pH of 8 but still be high enough given especially long residence times in distribution storage reservoirs. Similarly, the half-saturation constants for DO for *Nitrosomonas* and *Nitrobacter* have been reported between 0.3 and 1.3 mg/L O_2 and oxygen inhibition occurs somewhere below 1.0 mg/L O_2, as reported in chapter 6. DO levels are typically much higher in drinking water, resulting in lesser impact of this variable on the growth of nitrifiers. Nitrifying bacteria can grow in drinking water at various temperatures. Many of the differences between wastewater nitrification and drinking water nitrification may be due to the fundamental differences in microbial ecology beyond the scope of this brief review.

CONCLUSIONS

Nitrification can occur within the water treatment process if there are elevated levels of ammonia in the source water. The strategy is typically to promote nitrification within a filter bed to provide surface for attached growth and maintain low and steady filtration rates. Nitrification can also occur in the holding or sedimentation basins.

Lessons learned from nitrification practice in wastewater treatment indicate that suspended-growth processes are much more susceptible to washout and temperature variations than attached-growth processes. Attached-growth tertiary nitrification is more robust and can be maintained at much shorter hydraulic retention times.

Unwanted nitrification in drinking water distribution systems (discussed in detail in chapter 3) could be best avoided by addressing the attached growth on the submerged pipes, walls, and floors of the water system infrastructure. Biofilms/deposits

may shelter nitrifying bacteria from chloramine and temperature effects; nitrification has been known to occur in relatively cold waters, given long detention times and the presence of deposits or biofilm, which may prevent washout in spite of low growth rates in cold water. Suspended growth of nitrifying bacteria in the bulk water will occur only under favorable circumstances and cause a nitrification episode (explosive growth of nitrifying bacteria in the bulk water, resulting in the loss of chloramine residual) if the attached nitrifying biomass remains unchecked.

Lessons derived from wastewater treatment would indicate that the best nitrification control strategy for a drinking water distribution storage reservoir would be in a completely mixed tank without excessive deposits or biofilm, with the water turnover high enough to cause AOB washout. A completely mixed tank provides the highest possible chloramine (biocide) concentration and lowest possible free ammonia concentration (lowest possible nitrifier growth rate).

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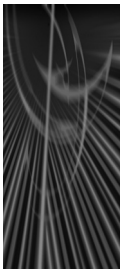

Chapter 3

Nitrification in Drinking Water Distribution Systems

Andrzej Wilczak

INTRODUCTION

This chapter discusses available information on the occurrence of nitrification in drinking water distribution systems and provides an overview leading to a more in-depth discussion of nitrification microbiology, monitoring, prevention, response, and engineering improvements in the subsequent chapters of this manual. The key findings of this review are summarized in Table 3-1.

NITRIFICATION IN DRINKING WATER DISTRIBUTION SYSTEMS

A baseline level of continuous biological nitrification occurs to some extent in all chloraminated distribution systems, as indicated by low concentrations of nitrite (below 0.01 mg/L N) typically measured year-round in the bulk water of full-scale sampling sites. These background nitrite levels are of no water quality concern as long as the conditions that give rise to them do not progress into a nitrification episode. A nitrification episode typically begins with steadily decreasing total chlorine residual, increasing heterotrophic plate count (HPC) bacterial counts, a free ammonia level decreasing to zero or nondetectable, and an increasing nitrite level up to and above 0.05 mg/L N. The rapid increase of ammonia-oxidizing bacteria (AOB) in the bulk water eventually causes a complete, or almost complete, loss of total chlorine residual, conversion of free ammonia to nitrite, and often a decrease in pH. Further explanation of conducting nitrification episode assessment and response is provided in chapter 9.

Occurrence of Nitrification in Distribution Systems

AOB need a source of ammonia for energy, are slow growers, and are also fairly resistant to chloramine. Because of these characteristics, AOB are well suited to living in chloraminated distribution systems, proliferating especially in water storage reservoirs and dead-end mains. Nitrification has been reported to occur in water distribution systems using chloramine throughout the United States, Europe, and Australia. Region or climate does not seem to make a difference in repeated occurrence of nitrification

Table 3-1 Key points from chapter 3

Nitrification in Drinking Water Distribution Systems	• AOB are fairly ubiquitous in chloraminated distribution systems, with the possible exception of areas closest to the water treatment plant. Low-flow dead-end mains created by design or closed valves, oversized mains, and low-turnover water storage reservoirs are primary nitrifying areas. • If the rate of AOB growth exceeds the rate of AOB inactivation, nitrification will proceed in the presence of a chloramine residual. Low levels of AOB are detected even at chloramine residuals as high as 5 mg/L Cl_2. • Nitrification episodes can affect the majority of utilities that chloraminate, especially in summer at temperatures greater than 15°C. Some systems experience nitrification in winter even in cold water (below 5°C) due to increased water age. Nitrification, if not controlled, can be a year-round phenomenon. Low-level nitrification probably occurs in parts of all chloraminated systems. • Nitrifying bacteria remain present in drinking water distribution systems in the winter. Their metabolic activity decreases to a point where they no longer create detectable signs of nitrification but they are still present and will resume activity as soon as water temperature increases. • Nitrification in drinking water distribution systems can occur over a wide range in pH from 7 to 10 and at low oxygen levels due to long detention times in the system. • One of the first molecular biology speciation studies observed that *Nitrosomonas oligotropha*, a group of AOB known to grow at low ammonia concentrations, was the predominant AOB isolated from full-scale distribution systems. *Nitrospira*, a group of NOB, were detected in nearly all distribution system samples. • Nitrification episodes in water storage reservoirs occurred when AOB levels increased initially in the bulk water to 5 to 30 MPN/mL from previously nondetected levels. Typically, increased HPC bacterial counts preceded and nitrite concentrations followed an increase in AOB concentrations. • Greater numbers of AOB grow in sediments and in pipe/reservoir wall biofilms (tens or hundreds of thousand per square centimeter) than in the bulk water; thus one can characterize nitrification as a biofilm phenomenon. Higher levels of AOB were found in pipe sediments than pipe biofilms, thus one of the reasons that water age contributes to nitrification is in the collection and deposition of sediments. • Nitrifying bacteria can form cell aggregates called cysts or zooglea increasing their protection from disinfectants. • AOB in distribution systems appear more resistant to chloramine than was expected, possibly due to biofilm protection and cell aggregation. AOB enumeration methods and the types of bacteria investigated may also be responsible for this discrepancy. • Nitrification can occur in pipes made of any material. Concrete-lined pipes had the lowest levels of AOB and HPC bacteria. The levels of AOB in cast-iron pipes were inconsistent, possibly due to microhabitat differences. • Corrosion control programs may help minimize pipe biofilms and sediment or micro-niche development, as well as in chlorine decay, and aid in nitrification control.

NOTE: AOB, ammonia-oxidizing bacteria; HPC, heterotrophic plate count; MPN, most probable number; NOB, nitrite-oxidizing bacteria.

problems (Wolfe and Lieu, 2001); however, seasonal variations in water temperature may impact when nitrification occurs. Utilities in the northern United States and in Canada typically experience nitrification in the summer only, whereas the systems located in more temperate climates may observe the activity of AOB year-round, with nitrite-oxidizing bacteria (NOB) being more active in the summer and fall seasons.

The water temperature is the main determinant, and the systems where water temperature exceeds 15°C for several months are more susceptible to nitrification.

Chloramine is not conservative in drinking water. As soon as water enters the distribution system, the chloramine residual begins to decay due to bulk water reactions and pipe wall/sediment reactions. The concentration of chloramine decreases as the water flows (ages) throughout the distribution system while the concentration of ammonia increases as a result of chloramine demand and decay reactions. Because of this, nitrification has a better chance of occurring at points farther from the treatment plant than at points near the treatment plant (Harrington et al., 2003), assuming water age is proportional to distance, or at any location where water stagnates. A 1996 American Water Works Association Research Foundation (AwwaRF) survey (Wilczak et al., 1996) indicated that nitrification might be occurring in 63% of utilities that use chloramine. A more recent AwwaRF survey (Kirmeyer et al., 2004) reported that 54% of polled utilities experienced nitrification during the summer. These findings likely reflect the perception of utility personnel about the frequency of major nitrification episodes. However, background nitrification is probably more prevalent and likely occurs in the majority of chloraminated systems at locations near the floor and walls of the reservoirs and in pipelines farther away from the treatment plants where the combination of factors (oversized mains, dead-end configurations, closed valves) allow for AOB growth. Some utilities may not realize the extent of nitrification in the distribution system depending on the scope of the monitoring program (extent of sampling locations, placement of those locations, parameters chosen for monitoring at those locations).

Temperature and pH Impacts on AOB Growth in the Distribution System

In drinking water distribution systems, nitrification has occurred at a wide range of temperatures, from 5 to 26°C (Kirmeyer et al., 1995; Odell et al., 1996; Wilczak et al., 1996), but is most often seen at temperatures above 15 to 16°C. Wolfe et al. (1990) surveyed the presence of AOB in a drinking water distribution system receiving chloraminated water; AOB were detected when the water temperature was above 16 to 18°C. Skadsen (1993) observed nitrification in full-scale drinking water distribution systems at water temperatures of 14 to 25°C.

Water temperature in distribution system pipes and reservoirs can vary widely, e.g., from 0 to 30°C, depending on the season and the location within the system. The ideal temperature range for nitrifying bacteria regrowth is 25 to 30°C, and the decomposition rate of chloramine increases with temperature wherein more free ammonia will be released. The combination of these three factors at higher temperatures: (1) an increase of bacterial growth rate, (2) the release of more substrate (ammonia), and (3) the reduction in disinfectant (chloramine), may explain why nitrification increases somewhat exponentially with increasing water temperature. Some utilities have reported more nitrification episodes during the summer (Cohen et al., 2001). Elevated reservoirs and standpipes may experience significant nitrification in the summer due to very warm water, with thermal stratification conducive to and/or resulting from water stagnation. Regrowth and nitrification can occur at temperatures as low as 5°C due to increased water age in the winter months (Wolfe et al., 1988).

Pintar et al. (2000) observed the growth of AOB in a bench-scale distribution system even at 6°C. An AOB biofilm was established at both 22°C and 12°C and both higher (0.2 to 0.6 mg/L) and lower (0.05 to 0.1 mg/L) monochloramine residual. A further temperature decrease from 12°C to 6°C did not have an impact on an established nitrifying biofilm. Evidence from this bench-scale distribution system suggests that the full-scale distribution systems may also be impacted by AOB during winter conditions. At lower temperatures (12°C) and higher residuals, significantly lower levels of

AOB were detected (0.0001 to 1 MPN/cm^2) than at low chloramine residuals (typically 1 to 10 MPN/cm^2). At higher temperatures (22°C), chloramine residual did not affect AOB levels; they were higher between 1 and 100 MPN/cm^2 (Pintar and Slawson, 2003).

In drinking water distribution systems, nitrifying bacteria can grow over a pH range of 7 to 10 due to long residence times that allow them to proliferate under less-than-optimum growth rate conditions. In a pilot system fed with a conventional coagulation process, Harrington et al. (2002) observed that nitrification occurred faster at pH 8.5 and pH 8.9, than at pH 7.9. In the pilot system fed with an enhanced coagulation process, nitrification occurred faster at pH 8.6 than at pH 8.2. Nitrification was significantly delayed in the system operated at a pH of 7.9 (Harrington et al., 2002). Since the rate of chloramine decay and free ammonia release increases at lower pH values, especially below 8.0, the majority of water systems operate at higher pH for chloramine stability and corrosion control (see chapter 4 for discussion of chemistry of chloramine decomposition).

Skadsen and Sanford (1996) reported that an elevated pH of 9.3 versus 8.5 improved the control of nitrification in drinking water distribution systems but did not completely eliminate the problem. Kirmeyer et al. (1995) and Odell et al. (1996) reported that nitrification has occurred in drinking water distribution systems with pH levels ranging from 6.6 to 9.8. In a water quality survey of 10 drinking water distribution systems, nitrification (as indicated by an increase in nitrite and nitrate concentrations above 50 µg/L N) was observed over a wide pH range, from 6.5 to 9.5 (Wilczak et al., 1996).

Species of Nitrifying Bacteria Present in Distribution Systems

The first identification studies focusing on the species of AOB and NOB proliferating in distribution systems have been published only recently. Regan et al. (2002, 2003) analyzed samples from several West Coast and Midwestern drinking water distribution systems using molecular methods for AOB and NOB identification. Bulk water samples from several reservoirs and biofilm coupon samples positioned near the top and bottom of the reservoirs were collected during known periods of nitrification. Hydrant samples were also collected from one utility at the time of no known nitrification. AOB communities were dominated by *Nitrosomonas oligotropha*, a group of AOB known to grow at low ammonia concentrations relative to other *Nitrosomonas* species. *Nm. oligotropha* exhibits a lower half-saturation constant for ammonia than other tested *Nitrosomonas* and experiences substrate inhibition at considerably lower concentrations. This characteristic would explain the proliferation of this organism in drinking water distribution systems that have relatively low levels of ammonia available for metabolism.

The NOB evaluation showed the ubiquitous detection of *Nitrospira* in each of the systems, with occasional detection of *Nitrobacter* (Regan, 2001). *Nitrospira* NOB were detected in nearly all distribution system samples tested. Recent studies have also detected *Nitrospira* strains in freshwater treatment systems. However, the majority of NOB studies have been performed on *Nitrobacter winogradskyi* and, until recently, it was believed that other NOB genera only grew in marine environments. NOB may play an important role in the ecology of nitrification and biological regrowth in chloraminated water systems. NOB oxidize nitrite to nitrate, thereby reducing the chloramine demand of nitrite produced by AOB. NOB may also contribute to the growth of heterotrophic bacteria by producing soluble organic products (Regan, 2001). NOB lag behind AOB during nitrification episodes, possibly because when nitrite is exhausted, *Nitrobacter* becomes inactivated and loses its ability to oxidize nitrite. For

example, *Nitrobacter* lost 50% of its activity during 2 days without nitrite (Painter, 1970). An in-depth discussion of nitrifying bacteria speciation and growth conditions is presented in chapters 5 and 6.

Resistance of AOB to Chloramine

Nitrification can progressively start even in the presence of low to medium chloramine residuals (e.g., 1 mg/L Cl_2), and once nitrifying communities are developed their growth cannot be easily stopped even by applying chloramine doses in excess of 4 mg/L Cl_2, as shown below by the examples from several water systems. If the rate of AOB growth exceeds the rate of AOB inactivation, nitrification will proceed in the presence of chloramine residual. More detailed discussion of AOB inactivation is presented in chapter 6.

Cunliffe (1991) examined 1,184 samples collected from five chloraminated drinking water supplies for the presence of nitrifying bacteria. Nitrifying bacteria were detected in 64% of all samples and in 21% of samples with more than 5.0 mg/L monochloramine (Table 3-2). In a water quality survey of 10 drinking water distribution systems, Wilczak et al. (1996) observed increases in nitrite and nitrate concentrations above 50 µg/L N in the distribution systems, even at high chloramine concentrations in finished water entering the distribution systems (3 to 6 mg/L Cl_2).

Kirmeyer et al. (1995), Odell et al. (1996), and Harrington et al. (2002) observed that a chloramine dose above 2.0 mg/L may prevent the onset of nitrification. However, once a population of nitrifying bacteria was established, a similar chloramine concentration did not inhibit the growth of nitrifying bacteria.

Skadsen (1993) observed nitrification (as indicated by a decrease in chloramine residual, an increase in HPC, and/or an increase in nitrite concentration) in a full-scale drinking water distribution system with a monochloramine residual of 4.6 mg/L. The pH was 8.7 to 8.8 at the finished water reservoir, and it may have decreased by 0.5 to 1.0 pH unit in the distribution system. Signs of nitrification persisted even after increasing the chloramine dose to 8.0 mg/L. The water temperature was 14 to 25°C and the chlorine to ammonia-N (Cl_2:NH_3-N) ratio was 3.6:1 (Skadsen, 1993). Even after increasing the Cl_2:NH_3-N ratio to >4.5:1, nitrification was still detected in this distribution system. Nitrification was finally stopped using 0.7 to 1.8 mg/L free chlorine in

Table 3-2 Frequency of detection of nitrifying bacteria in five chloraminated South Australian water systems

Total Chlorine Residual (mg/L)	Number of Samples Tested	Samples Containing Nitrifying Bacteria (%)	Median Number of Nitrifying Bacteria (#/mL)
0.1–0.2	343	88	130
0.3–1.0	156	71	4.1
1.1–2.0	215	64	2.0
2.1–3.0	182	57	0.5
3.1–4.0	134	46	<0.2
4.1–5.0	62	42	<0.2
>5.0	92	21	<0.2
Total	**1,184**	**64**	**2.0**

Source: Cunliffe, 1991.

the distribution system (Skadsen, 1993). These reports do not contain information about the rates of chloramine demand and decay, which are critical to the ability of chloramine to counteract a nitrification episode.

Woolschlager et al. (2001) developed a Comprehensive Disinfection and Water Quality Model that accounts for the ammonia-producing reactions and the dynamics of suspended and fixed bacteria, including nitrifiers, within drinking water distribution systems. Results from the model indicate that nitrification control by increasing chloramine residual is ineffective. The study found that increasing the chloramine residual (up to a concentration similar to that measured at the treatment plant effluent, 3.3 mg/L Cl_2) to inactivate nitrifiers was ineffective. The ammonia released from chloramine decay fueled nitrifier growth, outpacing disinfection dynamics.

Interactions Between HPC and Nitrifying Bacteria

Competition between heterotrophic and nitrifying bacteria for oxygen and biofilm space may impact the effectiveness of nitrification, especially when the biodegradable dissolved organic carbon (BDOC) concentration is high. A beneficial interaction between nitrifying and heterotrophic bacteria can also occur when BDOC in the water is low. Aerobic heterotrophs usually outcompete nitrifiers, with the result that organic oxidation proceeds first, followed by nitrification, provided that sufficient oxygen remains. This occurs because the autotrophic growth rate is slower than the heterotrophic growth rate. Heterotrophic bacteria usually outnumber nitrifying bacteria because the generation time of nitrifying organisms is 8 to 36 hr or longer, even under optimal conditions (the typical generation time for HPC bacteria is on the order of 10 times shorter). Heterotrophs also appear to be less susceptible than nitrifiers to shear losses caused by high water flow rates (Bouwer and Crowe, 1988). The interactions between nitrifiers and other bacterial communities are further discussed in chapter 5.

Although nitrifiers do not require a medium (surfaces) on which to grow, they will adhere to one if present. In the marine environment, nitrifying bacteria do not remain in the water but are found in deposited sediments. An important feature of nitrifying bacteria is that they can grow in clumps or aggregates. A *Nitrosomonas* culture, when centrifuged, loses a large proportion of its activity (more than 80%), which may be attributable to the dispersal of zoogloea formed by the organisms. *Nitrosomonas* appears to be protected from the action of toxic substances by a mucilage (Painter, 1970). Examples of cell aggregates are shown in chapter 5 (Figures 5-1 and 5-2). This is significant because it points out that nitrification in drinking water is essentially a biofilm phenomenon, as evidenced by the enumeration studies discussed further in this chapter. Aggregation of bacterial cells can possibly explain some of the resistance to chloramine disinfection.

Note on the Enumeration of Nitrifying Bacteria in the Case Studies

Actual levels of AOB are likely to be much higher than reported in case studies in this chapter, given the low recovery efficiency of the MPN technique (Wolfe and Lieu, 2001). Brion and Billen (2000) calculated that the MPN counts of nitrifying bacteria converted to biomass were 2 to 3 orders of magnitude lower than the estimates deduced from the measurements of potential activity in wastewater samples. Also, MPN counts from soil and sediment samples were only 0.1 to 5% of the estimated populations that would be required to produce the observed nitrifying activity. The method of enumeration affects recovery and quantitation. For example, the fluorescent antibody technique underestimates nitrifiers' counts because not all of a sample's serotypes can be detected and so it produces estimates even lower than the MPN technique. Estimates derived from the

nitrifying activity measurements in terms of oxygen consumption rate in wastewaters (similar to BOD_5 technique) were deemed more realistic and in agreement with treatment models (Brion and Billen, 2000). Given these discrepancies, the MPN levels for nitrifying bacteria reported in this chapter for drinking water distribution systems should be considered underestimated and used perhaps only in a relative way. Chapter 5 discusses the details of different methods for isolation and enumeration of nitrifying bacteria.

NITRIFICATION IN PIPELINES AND EFFECTS OF BIOFILMS

The relative resistance of nitrifiers to chloramine does not fully explain the prevalence of nitrifying bacteria in water supplies. A second mechanism that may contribute to their persistence is their survival or growth in biofilms. Nitrifying bacteria can grow in aggregates and attach to surfaces and have been detected in large numbers in sediments. If the bacteria exist in biofilms, the organisms detected in bulk water samples with high total chlorine residuals may have been dislodged shortly before or during sampling. The frequent detection of nitrifying bacteria at the ends of distribution systems could be due to a combination of decreased water flows, which would favor the formation of biofilms, and lower chloramine residuals (Cunliffe, 1991).

Low-flow lines such as dead-ends, oversized pipes in residential neighborhoods needed for fire-flow requirements, mains with closed valves such as at pressure district boundaries, as well as reservoirs that have long hydraulic residence times are the most susceptible places for nitrification to develop (Cohen et al., 2001). Dead-end pipelines should be avoided or special precautions should be taken to preclude excessive water age. A valve-exercising program can be used to help identify inappropriately closed valves. It is not uncommon in water systems for at least 10% of the valves to be closed, thereby creating artificial dead-ends and potential water quality problems (Kirmeyer et al., 2000). Water main replacement should consider downsizing water mains where excessive water age is occurring.

It is likely that nitrification can occur irrespective of pipe material—plastic, polyvinyl chloride (PVC), asbestos-cement, ductile iron, and cast iron. Certain pipe materials may provide more favorable conditions for nitrification to occur. For example, unlined cast-iron pipes or old mortar-lined iron pipes with heavy tuberculation provide a good environment for nitrifying bacteria growth. Also, corrosion in these types of pipes will contribute to chlorine demand (Cohen et al., 2001). Accumulated sediment and biofilm can protect the AOB from bulk water chloramine residual. Higher concentrations of AOB were detected in reservoir and pipe sediment materials than in pipe biofilm samples (Wolfe et al., 1990). The AOB levels in pipe sediment were around 10 MPN/mg whereas in the pipe wall scrapings levels were between <0.2 MPN and 7.4 MPN/mg. The important factor that contributes to the survival of AOB in the distribution system and reservoirs is their presence in the sediment and biofilm material, presumably because of the larger amounts of essential nutrients and protection from disinfectant (Wolfe et al., 1990). Some information exists to indicate that AOB produce a capsule layer and grow in clumps. It is possible that they would attach to the underside of the floating cover or to the reservoir walls and floor. Some evidence indicates that the attachment of nitrifiers to solid surfaces enhances their growth and renders them more resistant to toxic compounds than freely suspended cells (Wolfe et al., 1988).

Lipponen et al. (2002) surveyed 15 drinking water distribution systems in Finland for the presence of AOB and NOB, finding high concentrations of these bacteria, especially in pipe sediments. The surveyed sites had only traces of total chlorine residual and the estimated MPN/g AOB concentrations in the pipe sediment were in the millions to hundreds of millions per gram. The NOB MPN/g of pipe sediment were in the hundred thousand concentration range. The water samples contained a maximum of 390,000 MPN/L AOB and 300,000 MPN/L NOB, which would indicate a severe

nitrification episode in spite of the low temperatures (5 to 19°C, average 12°C). No further operational details of the surveyed systems were presented, except for a low chloramine residual entering the systems below 0.7 mg/L (a typical disinfectant residual for European practice).

Camper et al. (1996) reported that a significant fraction of the bacteria growing in distribution systems was associated with the biofilms. If the chloramine demand exerted by the biofilm is sufficiently large, the biocide will only penetrate the outer part of the biofilm and ammonia will be released to the interior of the biofilm. The development of biofilm will depend on the type of material used. Concrete-lined pipes had the lowest level of AOB and HPC in comparison to other materials (Stewart and Lieu, 1997). This may be due to the alkaline nature of concrete and the impact of high pH on AOB. The levels of AOB were inconsistent in the cast-iron pipes, possibly due to microhabitat differences. Tubercules on the iron pipe may provide a protective environment for the bacteria. AOB were found in numbers as high as 100,000/cm^2 (or 10,000/mg) in distribution system biofilms, suggesting that biofilms may act as a reservoir of AOB in the distribution system. However, in some pipeline biofilm samples, toxic material probably inhibited the recovery of AOB at the lower dilution, but not the higher dilutions (Stewart and Lieu, 1997). Various metals are toxic and inhibit the respiration of nitrifying bacteria. The complete or substantial inhibition of oxygen uptake by *Nitrosomonas* occurs at 0.01*M* of iron, aluminum, copper, zinc, lead, and manganese (several hundred milligrams per liter) and at 0.0002*M* (12 mg/L) of nickel (Painter, 1970). The effect of metals on growing cultures is much more severe: complete inhibition of growth occurred at 0.25 mg/L nickel, 0.1 to 0.5 mg/L copper.

Ford (1980) reported that the nitrifying bacteria he studied were sensitive microorganisms that may have experienced severe upsets in the presence of very small concentrations of inhibitory substances. According to Ford (1980), these inhibitory substances include heavy metals, cyanides, halogenated compounds, phenols, mercaptans, and thiourea. Watson et al. (1989) also reported that many compounds at low concentrations (such as copper-binding agents, acetylene) inhibit the oxidation of ammonia to nitrite, whereas the oxidation of NH_2OH (an intermediate of the ammonia oxidation reaction) to nitrite is unaffected or much less susceptible. Metal ions such as copper, nickel, or chromium can also inhibit nitrification (Ford, 1980). The complete or substantial inhibition of oxygen uptake by *Nitrosomonas* occurs at 0.01*M* of iron, aluminum, copper, zinc, lead, and manganese and at 0.0002*M* nickel (Painter, 1970).

Implementation of a corrosion control program may help minimize pipe biofilms, improve chloramine residuals and decrease HPC bacterial counts, and aid in nitrification control. In one case, a utility implemented a 3-year corrosion control program (Cohen et al., 2003) in which unlined cast-iron pipes comprise about 53% of the 410 miles of the water distribution system. A polyphosphate-blend (approximately 77% polyphosphate and 23% orthophosphate) corrosion inhibitor was shown to produce softer corrosion products and was less cohesive than zinc orthophosphate-based corrosion inhibitors. The use of a polyphosphate blend could produce corrosion products that would be easier to remove by flushing. Application of this blend over 3 years improved total chlorine residuals. Approximately 50% of samples were less than 1.0 mg/L Cl_2 before corrosion control while afterward 100% were more than 1.0 mg/L Cl_2 and HPC bacterial counts fell from 1,600 colony-forming units (cfu)/mL to near zero (Cohen et al., 2003).

Examples of Nitrification Episodes and Frequency of AOB Detection

Cunliffe (1991) depicted a nitrification episode for a site located near the end of the chloraminated system in South Australia (Figure 3-1). The total chlorine residual decreased from between 1.5 and 2.5 mg/L to <0.1 mg/L Cl_2. The numbers of nitrifying

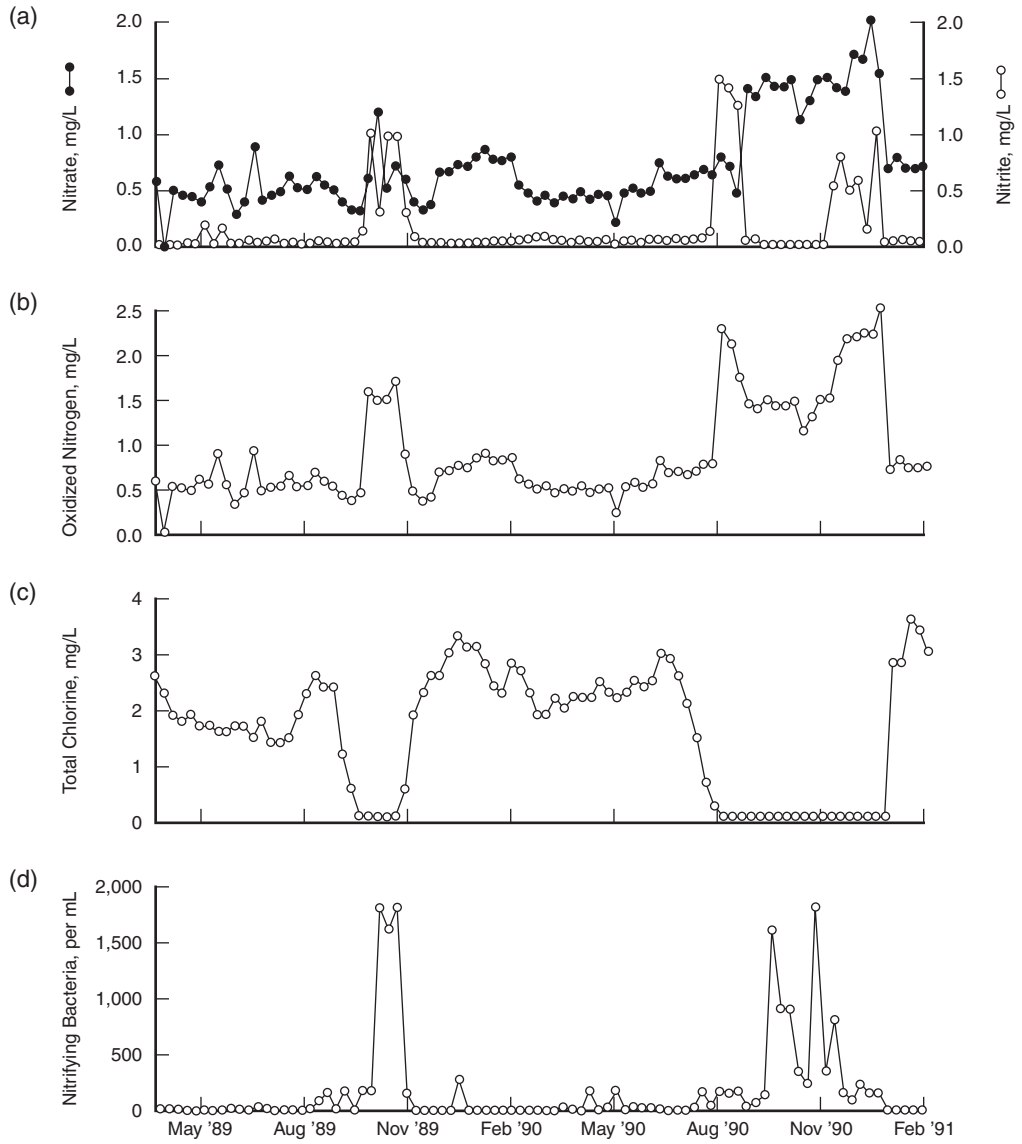

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Figure 3-1 Nitrification episode in a South Australian distribution system. Relationship between: (a) nitrite and nitrate concentrations, (b) oxidized nitrogen concentrations, (c) total chlorine residual, and (d) numbers of nitrifying bacteria.

bacteria and concentrations of oxidized nitrogen, nitrite, and nitrate all increased. Typically, nitrite concentrations increase relatively quickly but are not always sustained. When nitrite is detected, AOB are typically well established in biofilms attached on the surfaces of materials. Therefore, once AOB are established, it is conceivable that nitrite levels can increase noticeably within hours (Stewart and Lieu, 1997). Notice also that the AOB concentrations shown in Figure 3-1d increased before the jump in nitrite levels and loss of chloramine residual. They started increasing about 1 month before the nitrite increase. Unfortunately, AOB enumeration is a long process (see chapter 5 for

Table 3-3 Occurrence of nitrifying bacteria in a chloraminated distribution system in Australia

Distance From Dosing Station (km)	Positive Samples (%)	Median Number of Bacteria (#/mL)	Median Chloramine Residual (mg/L Cl_2)
Before	91	2.5	<0.1
1.5	8	<0.2	6.4
27	0	<0.2	3.9
42	5	<0.2	5.6
83	53	0.2	2.2
101	33	<0.2	2.5
110	35	<0.2	2.3
125	63	0.9	2.5
129	100	3.5	2.2
129	67	1.3	2.3
143	88	3.5	2.0

Source: Cunliffe, 1991.

discussion of isolation and enumeration techniques); therefore, nitrites remain a better indicator. HPC bacterial counts typically increase before a nitrification episode and may be used in some systems for diagnostic purposes.

The frequency of detection and the median number of AOB in the South Australian water distribution system decreased as the total chlorine residual increased, but nitrifying bacteria were still detected in 21% of samples that contained more than 5.0 mg/L of total chlorine. Table 3-2 presents the frequency of detection in the chloraminated water system between 1988 and 1990 (no temperature or pH conditions were given). Nitrifying bacteria were detected in 64% of the samples collected (Cunliffe, 1991).

Surveys of individual systems showed that there is an association between distance from the chloramine dosing station and the frequency of detection of bacteria. The results from a survey performed in 1988 and 1989 are shown in Table 3-3 (Cunliffe, 1991). Percent positive samples for AOB and bacterial concentrations increased with the distance in the distribution system in spite of maintaining a chloramine residual at or above 2 mg/L Cl_2.

NITRIFICATION IN WATER STORAGE FACILITIES

Reservoir Water Age and Mixing

Finished water storage facilities have been used to equalize water demands or shave off peaks in pumping, reduce pressure fluctuations in the distribution system, and provide reserves for fire fighting, power outages, and other emergencies. Excessive water age in many storage facilities is probably the most important factor related to water quality deterioration. Excessive water age is caused by: (1) underutilization, i.e., water is not cycled through the facility, and (2) short-circuiting within the reservoir. If short-circuiting is severe, the actual water age within a storage facility can vary significantly from the theoretical age and may range from a few minutes to weeks or months. Reservoirs located too low in a pressure zone that is not exchanging

water (so-called floaters) will likely show nitrifying activity first, due to increased water age. On the other hand, tanks located high in a pressure zone may be prone to nitrification since they will have the longest water age by distance from the entry point. They may also be seeded with nitrifiers from the lower pressure zones.

Few guidelines are available on water turnover rates. The state of Georgia and the country of Scotland recommend 50% daily turnover, whereas the state of Virginia recommends 33%. A maximum 1- to 3-day turnover is recommended in Switzerland and 5 to 7 days is recommended in Germany. These guidelines have not been specifically established for nitrification control. Even with good turnover, poor mixing can result with pockets of older water and low disinfectant residuals, and vice versa; even with good mixing, low residuals can result from excessive detention time (Grayman et al., 2000). Wolfe et al. (1988) observed that nitrification occurred in a large water storage facility in California in 1986 when the mean residence time was increased from 3.3 to 4.5 days.

Occurrence of AOB Within Water Storage Facilities

Ike et al. (1988) described a nitrification episode that occurred in California during the summer of 1987. The reservoir had a 200-acre-feet capacity and was covered with an elastomer cover. The detention time varied from 3 to 6 days at that time. The seasonal occurrence of AOB (at the top of the column) is shown in Figure 3-2.

Ike et al. (1988) reported that the number of AOB ranged from <0.18 MPN/mL during the winter months to 500 MPN/mL during a nitrification episode in the summer of 1986. During 1987, the first indication of an increase in AOB occurred on June 18. At that time, the water temperature was 18°C and the HPC was 400 cfu/mL; however, no nitrite was detected. By Aug. 5, 1987, the nitrite level had rapidly increased to 30 µg/L, the chloramine residual decreased to below 1.0 mg/L, and the level of AOB was 22 MPN/mL. In general, an increase in AOB was detected when the water temperature was over 18°C and the HPC was between 350 and 500 cfu/mL. Interestingly, nitrite was usually not detected until the AOB level reached about 1 MPN/mL. The detention time had been observed to affect nitrification in this flow-through reservoir. In general, when the detention time was decreased to 2 or 3 days, nitrite and the numbers of AOB decreased. Most likely, AOB populations were not able to impact the bulk water at such short detention times (Ike et al., 1988).

Wolfe et al. (1990) investigated the presence of nitrifying bacteria in a distribution system and found them throughout the system. The lowest AOB counts were detected in plant effluent (MPN from <2 to 15/mL), and the concentrations in reservoir effluents were comparable to those inside the reservoirs in the water column. During the summer months, AOB numbers in both reservoirs were approximately 10 times greater than they were in the reservoir influents. In the winter months, typically no AOB were detected in the reservoirs. In the summer months, the concentration of AOB in the reservoir column varied typically between an MPN of 10 and 20/mL. The beginning of the nitrification episode occurred in MWDSC's system when AOB levels were between 5 and 30 MPN/mL (Wolfe et al., 1990). The highest concentration observed was at an MPN of 280 to 820/mL in the reservoir in the summer during a nitrification episode. The numbers of AOB in the reservoirs were generally much higher in the water column than in the influent and approximately 100 to 1,000 times higher in the summer than in the winter months, indicating that these organisms were not only able to survive in the presence of 1.2 to 1.5 mg/L of monochloramine residual but were also capable of growing in the presence of these disinfectant residuals. AOB were detected only when the water temperature was above 16 to 18°C. Chloraminated systems may have to increase the residuals substantially above 1.5 mg/L to control nitrifiers' growth (Wolfe et al., 1988, 1990). In 1998, the utility increased chloramine residuals entering the flow-through reservoirs to 2.5 mg/L Cl_2.

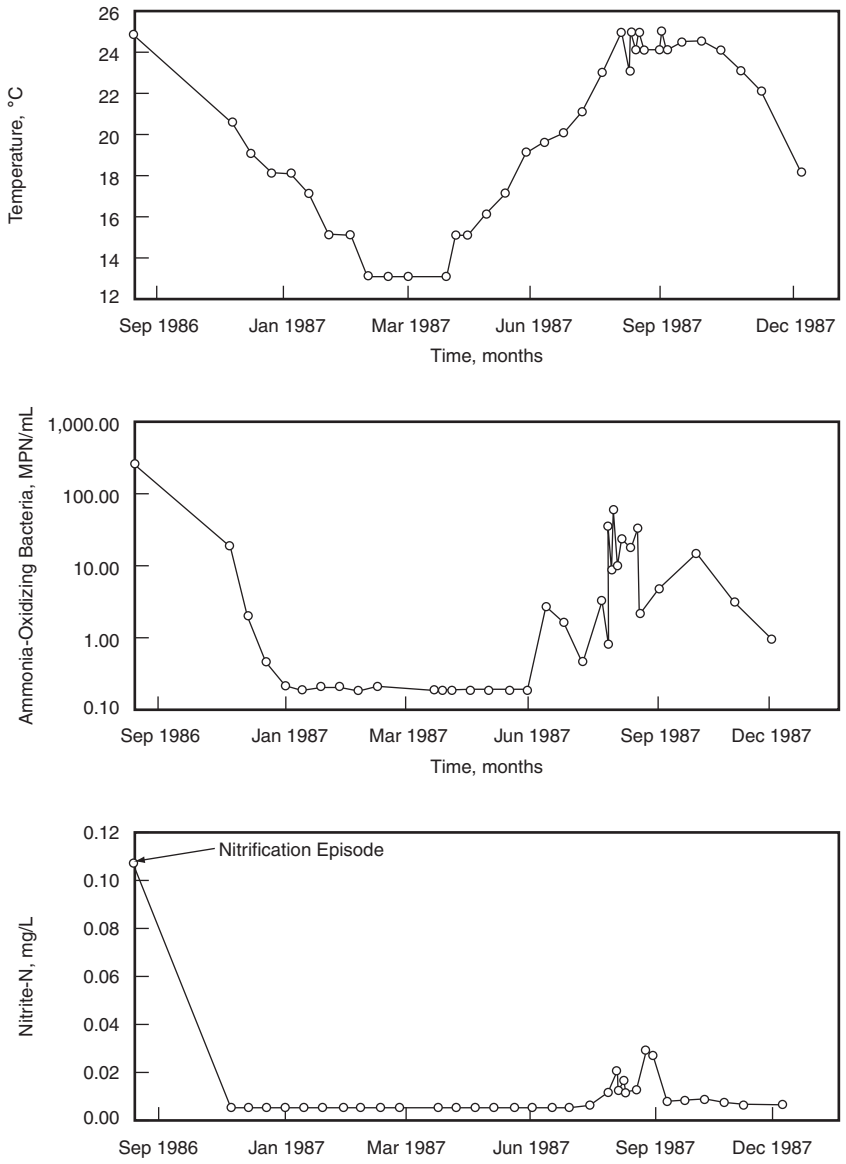

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Figure 3-2 Seasonal relationship between temperature, AOB, and nitrite in a California reservoir

Ike et al. (1988) sampled a reservoir throughout its depth for biological, chemical, and gravimetric parameters (results presented in Table 3-4). In the water column, AOB, nitrite, and temperature levels were the highest at the surface where the chloramine residual was the lowest. HPC levels appeared to be the same throughout the water column. The fact that lower levels of AOB, HPC bacteria, and nitrite were found in the influent as compared to within the reservoir indicates that the AOB were actively growing in the reservoir. AOB were also enumerated in biofilm and sediment samples collected from the underside of the cover and from the bottom and sides of the reservoir. The bottom sediment appeared to have more AOB per area than the cover biofilm. The material on the bottom of the reservoir was approximately 1 cm thick, brown in color,

Table 3-4 Biological and chemical analyses of samples collected from within a California reservoir

Site	Temperature (°C)	Total Residual Chlorine (mg/L Cl_2)	Nitrite (µg/L)	Ammonia Oxidizing Bacteria (MPN/mL)	HPC (cfu/mL)
Reservoir influent	23.5	1.5	<5	<0.18	9
	24.5	1.4	<5	<0.18	26
Reservoir effluent (Sept. 3 only)	24.5	1.5	12	10.2	390
Bulk water at 0.3 m	27.0	0.8	31	22	1,900
(1 ft) depth	24.5	0.9	19	1.9	1,100
Bulk water at 5 m	24.0	1.2	18	0.69	1,200
(16 ft) (middle)	24.5	1.3	18	0.18	1,400
Bulk water at 10 m	24.0	1.1	16	6.7	1,200
(32 ft) (bottom)	24.5	0.8	18	0.19	680
Cover biofilm				1,500*	94,000*
				52*	
Floor sediment				420,000*	3,800,000*
				39,000*	700,000*
				67†	1,400†
Side wall sediment				200,000*	550,000*

Source: Ike et al., 1988.

NOTES: Samples collected on August 5 and September 3, 1987.
cfu, colony-forming unit; HPC, heterotropic plate count; MPN, most probable number.

* MPN/cm^2.

† MPN/mg.

and flocculant-like in consistency. The total volatile solids of this material were 51%, which indicated that much of it would probably be organic. Although the material was suspected to be coagulant floc that had broken through the filters, low concentrations of aluminum were found. In contrast, the biofilm material beneath the reservoir cover was very thin and difficult to remove (Ike et al., 1988).

Baribeau et al. (2001) evaluated in detail three covered reservoirs in southern California (one steel and two concrete) to characterize the suspended and fixed biomass populations. The total chlorine residual in the reservoirs fluctuated typically between 1 and 2 mg/L and the temperature varied between 12 and 26°C. Coupons used to examine biofilm were made of the same material as the reservoir in which they were deployed (steel or concrete). AOB were detected in all reservoirs, in both bulk water and biofilm samples, and at all sampling depths. Higher AOB levels were detected in the upstream steel reservoir than the two downstream concrete reservoirs. Higher HPC and AOB levels were measured in the biofilm coupons collected from the bottom of the reservoirs (area constantly submerged) than on top of the reservoirs (intermittently exposed to air). AOB were detected in the biofilm coupons within 2 weeks following placement of coupons in the reservoir. There was a significant number of nondetectable coupon samples through 250 days of coupon placement, and an increase of AOB levels (between 20 and 200 MPN/cm^2 and higher) on the bottom coupons was consistent with an increase in HPC levels and a slight decrease in total chlorine residual (1.4 mg/L Cl_2). The concentrations of AOB in the bulk water samples typically varied between 0 and 10 MPN/mL. Total chlorine residuals after 250 days began to fluctuate below 1.5 mg/L Cl_2 instead of at relatively steady levels between

1.5 and 2.0 mg/L Cl_2 in the preceding period. Reservoir cycling was not sufficient to prevent nitrification. In one of the reservoirs, a severe nitrification episode occurred in winter when the water temperature was only 13 to 14°C. Chlorination at 2.5 mg/L free chlorine effectively decreased biomass concentrations in both bulk water and biofilm samples, although experience has shown that nitrification may reoccur within a period of a few weeks or months, depending on the source water. AOB were not detectable in the bulk water samples following chlorination and were reduced by 2 to 3.5 orders of magnitude in the biofilm samples (Baribeau et al., 2001).

Stewart and Lieu (1997) sampled a 2.75-mil gal coated steel tank in southern California and observed that although AOB were not detected in the water column, high levels of AOB and HPC bacteria colonized the biofilm layers attached to the side of the tank. The chloramine (2.0 mg/L) and nitrite (0.003 mg/L) levels were similar throughout the tank. The sides of the tank were not smooth and the paint coating was chipped in some areas. The AOB levels on the sides of the tank wall surface ranged from a low of 11 (middle level) to a high of 860 MPN/cm^2 (bottom level). The sludge sample also had high levels of AOB (4,000 MPN/mg) (Stewart and Lieu, 1997). Attachment to surfaces offers the bacteria protection from inactivation and serves as a sink for seeding the water column (Wolfe and Lieu, 2001).

Nitrification in water storage reservoirs may not only cause a loss of chloramine residual and an increase in HPC regrowth but could also lead to customer complaints. Organic compounds released by nitrifying bacteria and ammonia have been associated with taste and odor problems (Bouwer and Crowe, 1988). Burlingame and Brock (1985) reported customer taste and odor complaints that occurred during nitrification episodes in storage tanks (10 mil gal) in Pennsylvania. Strong musty odors and a chemical taste were detected in the effluent of the tanks in September 1983 after the chloramine residual fell to 0.0 mg/L and HPC counts exceeded 500 cfu/mL. The tanks were drained and refilled, which restored chloramine residuals and eliminated the taste and odor problem. Both tanks began to display a similar loss of residual in 1984; cycling was improved in the tanks and booster chloramination was conducted at the tanks—both resulted in maintenance of a residual above 1.0 mg/L throughout 1984 and no taste and odor complaints. An evaluation of historical data indicated that the reoccurring taste and odor events only occurred after chloramine residuals declined below 0.5 mg/L and bacterial counts correspondingly increased. Subsequent monitoring found the nitrite level to increase significantly when the chloramine residual disappeared during the summer.

Nitrifiers are very sensitive to near-ultraviolet (UV), visual, and fluorescent light; consequently, nitrification episodes in distribution systems only occur in the dark (in covered reservoirs, pipelines, taps, etc.). Nitrifiers, however, do have a mechanism for DNA repair; therefore, low levels of nitrifiers may be recovered from partially shaded reservoirs or channels (Wolfe and Lieu, 2001).

Carryover of Filter Media and Sediments Into the Distribution System

Microorganisms typically colonize sediments in reservoirs and pipes. The mineral fraction of sediment acts as a support for bacteria, while the number of organisms is driven by substrate concentration (Kirmeyer et al., 1999). Reservoirs that contain significant deposits can nitrify more frequently and some nitrification control/response methods may not be effective. Toward that end, a treatment process would need to maximize iron and manganese removal, minimize turbidity and coagulant breakthrough in the filter bed, and prevent sand leakage through filter underdrains.

A water treatment plant in California experienced sand leakage through the filter underdrains. Filters were rebuilt and sand traps were installed to monitor the sand loss in the new filters. Several of them still leaked some sand and needed repairs and one

had to be rebuilt. The filters failed because the underdrain caps were loose due to stripped or missing screws and media got underneath. The leaks were fixed by putting in additional screws and epoxy up to the top of the caps and by surrounding each cap with epoxy (pers. commun., J.F. Smith, 2003). The storage reservoir in the plant service area nitrified repeatedly until the sand accumulated on the reservoir floor was removed. Afterward, a stable chloramine residual was developed and nitrification in that reservoir was eliminated.

One method of preventing the accumulated sediments from reentering the distribution system once settling in a storage facility has occurred is to install a riser pipe on the outlet. Avoiding flow situations, which would scour the bottom surface, or changing the inlet/outlet to improve flow patterns may also keep sediments from reentering the distribution system (Kirmeyer et al., 1999).

CONCLUSIONS

AOB are ubiquitous in chloraminated distribution systems, with the possible exception of areas closest to the water treatment plant. The concentration of chloramine typically decreases as the water flows (ages) throughout the distribution system, while the concentration of ammonia increases as a result of chloramine demand and decay reactions. A continuous background level of nitrification is probably prevalent and likely occurs in the majority of chloraminated systems. Nitrification would be greatest at locations near the floor and walls of reservoirs and pipelines. Nitrification would be greatest where water age is highest, such as farther away from the treatment plants or in oversized water mains, and at dead-ends caused by configurations and closed valves where the combination of factors allows for AOB growth.

It is difficult to estimate retention times that promote nitrifying bacteria in drinking water storage reservoirs; however, they are likely to be very long. Nitrification in a drinking water storage facility or a pipeline occurs due to nitrifying bacteria growing in a biofilm or in sediment on the floor and on the walls of a reservoir or a pipeline. Bulk water nitrification occurs only if this biofilm nitrification remains unchecked.

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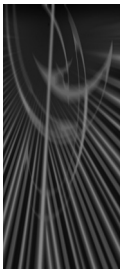


Chapter 4

Overview of Causes and Control of Nitrification in Water Distribution Systems

Andrzej Wilczak

INTRODUCTION

This chapter provides an overview of nitrification causative factors leading to an in-depth discussion of nitrification microbiology, monitoring, prevention, response, and engineering improvements in subsequent chapters. The causes of nitrification can be divided into three major categories: (1) water quality conditions, (2) distribution system operations and maintenance conditions, and (3) distribution system design conditions. The relative impact of these causes may be interrelated, and if some are addressed, others may become less significant. Typically, nitrification would result from a combination of several factors, and all of these should be addressed in chloraminated distribution systems. The key findings of this review are summarized in Table 4-1. Understanding of chloramine chemistry, especially its demand and decay reactions, is critical to maintenance of a total chlorine residual in the distribution system and control of nitrification. This factor is discussed in detail in the latter part of this chapter.

CONDITIONS PROMOTING AND LIMITING THE GROWTH OF NITRIFYING BACTERIA IN DRINKING WATER DISTRIBUTION SYSTEMS

Nitrifying bacteria are ubiquitous in chloraminated distribution systems and both ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) can proliferate under favorable conditions. Distribution systems have not been designed for quick water turnover and, additionally, chloramine stability may not be optimized.

The conditions causing or controlling nitrification in distribution systems can be divided into three categories: (1) water quality and treatment conditions, (2) distribution system operations and maintenance conditions, and (3) distribution system design conditions. Tables 4-2 through 4-4 summarize the water quality and distribution system

Table 4-1 Key points from chapter 4

Chloramine Demand and Decay—the Root Cause of Nitrification	• Water quality and treatment factors determine the stability of a chloramine residual and the related rates of nitrifying bacteria growth (see Table 4-2). • Reaction of chloramine with itself (autodecomposition) is termed *decay* and the reaction with other constituents—organic and inorganic—is *demand*. • Chloramine demand and decay in the distribution system release free ammonia that becomes substrate for the growth of nitrifying bacteria. • The need to maintain a high chloramine residual in the treatment plant effluent to avoid nitrification may indicate excessive chloramine demand or decay in the water entering the distribution system, excessive detention time in the distribution system, and/or lack of distribution system cleanliness.
Minimization of Chloramine Demand and Decay at the Treatment Plant—Prerequisites of Nitrification Control and Customer Satisfaction	• Chloramine demand of the bulk water should be removed or satisfied at the treatment plant to the greatest degree possible. Minimize chloramine decay by keeping high pH in the distribution system, avoiding water temperature increase, exposure to light. • Minimization of chloramine demand and decay in the distribution system coupled with other operational/maintenance/design strategies may allow for control of nitrification at lower disinfectant residuals leading to improved customer satisfaction. • Oxygenation of the raw water source (e.g., lake or artificial impoundment) may eliminate anoxia, and lower the overall oxidant demand (chlorine, ozone, peroxide, etc.) during water treatment. The resulting chloramine residual may be more stable and limit AOB growth in the distribution system. • TOC removal by coagulation/sedimentation, GAC adsorption, or membrane filtration will minimize the demand exerted by natural organic substances. • Remove substances that may exert chloramine demand in the bulk water, pipe wall and sediment, especially color, reduced manganese, reduced iron, nitrites. • Check ozone and biofiltration for creating excessive chloramine demand. If hydrogen peroxide is used for advanced oxidation, apply as little as possible. • Prevent the passage of the filter media into the distribution system. • Provide a short postfiltration contact time with free chlorine or chlorine dioxide prior to chloramine formation to satisfy a portion of disinfectant demand. The distance between chlorine and ammonia addition and corresponding free chlorine contact time will be a balance between required $C \times T$, DBP formation, and chloramine stability and should be evaluated on a case-by-case basis. • Application of chlorine dioxide as a preoxidant and/or primary disinfectant is very effective for nitrification control. The key is introduction of chlorite ion into the distribution system. Chlorine dioxide followed by ozonation will be ineffective, as all chlorite will be oxidized to chlorate ion. • Maintain pH >8.3 in finished chloraminated water if possible without causing scaling. Water pH in the distribution system and required minimum pH for chloramine stability should be evaluated on a case-by-case basis and reconciled with corrosion control program. • Chloramine demand/decay can be tested in the raw water and after each unit process to understand the impact of each treatment step. Plant effluent chloramine demand/decay should be measured periodically, as needed, especially to verify the impact of proposed treatment changes in the planning stage using bench or pilot treatment simulation.

Table continued next page

Table 4-1 Key points from chapter 4 (continued)

Distribution System Water Age and Biomass Residence Times—the Root Causes of Nitrification	• Water distribution system provides growth environment for certain types of AOB, particularly *Nm. oligotropha*: darkness, long detention time, and continuous supply of low levels of free ammonia. • The quiescent conditions of water storage reservoirs and pipe dead-ends associated with long water ages allow also for long residence times of AOB and NOB in spite of their slow growth rates. Similarly, corrosion and tuberculation of pipes may also provide attached growth conditions and protect the bacteria from shear (washout) and disinfectant.
Distribution System Operations and Maintenance Practices for Control of Nitrification	• Minimizing water age through operational means, maintaining system cleanliness, and proper corrosion control are all prerequisites of chloraminated system operation and nitrification control (see Table 4-3). Water age can be minimized through storage operating levels, water demand, pumping schedules, flushing. • System cleanliness can be maintained through reservoir cleaning program and pipe flushing. • Some systems apply periodic free chlorination of the system and blending of different water sources, if feasible, to control nitrifiers.
Distribution System Engineering Improvements for Control of Nitrification	• Water age is fixed to a certain extent due to historic system development and configuration. Configuration of water storage reservoirs inlet and outlet may create stagnant water zones that can be eliminated through mechanical mixers, changes in operations, and redesign of inlet and outlet (Table 4-4). • Pipeline materials can impact chloramine demand and biofilm growth. • Chloramine boosting can counteract the effects of water age and pipe walls by recombining free ammonia and eliminating the food source for AOB.

NOTE: AOB, ammonia-oxidizing bacteria; DBP, disinfection by-product; GAC, granular activated carbon; NOB, nitrite-oxidizing bacteria; TOC, total organic carbon.

conditions and their impact on promoting or limiting the growth of nitrifying bacteria. Tables 4-2 through 4-4 could be utilized as a general guideline to nitrification control with the understanding that the conditions listed may apply to a different extent for a given water system. Site-specific evaluations are necessary to implement nitrification control and prevention practices. The conditions and practices briefly summarized in these tables are discussed in detail in the subsequent chapters of this manual.

Systems preparing for chloramine conversion should also prepare for nitrification control by implementing appropriate practices, as listed in this manual. In general, problem areas of old water encountered with free chlorine in the distribution system often continue to generate water quality challenges after chloramine conversion. Typically, optimization of chloraminated distribution system operations takes a few years of progressive improvements in chloramine formation, water quality monitoring, and operational tools for the control of nitrification. Where necessary, it may take engineering improvements of the source, treatment, and/or distribution systems to resolve persistent trouble areas.

Water Quality and Treatment Conditions

Water quality and treatment conditions primarily impact the chloramine residual's stability and the growth rate of nitrifiers (see Table 4-2). The chloramine residual is impacted by:

- chloramine dose entering the system,
- chlorine to ammonia weight ratio,

- chloramine demand (affected by total organic carbon [TOC] and treatment factors), and
- chloramine decay (affected by temperature, pH, alkalinity).

The nitrifiers' growth rate is impacted by many factors, as discussed in chapter 6.

Chloramine residual. In general, higher residuals (greater than 2.0 mg/L Cl_2) appear to be more effective in preventing nitrification by limiting excessive growth of AOB. The Stage 1 Disinfectant/Disinfection By-product (D/DBP) Rule establishes a maximum residual disinfectant level for total chlorine of 4.0 mg/L Cl_2, measured as a running annual average. One drawback of using higher chloramine residuals is that higher free ammonia levels are potentially available to the AOB as the chloramine residual decays in the system. Using higher chloramine residuals in the distribution system has other potential disadvantages including increased DBP formation; lower customer acceptance and satisfaction with taste, odor, and general water quality; and increased concerns by special customers such as bottled water producers, beverage producers, aquarium stores, and dialysis providers. For example, one Australian utility practices chloramination at 1.5 mg/L Cl_2 leaving the plants and maintains disinfectant in its vast distribution system (280 water storage reservoirs and 21,000 km of pipelines) without major nitrification episodes through booster chlorination and other practices. Customer satisfaction is a key reason for not increasing chloramine residual (pers. commun., J. Broad, 2005). Also, once nitrification is established in the distribution system, even a high chloramine dose appears irrelevant (up to 8.0 mg/L) (Skadsen, 1993) and will not control nitrification. Chloramine demand and decay rate are key parameters that will determine whether and which residual levels will be sufficient to control nitrification. Further information on chloramine demand and decay can be found in chapter 4.

Chlorine to ammonia-N ratio. The chlorine to ammonia-N weight ratio necessary to form monochloramine varies from 3:1 to 5:1. In general, higher chlorine to ammonia-N weight ratios (up to 5:1) are preferred at the entry to the distribution system since less ammonia is initially available for nitrification. However, as chloramine decays, the chlorine to ammonia-N ratio decreases. Therefore, more attention is given to recombining liberated free ammonia in the distribution system by booster chlorination to maintain the chlorine to ammonia-N weight ratio near 5:1 throughout the system. Maintenance of the ratio close to 5:1 may be difficult and sometimes associated with dichloramine formation, associated tastes and odors, as well as increased potential for DBP formation. Further information about ammonia feed control can be found in chapter 8 and about booster chlorination in chapter 10.

Impacts of water treatment. An optimized water treatment process is generally expected to improve chloramine stability and reduce susceptibility to nitrification. It may not always be the case, as discussed later in this chapter. It is, therefore, important to make sure treatment processes are optimized for chloramine stability and nitrification control. Chapter 2 discusses the potential impacts of nitrification within a treatment plant on the distribution system, while chapter 4 presents detailed information on the impacts of treatment changes on chloramine stability. In general, the removal of particulate matter and TOC during treatment is beneficial to nitrification control. Attention must be paid to oxidation and disinfection sequence to make sure that chlorine/chloramine demand is satisfied as much as possible within the treatment train and exerted less in the distribution system. In general, waters low in TOC and biodegradable dissolved organic carbon (BDOC) would have more stable chloramine, but this is not always the case. Therefore, experimental checking of demand and decay using the "bottle test" is recommended.

Water temperature. The water temperature in the distribution system mains and storage facilities generally varies depending on the season and the location within the system. The temperature impacts the growth rates of AOB and NOB. The ideal

Table 4-2 Causes and control of nitrification: Water quality and treatment conditions

Parameter or Condition	Causes of Nitrification	Control of Nitrification	Feasibility of Implementation for Nitrification Control
Chloramine residual entering distribution system	Low chloramine residual may not be sufficient to reach the ends of the distribution system and inactivate nitrifiers. Higher chloramine dose means adding more ammonia into the water.	The utilities in the United States have been increasing chloramine residuals entering the system (e.g., 2.5 mg/L Cl_2 in California and 4.0 mg/L Cl_2 in Florida), which appears to help control nitrification.	Easy to implement and help limit microbial growth, but adding more ammonia may be detrimental.
Cl_2-to-NH_3-N ratio entering distribution system	Overfeeding ammonia at the treatment plant due to poor controls is a major cause of nitrification.	Minimizing free ammonia entering the system is extremely important. Maintain Cl_2:NH_3-N weight ratios > 4.5:1 at the entry point, if possible.	Easy to implement and must be controlled.
Chloramine demand	Chloramine demand reactions with both organic and inorganic constituents release free ammonia and reduce total Cl_2.	Chloramine demand should be satisfied as much as possible during treatment by coagulation, oxidation, and filtration.	Easy to satisfy portion of the demand in conventional treatment and chlorination.
Chloramine decay	Monochloramine is unstable and decays (decomposes) as a function of pH and temperature releasing free ammonia.	Decay is minimized above pH of 8.5 and by avoiding pH drops in the system.	Should be minimized. Easy to control with proper pH.
TOC (NOM)	High TOC exerts chloramine demand and promotes the release of free ammonia.	Low TOC minimizes the initial chloramine demand.	Costly to remove TOC with GAC or nanofiltration beyond enhanced coagulation.
Temperature	Nitrifiers grow faster above 15°C. Warm water exacerbates nitrification.	Cold water in winter limits nitrification for many systems. Nitrifiers exhibit slow metabolic activity even at low temperatures.	In general, not controllable. Blending source waters or shading reservoirs, mixing to limit temperature stratification may help.
pH	Chloramines do not seem effective for AOB inactivation above pH of 8.0. Dichloramine is a better bactericide but generates offensive taste and odors.	Monochloramine decay is minimized above pH of 8.5. Some utilities observed high pH (above 9.0) to better control nitrification.	Easy to control. Should be implemented if no precipitation occurs.
Alkalinity	Low alkalinity may contribute to wide pH shifts in the distribution system, while high alkalinity may contribute to increased chloramine decay. Nitrification consumes alkalinity.	Higher alkalinity water would be more desirable to maintain pH, chloramine residual, and corrosion control.	Addition of lime or soda ash is easy and can be implemented for pH and alkalinity control.

NOTE: AOB, ammonia-oxidizing bacteria; DBP, disinfection by-product; GAC, granular activated carbon; NOB, nitrite-oxidizing bacteria; NOM, natural organic matter; TOC, total organic carbon.

temperature range for nitrifying bacteria regrowth is 25 to 30°C; however, regrowth and nitrification can occur at temperatures as low as 5°C or even less in systems with long detention times (Pintar et al., 2000). Also, the chloramine decay rate will increase as temperature increases and more free ammonia will be released. Some utilities experience more nitrification episodes during the summer.

Water pH and alkalinity. As with water temperature, pH affects both the AOB growth rate and chloramine decay rate. Although the optimal pH range for nitrification is 7.5 to 8.0, nitrification can occur at pH values of 6.6 to 9.8. In general, the pH will decrease during nitrification depending on the alkalinity of the water. However, the pH data should be evaluated carefully, because pH may vary throughout the system, depending on factors such as the water-buffering capacity, pipe material, and corrosion. Chloramine decomposition and free ammonia release will generally be slower at pH values above 8.5. Low alkalinity and buffering capacity may result in accelerated loss of residual if pH decreases below 8.0. It has been suggested that pH depression may be even more significant at the pipe wall and boundary layer, further contributing to localized pH depression and accelerated corrosion of the pipe wall.

Presence of chlorite ion. Chlorite ion has been observed to selectively inactivate AOB. The chlorite ion has not been added to drinking water to control nitrification because it is regulated and has a maximum contaminant level. Chlorite has been present as a by-product of chlorine dioxide addition. The instances of utilities using chlorine dioxide for primary disinfection and chloramine as secondary disinfectant are proving that chlorite is a nitrification inhibitor. More information on this subject is contained in chapters 6 and 8.

Distribution System Operations and Maintenance Conditions

Distribution system operations and maintenance conditions are related to minimizing water age through operational means, maintaining system cleanliness, and optimized corrosion control. Some utilities go through a periodic free chlorination of their system or blend different water sources, if feasible, as a means of controlling nitrification (see Table 4-3).

Distribution system configuration. Detention time, or water age, which is the time that the water stays in the distribution pipes, tanks, and reservoirs, plays an important role in the development of nitrification. Areas with longer detention times are more likely to have lower disinfectant residuals, higher ammonia concentrations, and sediment, and, therefore, are more likely to experience nitrification. Additionally, these areas allow for longer residence time of the nitrifying bacteria to grow and metabolize in spite of their long generation times. Adjustment of water storage operating levels, water demand, and pumping schedules is also necessary. Chapter 8 presents operational techniques to prevent nitrification.

Flushing. Flushing is one of the best temporary control measures for nitrification by removing the water, biofilm, and sediment containing nitrifying bacteria. Systematic flushing is also a preventive measure. Flushing requires bringing unaffected water that has a high total chlorine residual (e.g., >1.5 mg/L Cl_2) and low nitrite/nitrate levels (<0.010 mg/L N nitrite) into the affected area. Unidirectional flushing accomplishes this and moves the affected water and sediment out of the system rather than downstream to other areas where it can spread the problem. After the total chlorine residual increases and nitrite-N level decreases below the alert levels, flushing can be stopped. Flushing may not be available in certain areas of drought and arid conditions. Flushing is discussed in chapters 8 and 9.

Reservoir cleaning program. Removal of the deposits from water storage facilities is a prerequisite to nitrification control. The deposits of residual turbidity,

Table 4-3 Causes and control of nitrification: Distribution system operations and maintenance conditions

Parameter or Condition	Causes of Nitrification	Control of Nitrification	Feasibility of Implementation for Nitrification Control
Water age due to operations	Excessive water age is one of the primary causes of nitrification. Allowable water age is site specific, depends on many factors.	Appropriate pumping schedules, reservoir cycling, seasonal reservoir outages will limit detention time to a certain extent.	Requires pro-active, innovative approaches, more complicated system operation.
Water storage operating levels	Water systems have been traditionally operated with full storage for maximum fire protection and water demands.	Chloraminated water storage tank levels need to be either lowered or operation should allow for significant water cycling.	Decrease of water storage and water age is a balancing act between water quality and supply.
Water demand	Discharging water to lower zones recycles old water and causes problems in all zones.	Continuous bleeding of long dead-end or oversized pipelines is helpful.	Could be considered for long dead-end pipes.
Pumping schedule	Pumping to demand typically leaves the reservoirs full and increases water age.	Pumping not to demand and pumping synchronized in a cascade will lower reservoir water age and promote mixing.	Relatively easy for most systems.
System flushing	High water age, chloramine reactions with the pipe wall, biofilm growth and debris accumulation in pipes.	Unidirectional flushing can reduce water age, some deposits, and clean pipe walls. Routine distribution system maintenance aids in identification of closed valves.	Relatively inexpensive for small pipes. Flushing may not be sufficient in areas receiving nitrifying water.
System cleanliness	Deposits and biofilms cause disinfectant demand and promote on-going nitrification. Reservoir roof leaks contribute to demand.	Reservoir cleaning program is crucial for maintenance of chloramines. Maintain integrity of roofing.	Relatively inexpensive. Large reservoirs can be expensive to clean.
Periodic free chlorination of parts or entire system	Free chlorination, especially frequent chlorination of nitrifying water storage reservoirs, is not a long-term solution and is an indication of other parameter(s) or condition(s) not being optimized.	Periodic free chlorination of the entire system or its portions may successfully control nitrification short-term. Although this strategy is used, there may be a trend away from this approach.	Easy to implement in small scale and successful short-term strategy; not as good long-term. May cause high DBP levels and taste and odor complaints.
Blending with other source water	Blending itself will not inactivate nitrifiers and may only suppress their activity; e.g., seasonally.	Blending water with lower NOM, or colder water may help control nitrification.	Easy to implement if alternative water source with appropriate characteristics is available and hydraulics allow for it.
Corrosion control	Lack of proper corrosion control may lead to pipeline tuberculation and biofilm growth and lead to persistent nitrification.	Proper corrosion control is a prerequisite of maintaining water quality in the distribution system and long-term successful nitrification control.	May or may not be easy to implement. Establishing proper corrosion control may require long-term studies and adjustments.

NOTE: NOM, natural organic matter.

coagulants, corrosion by-products, and occasionally filter media serve as a support environment for the growth of nitrifying bacteria. Accumulated sediment and biofilm in reservoirs and pipes can protect the AOB from bulk water chloramine residual. Therefore, a cleaning program is essential though may not be sufficient for maintaining a chloramine residual inside storage facilities. Reservoir cleaning activities are discussed in chapter 8.

Changing the disinfectant residual from chloramine to free chlorine. Changing the type of disinfectant residual from a combined to a free chlorine residual might be necessary when nitrification causes Total Coliform Rule violations or when other options are not effective. If done properly, a residual change is an effective measure to control nitrification, especially in storage tanks and small isolated areas of the system. Some utilities change over the disinfectant in their entire distribution system for a period of time each year as a preventive measure. Chapters 8 and 9 discuss the changeover of the disinfectant to free chlorine either as a preventive measure or as a response to nitrification.

Blending. Blending sources with different water quality characteristics on a seasonal or continuous basis may provide for more stable water and less favorable AOB growth conditions. Chapter 8 gives some information on this subject.

Optimized pipe corrosion control program. Corrosion control will reduce the reaction between chloramine and corrosion products and reduce chloramine demand. It also will reduce pipe wall environments and sediment that promote conditions more favorable to nitrifying bacteria. Corrosion control, secondary disinfection, and nitrification control programs should be integrated to make sure all water quality objectives are met. Corrosion control methods are discussed in chapter 8.

Distribution System Design Conditions

Distribution system design conditions are related to distribution system configuration and its impact on water age and nitrification. Pipeline materials may impact nitrification control. Boosting the chloramine residual is a renewed approach and requires investment in storage, feed, and control equipment (see Table 4-4).

Distribution system configuration. Systems designed with too much storage capacity will be more difficult to operate for nitrification control. Reservoir outages—permanent or seasonal—can be a relatively easy improvement. Where necessary, the redesign of storage facilities, pressure zones, and pipelines can provide a long-term solution. Further information is presented in chapters 8 and 10.

Distribution system pipes. Low-flow lines such as dead-ends and oversized pipes in residential neighborhoods needed for fire-flow requirements are the most susceptible pipe situations for nitrification to develop. It is likely that nitrification can occur irrespective of any pipe material—plastic, polyvinyl chloride (PVC), asbestos-cement, ductile iron, and cast iron. Certain pipe materials may provide more favorable conditions for nitrification to occur. Also, corrosion in these types of pipes will contribute to chlorine demand, which accelerates disinfectant loss. Further information is presented in chapters 8 and 10.

Internal mixing in water storage reservoirs. Storage tanks should ideally be well mixed to avoid dead zones that may contribute to increased nitrification. This mixing may be achieved through various means: high-momentum pumping, mechanical mixers, separation of inlet and outlet, and inlet/outlet modifications. Mixing is discussed in chapters 8 and 10.

Chloramine residual boosting. Elimination of a free ammonia residual and the maintenance of a relatively high chloramine residual throughout the distribution system is a preferred long-term solution. Boosting has not been widely used in the past in North America but it is becoming more common, as presented in chapter 10.

Table 4-4 Causes and control of nitrification: Distribution system design conditions

Parameter or Condition	Causes of Nitrification	Control of Nitrification	Feasibility of Implementation for Nitrification Control
Water age due to system configuration	Oversized storage reservoirs and water mains are primary locations for nitrifiers' growth. Reservoirs located low in the zone typically do not exchange water and nitrify.	Proper cycling and seasonal reservoir outages limit detention time. Reservoirs located low in the zone and dead-end pipes could be taken out of service.	Can be limited by system design and expensive to modify. Outages of redundant storage are relatively easy.
Pressure zone configuration	Sequential pressure zones increase water age. Most systems reporting nitrification have long and complex distribution systems.	Boosting chloramines may be necessary to maintain residual in sequential pressure zones.	Expensive to modify pressure zones. Operational practices typically implemented instead.
Pipeline configuration	Dead ends cause water stagnation and long detention time and may increase water temperature in shallow pipes in the summer.	Looped pipelines help water circulation and eliminate dead ends.	Expensive to modify. Valve exercise and flushing typically implemented instead.
Pipeline materials	Unlined cast-iron pipes and other iron pipes may corrode easier, exert chloramine demand, form tubercles, and shield nitrifiers.	High quality water, eliminating stagnation, lining the pipelines, and proper corrosion control limit the impact of pipeline material.	Expensive to replace pipes. Operational practices typically implemented instead.
Reservoir mixing	Poor mixing or baffling causes water stagnation and localized older water.	Complete mixing is a desired condition for distribution system storage reservoirs.	Relatively easy to implement. Can be achieved with pumping, mixers, and inlet modifications.
Reservoir inlet/ outlet	Common inlet/outlet may lead to stagnation and stratification. Nitrification can occur also with separate inlet/outlet.	Separating inlet and outlet may help with water circulation. Flapper valves are much cheaper alternative.	Expensive to modify. High momentum pumping could be implemented instead.
Chloramine residual boosting in distribution system	Free ammonia is required in order to boost with chlorine to avoid breakpoint. This may limit the number of applications. Boosting with chlorine and ammonia is less desirable because of two chemicals and the need to balance them. Storage of chemicals in many and/or remote locations is less desirable.	Binding free ammonia and increasing chloramine residuals (1.5–2.5 mg/L Cl_2) in the distribution systems appears to help control nitrification. This may be especially valuable in large storage reservoirs near distribution system entry where free ammonia is still available.	Boosting is more difficult to implement but could be the best long-term strategy. Booster stations are still experimental although more utilities are attempting to test their effectiveness.
Sunlight	Exposure to sunlight accelerates chlorine decay and liberates free ammonia. Covering reservoirs will increase nitrification potential, as nitrifying bacteria grow better in darkness.	Sunlight may inhibit but may not inactivate nitrifiers.	Very few uncovered treated water reservoirs remain in operation at this time.

Sunlight. Exposing stored water to sunlight should be avoided in spite of nitrifiers growing preferentially in the dark. Exposure to sunlight in open finished water storage reservoirs causes decay of chlorine and resulting liberation of free ammonia.

CHLORAMINE DEMAND AND DECAY AS A MAJOR CAUSE OF NITRIFICATION

Chloramine is more stable than free chlorine; however, it slowly decomposes, releasing free ammonia. Therefore, the agent responsible for controlling AOB growth is diminishing through the distribution system while the agent responsible for fueling AOB growth is accumulating (Harrington et al., 2003). Understanding the factors responsible for chloramine decomposition is crucial to nitrification control. This section presents a detailed discussion of the subject matter.

The rate of combined chlorine loss is not constant but varies as a result of many reactions depending on water quality, water treatment, and the conditions of the distribution system. The loss of chloramine residual due to reaction with itself (autodecomposition) is termed *decay*, whereas all other reactions with the chloramines (e.g., with the natural organic matter [NOM], or reduced inorganic species, etc.) are termed *demand*. Minimization of chloramine demand and decay and associated ammonia release is an important nitrification control method (Wilczak et al., 2003).

Chloramine Autodecomposition

Monochloramine decomposes through (a) hydrolysis and (b) acid-catalyzed disproportionation. Hydrolysis is slow and yields small quantities of hypochlorous acid reacting to form dichloramine:

$$NH_2Cl + H_2O \rightarrow HOCl + NH_3 \quad (4\text{-}1)$$

Lower pH levels lead to the formation of dichloramine that rapidly decomposes:

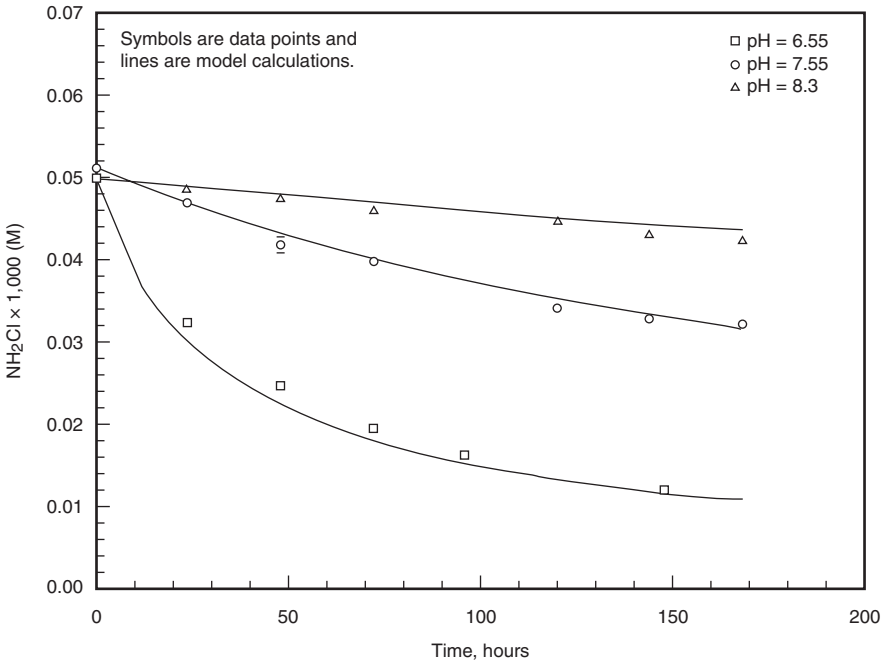
$$2NH_2Cl + H^+ \rightarrow NH_4^+ + NHCl_2 \quad (4\text{-}2)$$

The net decay of monochloramine via autodecomposition is simplified as follows:

$$3NH_2Cl \rightarrow N_2 + NH_3 + 3H^+ + 3Cl^- \quad (4\text{-}3)$$

This reaction produces 1 mole of ammonia for every 3 moles of monochloramine consumed. Note from the above equations that autodecomposition is accompanied by a reduction in pH. The autodecomposition rate increases at lower pH levels, as demonstrated by the second reaction. Elevated inorganic carbon concentrations, temperature, chlorine to ammonia ratio, as well as initial chloramine concentration contribute to faster autodecomposition of monochloramine (Valentine et al., 2000, 1998).

Water pH is one of the most important factors controlling the rate of monochloramine decay (Figure 4-1). Therefore, establishing the proper pH level is essential not only for corrosion control and water stability but also for maintaining chloramine residual and limiting nitrification. Thomas (1987) stated that the rate of chloramine decay doubled for a decrease in pH of 0.7 units. Bone et al. (1999) found that the difference in chloramine decay rate between pH 9 and pH 8 was smaller than the observed difference between pH 8 and pH 7.5. The half-life of monochloramine decreased from an estimated 300 hours at pH 7.5 to only 40 hours at pH 6.5 (Valentine et al., 1998). The half-life of chloramine in a California water decreased from 24 days at pH 8.5 to only 11 days at pH 7.5 (Karimi et al., 2001). Significant pH shifts and excessive chloramine decay due to depressed pH could occur in low-alkalinity, poorly buffered but otherwise high-quality water (Smith, 2002). The efficacy of chloramine for AOB inactivation at high pH is questioned (Oldenburg et al., 2002).



Source: Valentine et al., 1998.

Figure 4-1 Effect of pH on monochloramine decay (autodecomposition) as a function of pH at 25°C; 4 mg/L Cl_2 = 0.056 mM NH_2Cl

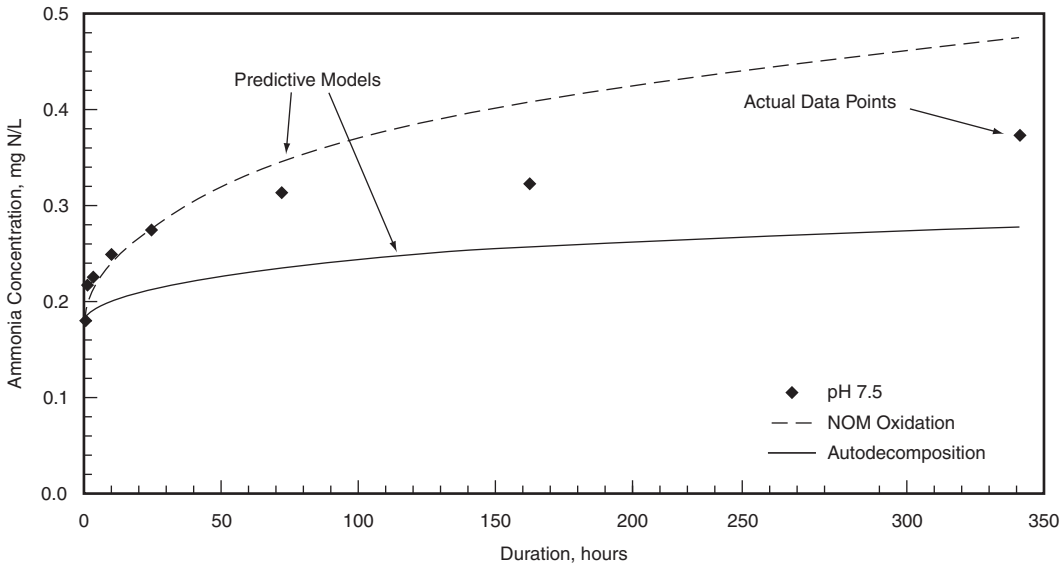
Thomas (1987) estimated that the rate of chloramine decay doubled for a temperature increase of 10°C. Valentine et al. (1998) observed that increasing the temperature from 4°C to 35°C increased the monochloramine decay rate 6.5-fold at pH 7.5. The half-life of chloramine in a California water decreased from 32 days at 10°C to 15 days at 25°C (Karimi et al., 2001).

Lowering the chlorine to ammonia weight ratio to 3:1 typically decreases the monochloramine decay rate. Valentine et al. (1998) reported that the effect of Cl_2:NH_3-N ratio became less important at pH 8.3 and higher. However, the Cl_2:NH_3-N ratio should be balanced at the treatment plant between 4.5:1 and 4.7:1 to limit excess ammonia and avoid dichloramine formation. Higher initial chloramine concentrations (3 to 4 mg/L Cl_2) were associated with a faster residual decay than for initial concentrations of 1 to 2 mg/L Cl_2 (Valentine et al., 1998). Nevertheless, these relatively high plant-effluent total chlorine residuals (3 to 4 mg/L Cl_2) are necessary to control nitrification for many systems—boosting chloramine residual in the system could counteract this faster decay rate. Since the fastest chloramine formation occurs at pH 8.3 (Kirmeyer et al., 1993), the slowest decomposition occurs above pH 8.0, and the chlorine to ammonia ratio becomes less important above pH 8.3, chloramine residuals in the system would be best maintained at pH >8.3. This also avoids the taste and odor problems associated with dichloramine.

Chloramine Reactions With Natural Organic Matter

Monochloramine demand exerted by NOM oxidation is conceptualized as follows:

$$NOM + NH_2Cl \rightarrow NH_4^+ + NOM + Cl^- + products \quad (4\text{-}4)$$



Source: Bone et al., 1999.

Figure 4-2 Evidence of different mechanisms of ammonia release from chloramine decay in conventionally coagulated water at pH 7.5

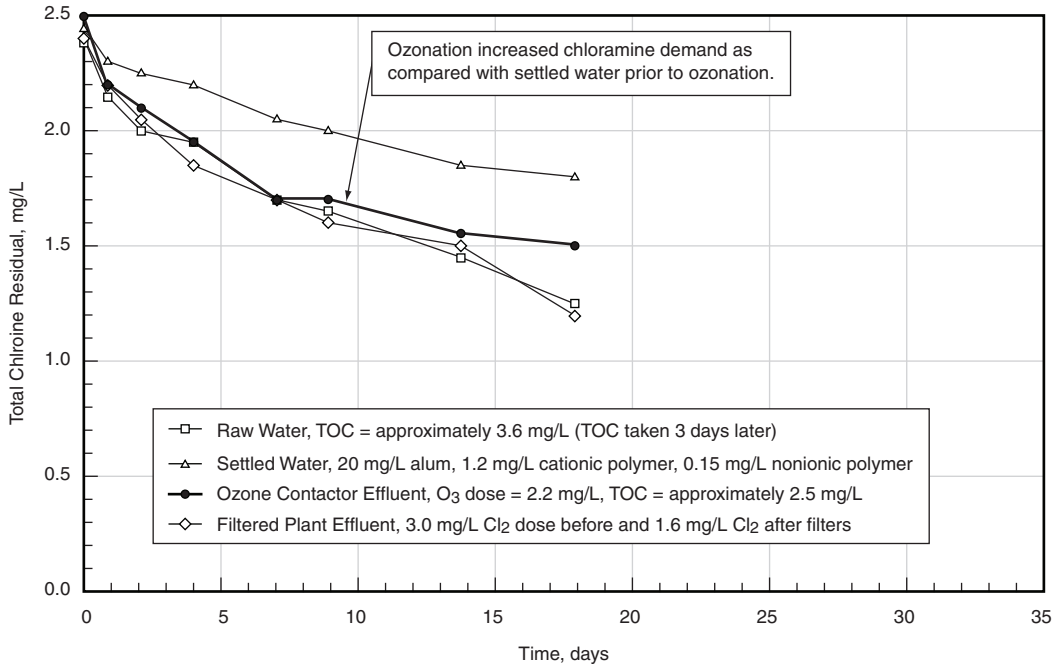
In this reaction, 1 mole of free ammonia is released for each mole of monochloramine consumed. The reduction of monochloramine by NOM thus releases more ammonia than autodecomposition (Bone et al., 1999; Valentine et al., 1998; Harrington et al., 2003). Bone et al. (1999) presented ammonia release data showing that most of the initial ammonia release was from NOM oxidation and most of the later ammonia release was from autodecomposition (Figure 4-2). Thomas (1987) observed that chloramine demand doubled for a dissolved organic carbon (DOC) increase of 4 mg/L. Chloramine reactions in natural treated waters are complex; typically, a fast initial demand is followed by slow autodecomposition.

TREATMENT OPTIONS TO MANAGE CHLORAMINE DEMAND AND DECAY

Conventional and enhanced coagulation followed by sedimentation remove a significant portion of reactive TOC and have beneficial effects on chloramine stability, as shown later in this section. Processes downstream of coagulation and sedimentation, however, especially advanced oxidation, biofiltration, final disinfection, and chloramine formation sequence, may have an overriding effect on chloramine stability and associated nitrification potential (Wilczak et al., 2003).

Conventional and Enhanced Coagulation Versus TOC Removal

Conventional coagulation followed by sedimentation had a beneficial effect on chloramine demand resulting in more stable total chlorine residual as compared with the raw water, as shown in (Figure 4-3). The plant treats reservoir water with moderate TOC and alkalinity (typically 4 mg/L and 100 mg/L $CaCO_3$, respectively). The



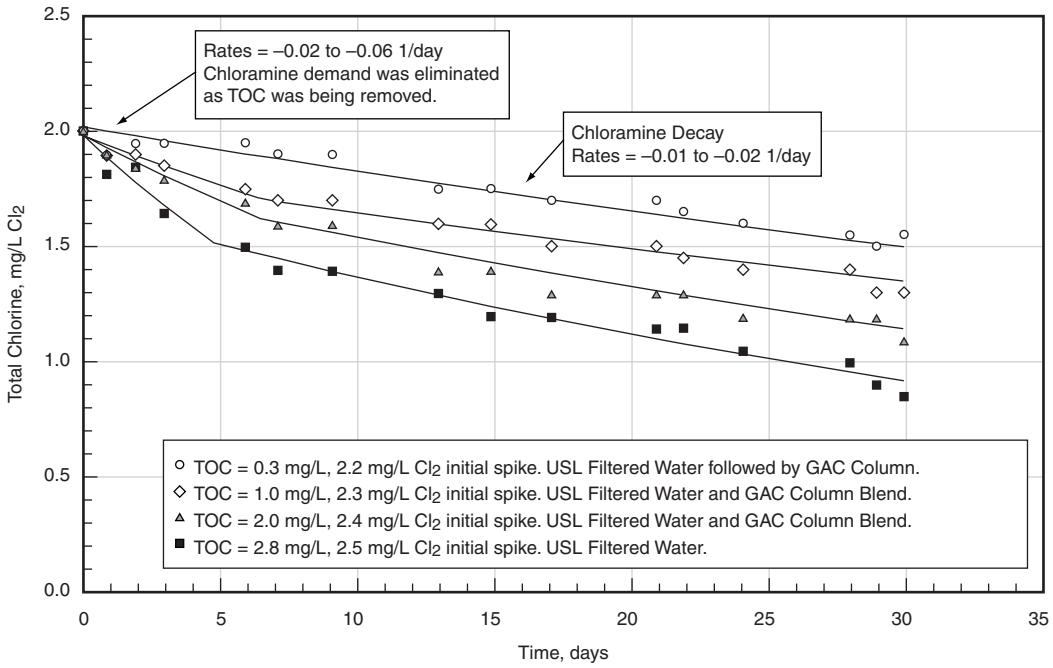
Source: Wilczak et al., 2003.

Figure 4-3 Impact of coagulation and ozonation on chloramine demand. Chloramine demand/decay profile; 20°C, pH = 8.9.

plant employs conventional treatment with intermediate ozonation and anthracite/sand filters followed by chlorination and chloramination. This type of analysis—graphing total chloramine demand after various treatment processes—may be useful for operators to understand the impact of each treatment process on chloramine reactions. Coagulation and sedimentation eliminated a substantial amount of the disinfectant demand, as evidenced by increased stability of chloramine in the settled water as compared with the raw water (see Figure 4-3 for settled water).

Little difference in chloramine demand and ammonia release rates was observed between waters after conventional and enhanced coagulation (3.4 versus 2.9 mg/L residual DOC) by Bone et al. (1999). However, for the same water supply, enhanced coagulation may delay the onset of nitrification and nitrification episodes may be less frequent, as reported by Harrington et al. (2002). However, nitrification occurred in these studies even with enhanced coagulation; consequently, by itself, TOC removal will not be sufficient to prevent the activity of nitrifying bacteria.

Only small improvements in the chloramine stability can be achieved through enhanced coagulation or even granular activated carbon (GAC) adsorption of TOC. Studies were conducted at a plant treating reservoir water with moderate TOC and alkalinity (typically 5 mg/L and 120 mg/L $CaCO_3$, respectively). The plant employs conventional treatment with intermediate ozonation and anthracite/sand filters followed by chlorination and chloramination. No impact on chloramine demand in water was observed as a result of improved TOC removal in pilot tests of enhanced coagulation with alum and ferric chloride salts. Very little difference in chloramine demand was observed when TOC was removed from the settled water (without ozonation) by a small activated carbon column; however, tests on ozonated and ozonated/biofiltered waters indicated a greater impact of TOC removal (Wilczak et al., 1999). Presumably



Source: Wilczak et al., 2003.

Figure 4-4 Effect of TOC removal by GAC adsorption on chloramine demand. Ozonated, filtered effluent and GAC effluent blends; 20°C, pH = 8.5.

the nature of NOM changed due to ozonation (see next section). An example of the impact of TOC removal on chloramine demand in ozonated/GAC biofiltered water is shown in Figure 4-4. The initial chloramine demand due to NOM was completely eliminated as TOC was removed by the GAC adsorption with only autodecomposition (decay) component at the lowest TOC level. Figure 4-4 shows the change in the rate expression occurring after 5 to 7 days for the tested water. Once the NOM demand was satisfied, chloramine decay could be characterized by autodecomposition alone. This was also observed for chloramine residual boosted after several days of holding (Smith, 2002). The impact of NOM removal on chloramine demand will depend on the nature and reactivity of NOM. One would expect modest gains except for the most reactive NOM and/or high TOC removal.

Some utilities may wish to investigate the use of more advanced and expensive NOM removal strategies such as GAC adsorption and nanofiltration (NF) discussed later in this chapter. These would require significant capital investment and there may be more cost-effective ways of achieving the same goal unless there are other reasons to use these processes, e.g., removal of organic microcontaminants of concern. For example, management of the source water quality, where possible, may decrease raw water TOC and the need for expensive NOM removal processes. Chloramine is quite stable in some coagulated/settled waters, and the addition of oxidation processes (for other purposes) should be carefully investigated for their impact on chloramine demand and decay (Wilczak et al., 2003). Proper pH conditions, proper chloramine residual and free ammonia leaving the treatment plant, satisfying chloramine demand at the treatment plant, boosting chloramine in the distribution system, reduction of excess storage, and elimination of dead zones may be more cost-effective alternatives to control nitrification than NOM removal. On the other hand, installation of GAC or NF to remove TOC or

other DBP precursors may eliminate the need for chloramination, depending on the volume of water treated, size of the system, and ability to maintain free chlorine residual in the distribution system without forming excessive amounts of DBPs.

Effect of Oxidants/Disinfectants

Oxidation satisfies a portion of the chloramine demand, thus lowering the overall disinfectant residual loss. Bone et al. (1999) showed that a longer contact time with free chlorine (45 minutes versus 1 minute) stabilized chloramine residuals and less free ammonia was released. Raw water chlorination did not impact chloramine stability in finished water; ozonation, biofiltration, and postfilter chlorination appeared to have an overriding effect (Wilczak et al., 2003).

Intermediate ozonation of coagulated and settled water increased the total chlorine demand at two evaluated water treatment plants (Wilczak et al., 2003). Figure 4-3 depicts the results after each treatment process. Ozonation at approximately 1:1 ozone/TOC mass ratio increased chloramine demand, as compared with settled water. A combination of ozone and hydrogen peroxide was used to control taste and odor at another plant. Typically, the plant used a combination of ozone and hydrogen peroxide at a mass ratio of 5:1 or greater. The slight residual peroxide was biodegraded in the filter media and did not react with chlorine applied after the filters. The chloramine stability was significantly degraded when higher doses of hydrogen peroxide (ozone to peroxide ratio of 4:1) were used to counteract elevated tastes and odors in the summer of 2001. Not only did the overall chlorine use increase at the plant from around 4.6 mg/L to 6.6 mg/L, but chloramine stability was also impacted. A rapid disintegration of total chlorine residual occurred, which was indicative of a different reaction taking place. The section of the distribution system supplied by the plant experienced rapid loss of chloramine residual followed by nitrification in storage reservoirs (Wilczak et al., 2003).

Raw Water Oxidation to Reduce Oxidant Use and Disinfectant Demand

The 41,000-acre-ft raw water reservoir in California serves as a supply of raw water for a treatment plant with a distribution system that has experienced unstable chloramine residual in previous years and nitrification in several service area water storage facilities. A hypolimnetic oxygenation system (HOS) was implemented for taste and odor control in May of 2002 ($1.2 million capital cost, $60,000 liquid oxygen cost/year) (Jung et al., 2003). HOS adds diffused oxygen into the hypolimnion layer below the reservoir thermocline to eliminate low- or no-oxygen conditions. The HOS system was first operated in a continuous mode for 2 months and then in a "pulse-feed" mode (at full capacity for fewer hours per day) from July 2002 through November 2002 and from April 2003 through November 2003. In 2002, ozone doses required at the water treatment plant for taste and odor control decreased by approximately 35% from the pre-HOS year. Also, hydrogen peroxide was not needed for advanced oxidation as in previous years. The chlorine dose decreased by 14% from the prior year (Jung et al., 2003). These lower oxidant demands resulted in a more stable chloramine residual leaving the plant throughout the year and lowered the incidents of nitrification in the distribution system. The savings in ozone generation that year offset HOS operational costs. The application of HOS in the second year of operation caused proliferation of filter-clogging algae in the raw water, which forced the plant to begin using prechlorination to control them. This was an unexpected outcome of HOS, pointing to a complex task of managing many treatment objectives.

Effect of GAC on Chloramine

Monochloramine reacts with GAC as follows:

$$NH_2Cl + H_2O + C^* \rightarrow NH_3 + HCl + CO^* \quad (4\text{-}5)$$

$$2NH_2Cl + CO^* \rightarrow N_2 + C^* + 2HCl + H_2O \quad (4\text{-}6)$$

where C* and CO* represent the carbon surface and oxidized carbon surface, respectively. The reaction of chloramine with GAC is based on attractive forces, not on the destruction of carbon (Komorita and Snoeyink, 1985). Dichloramine reacts faster with GAC than monochloramine (Komorita and Snoeyink, 1985). Dechloramination with carbon will occur until GAC is saturated (White, 1999). Some treatment plants pass chloramine through GAC filters. This practice is undesirable due to disinfectant destruction and application of ammonia to the filter bed (unless nitrification at the treatment plant is desired and controlled).

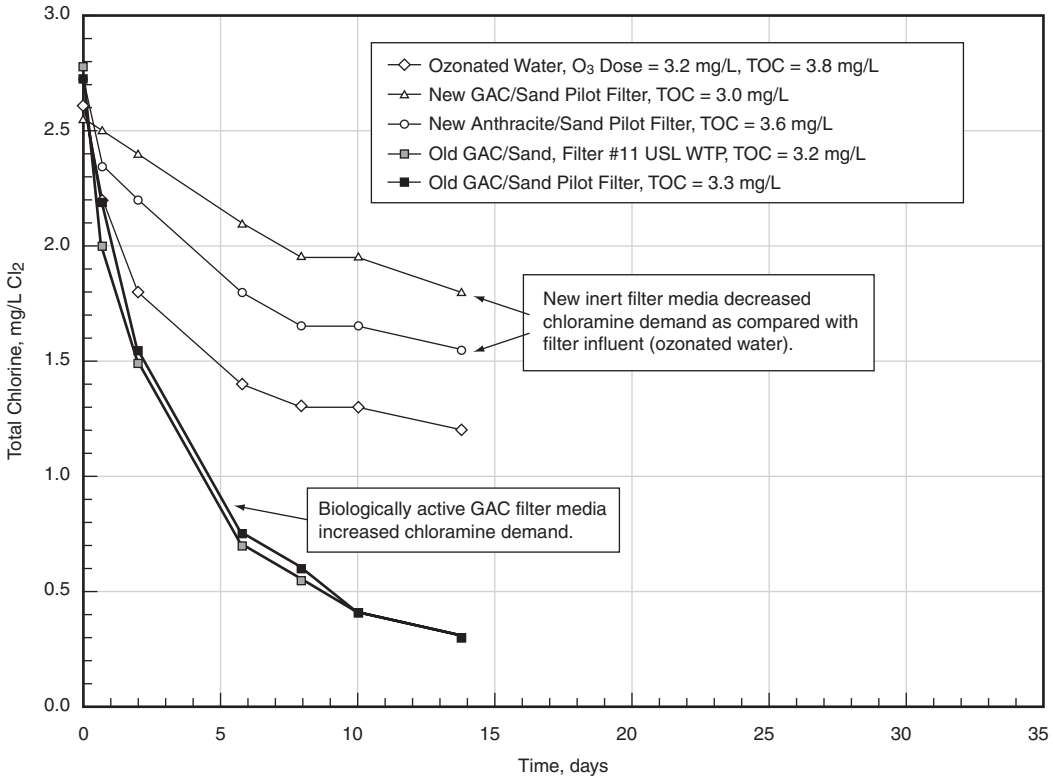
Filtration on inert and biologically active granular media. Filtration would be expected to be beneficial or neutral to chloramine stability. Decreased chloramine residuals were observed in the distribution system after installing ozonation and GAC biofilters at two treatment plants in Texas (pers. commun., T. Andrews, 2001). The free chlorine contact time after the filters and before ammoniation averaged less than 1 minute at one plant and around 11 minutes at the other. Increased chloramine demand was observed at both plants, but the demand was higher in the treated water from the plant with the shorter free chlorine contact time. To counteract this chloramine loss, the total residual chlorine entering the distribution system was increased to almost 4 mg/L. Before installing ozone/GAC biofiltration, anthracite/sand filters and free chlorination across the media were utilized for treatment without excessive chloramine loss in the distribution system. Similar cases were also reported by other utilities implementing ozonation as part of their treatment process.

Filtration of the ozonated water through biologically active GAC/sand media at two treatment plants in California substantially increased the chloramine demand in spite of lower TOC and lower BDOC (Figure 4-5). Free chlorine was first applied in the treatment train after the filters that contained sand and biologically active 11-year-old GAC, originally installed to control tastes and odors. The filters were backwashed with chloraminated water using a combination of surface and main water wash. Pilot filters were set up to investigate the impact of the filter media on chloramine demand: (a) biologically active GAC/sand media taken from one of the full-scale filters, (b) new GAC/sand media, and (c) new anthracite/sand media. New GAC or anthracite/sand did not exhibit any negative impact on chloramine demand, as shown by the excellent stability of chloramine in both pilot filter effluents (Figure 4-5).

The application of a more intensive air backwash in the pilot filters did not eliminate this increased chloramine demand in the biologically active pilot GAC/sand filter effluent. No GAC fines were visible on the 0.45-μm filter upon filtering 5 L of filter effluent, but rather a slight brown film was visually observed, possibly bacterial cell fragments. The hypothesis of suspended material shed from the filters and exerting chloramine demand was confirmed by membrane filtration studies, discussed below (Wilczak et al., 2003).

Membrane Filtration

In some cases, membrane filtration or some other advanced NOM removal process may be an excellent option to improve disinfectant stability, minimize DBPs, eliminate bacterial regrowth, and remove other contaminants of concern. Wilczak et al. (2003) conducted tests with settled, ozonated, and filtered water samples that were passed through the membrane modules and chloraminated. Ultrafiltration (UF) was



Source: Wilczak et al., 2003.

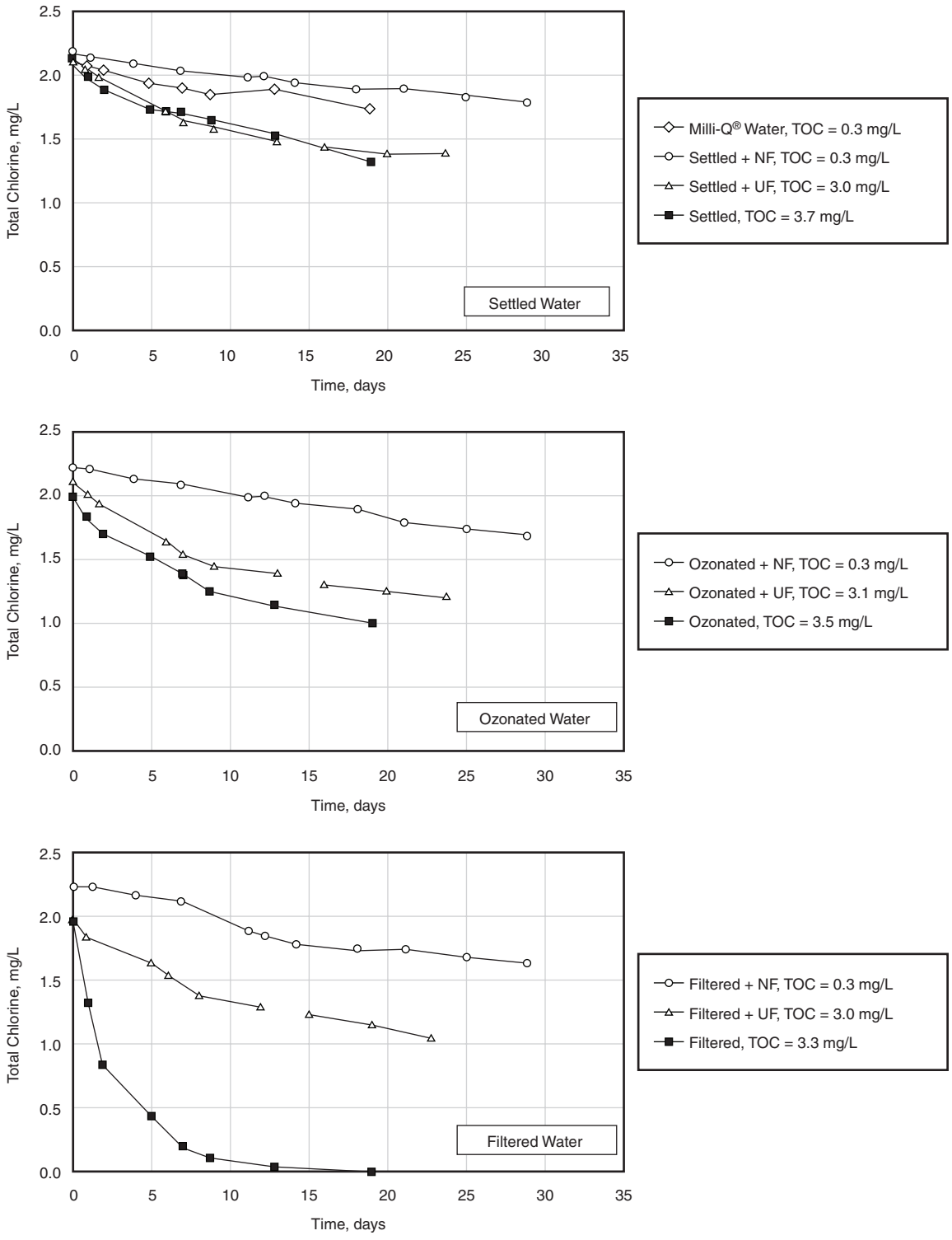
Figure 4-5 Effect of inert and biologically active filtration on chloramine demand. Ozonated and filtered water; 20°C, pH = 8.5.

expected not to impact chloramine stability, whereas NF was expected to improve disinfectant stability. Chloramine in NF permeate was very stable, regardless of whether settled, ozonated, or filtered water was processed (Figure 4-6). The decay rate in NF permeate was comparable to that in Milli-Q® (Millipore Corporation, Billerica, Mass.) water obtained as a control—no initial demand was observed in these test waters. These results indicate that utilities that employ nanofiltration may find that free chlorination in the distribution system becomes a viable alternative to chloramine.

Chloramine in the UF permeate was not as stable and no overall improvement was achieved with either settled or ozonated water. However, passing water through a UF filter improved chloramine stability dramatically. This result suggests that suspended materials shedding from the GAC/sand biofilters were responsible for excessive chloramine demand in that water (Wilczak et al., 2003).

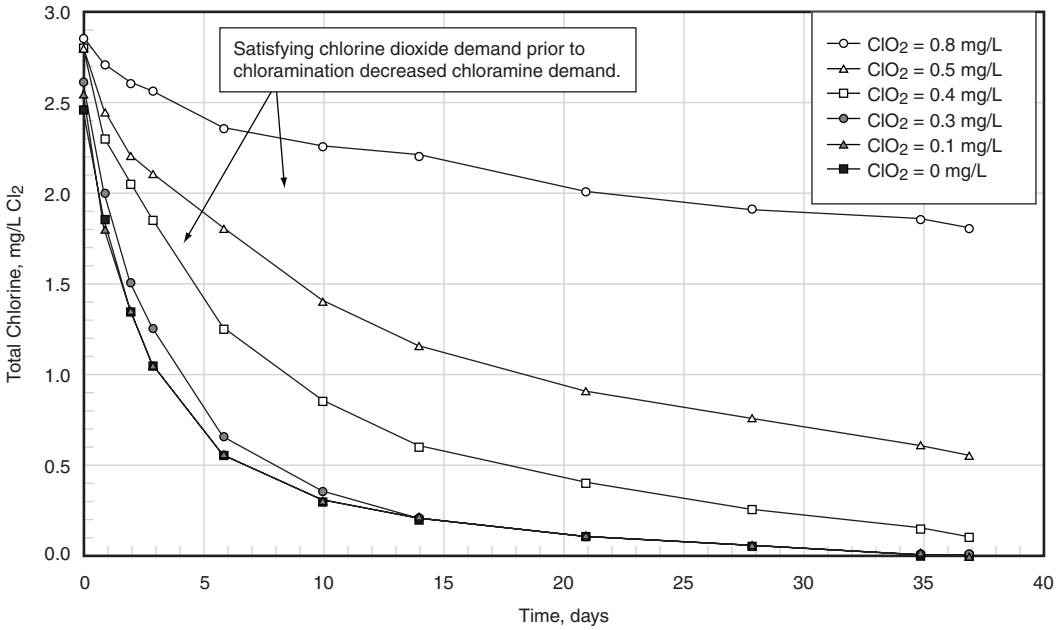
Chlorine and Ammonia Application Points

Kirmeyer et al. (1993) recommended contact time with free chlorine before ammonia addition to satisfy chlorine demand, obtain CT (disinfectant concentration multiplied by disinfectant contact time) credit, optimize the chlorine to ammonia ratio, and maintain a goal of 2 to 3 mg/L combined chlorine in finished water. According to Bone et al. (1999), free chlorine contact time prior to chloramination may serve to stabilize the chloramine residual by minimizing the extent of the chloramine/DOC reaction.



Source: Wilczak et al., 2003.

Figure 4-6 Effect of membrane filtration on chloramine demand. Settled, ozonated, and biofiltered (old GAC/sand) water, pH = 8.7; 20°C (no free Cl_2 contact time).



Source: Wilczak et al., 2003.

Figure 4-7 Effect of postfilter chlorine dioxide dose on chloramine demand. Filter effluent; TOC = 3.2 mg/L, O_3 = 0 mg/L, pH = 8.5, 20°C.

Application of free chlorine to exhausted GAC/sand biofilter effluent before chloramine formation improved chloramine stability. Satisfying even a small free chlorine demand (e.g., 0.5 mg/L) in the clearwell increased residuals in the system. These results point to the need to apply a strong oxidant to biofilter effluent for a short period of time prior to chloramination. The effect of chlorine dioxide applied to biofiltered water was similar to the effect of free chlorine; as higher doses of chlorine dioxide were applied, chloramine became more stable (Figure 4-7) (Wilczak et al., 2003). The impact of free chlorine or chlorine dioxide on chloramine demand was not as significant in the effluents from the new GAC/sand or anthracite/sand pilot filters as it was for the effluent of a biologically active filter. However, once biological activity develops in the filters, free chlorination of filter effluent prior to chloramination may become necessary (Wilczak et al., 2000).

Chloramine Stability in the Presence of Inorganics and Nitrifying Bacteria

Nitrite and chloramine react to form ammonia and nitrate (Margerum et al., 1994):

$$NH_2Cl + NO_2^- + H_2O \rightarrow NH_4^+ + NO_3^- + Cl^- \quad (4\text{-}7)$$

The reaction is relatively slow; e.g., hypochlorite ion is 1.8×10^5 times more reactive with nitrite than chloramine. Valentine et al. (1998) observed that 0.1 mg/L nitrite or bromide had very little effect but 0.5 mg/L accelerated monochloramine loss. Dibromamine can be formed and subsequently decompose if bromide ion is present (Lei et al., 2001). Valentine (1985) postulated that nitrification would accelerate the rate of monochloramine hydrolysis, which could also lead to indirect reaction between

nitrite and monochloramine through hypochlorous acid. Chloramine loss during nitrification is likely caused by depressed pH and higher concentrations of nitrites. McGuire (1995) reported that sulfide and manganese present in the raw water could break through the treatment process and degrade the chloramine residual in the distribution system.

Other Factors During Storage or Transmission

The exposure to sunlight decreased the half-life of chloramine by 50% and exposure of chloraminated water over a large surface area to wind and sunlight decreased this time even further (Kirmeyer et al., 1993). The half-life of chloramines was reduced from 3.8 days in the dark to 1.3 days in the sunlight in a California water (Karimi et al., 2001). Aeration can remove 10 to 15% monochloramine, up to 20% dichloramine, and 100% trichloramine, according to White (1999).

The reactions between monochloramine and ferrous iron contained in pipe wall deposits are faster at higher temperatures and ammonia is a primary product:

$$2Fe(II) + NH_2Cl + 6H_2O \rightarrow 2Fe(OH)_3(s) + NH_3 + Cl^- + 5H^+ \qquad (4\text{-}8)$$

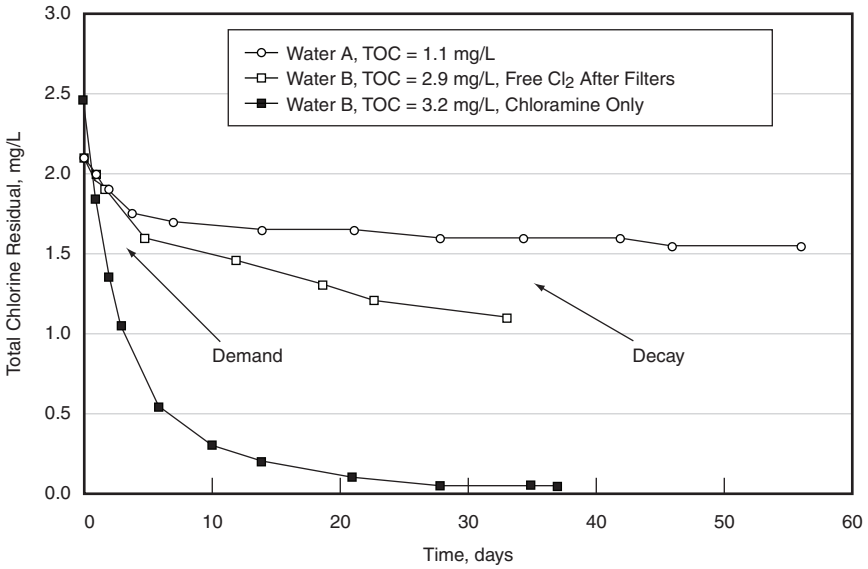
Monochloramine demand associated with 1 g/L pipe deposits ranged from 1 to 3 mg/L Cl_2 after 72 hours. Monochloramine was much less reactive with the deposits and exerted demand more slowly than free chlorine (Valentine et al., 2000).

Most studies do not differentiate between inorganic and organic chloramines, yet organic chloramines are present even in low-TOC waters. El-Farra and Andrews (2000) presented examples of organic chloramine formation and loss in a distribution system. Organic chloramines were generally more stable than monochloramine. Dead-end samples contained a higher percentage of organic chloramine than reservoir samples. Organochloramines are not studied frequently; the interference with total chlorine measurement is discussed in chapter 7.

EXAMPLE OF AN IMPACT OF CHLORAMINE DEMAND/DECAY ON NITRIFICATION

An acceptable detention time for a water storage reservoir is a function of many factors. Very stable chloramine residual and resulting low levels of free ammonia, low water temperatures, clean water storage tanks, and completely mixed reservoir contents without dead spots all discourage nitrification and allow for longer water storage. The impact of chloramine stability for two different source waters (A and B) and two treatment scenarios (Figure 4-8) on the incidence of nitrification in distribution storage reservoirs at one utility is discussed next.

Water A is very low in TOC and undergoes free chlorination in the transmission aqueducts, coagulation, and in-line filtration with anthracite/sand prior to final chloramination. The resulting total chlorine residual is extremely stable, as shown in Figure 4-8 (Wilczak et al., 2003). Water B is higher in TOC and undergoes conventional treatment followed by ozonation and biofiltration. During 1999 and 2000, exhausted GAC/sand biofilters were used followed by chloramine formation without any free chlorine contact time; the resulting total chlorine residual was very unstable, as shown by the solid squares in Figure 4-8. In 2001, new anthracite/sand filter media and a free chlorine contact chamber were installed at the water treatment plant treating water B prior to chloramine formation; the resulting total chlorine residual was more stable, as shown by open squares in Figure 4-8. If 1.5 mg/L Cl_2 were to be maintained in storage reservoirs to prevent nitrification, the allowable detention time for water A would be around 30 days, for water B free chlorinated first and then chloraminated the allowable detention time would be around 7 days, and for water B chloraminated only the allowable detention time would probably be only 2 days. This example shows the



Source: Wilczak et al., 2003.

Figure 4-8 Characteristics of chloramine demand/decay in a California plant's effluent waters, pH >8.5, 20°C

impact of chloramine stability on the acceptable detention time in storage reservoirs at one utility. These site-specific data may be developed to determine allowable detention time, depending on local regulations and site-specific requirements.

The corresponding free ammonia release rates are shown in Figure 4-9; more ammonia was released from chloraminated water B than from either water A or water B that was first free chlorinated. The ammonia released at 0.3 mg/L N would cause nitrifiers to grow much faster than at 0.15 mg/L ammonia released in water A. (See Figure 2-1 for AOB growth rates at different ammonia levels.)

Figure 4-10 shows the calculated chlorine to ammonia-N weight ratios based on the data reported in Figures 4-8 and 4-9. Although a high chlorine to ammonia-N weight ratio was initially applied (above 4.5:1 in each case), soon this ratio began to decrease as a result of total chlorine demand and decay and as a result of ammonia release. Chlorine to ammonia ratio may be boosted in the distribution system to counteract this undesirable trend toward lower values (recently, several systems have been implementing or investigating this approach). Chlorine to ammonia ratios at the treatment plant and at the entrance to the distribution system are well understood, but chlorine to ammonia ratios within the distribution system at the sites where nitrifying bacteria are actively growing are not well understood.

These differences in chloramine demand/decay characteristics directly impacted the maintenance of chloramine residual in distribution system water storage reservoirs. Table 4-5 presents the summary statistics for water storage reservoirs in water A and B service areas. The water A category was divided into two cases—smaller tanks and large reservoirs—since large reservoirs pose additional hydraulic complications that impact mixing and potentially increase water age in portions of these facilities. Approximately 70% of the smaller tanks (all with common inlet/outlet) served by water A maintained stable residual above 1.5 mg/L Cl_2 due to very stable chloramine, as indicated in Figure 4-8. On the other hand, the minority (27%) of very large reservoirs (25 to 150 mil gal in capacity) in the water A distribution system maintained the residual.

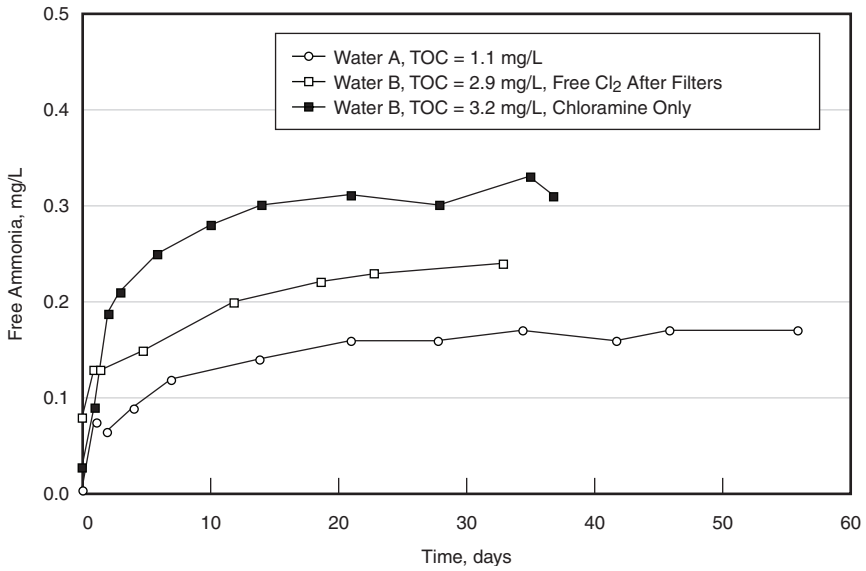


Figure 4-9 Free ammonia release from chloramine demand/decay in a California plant's effluent waters, pH >8.5, 20°C

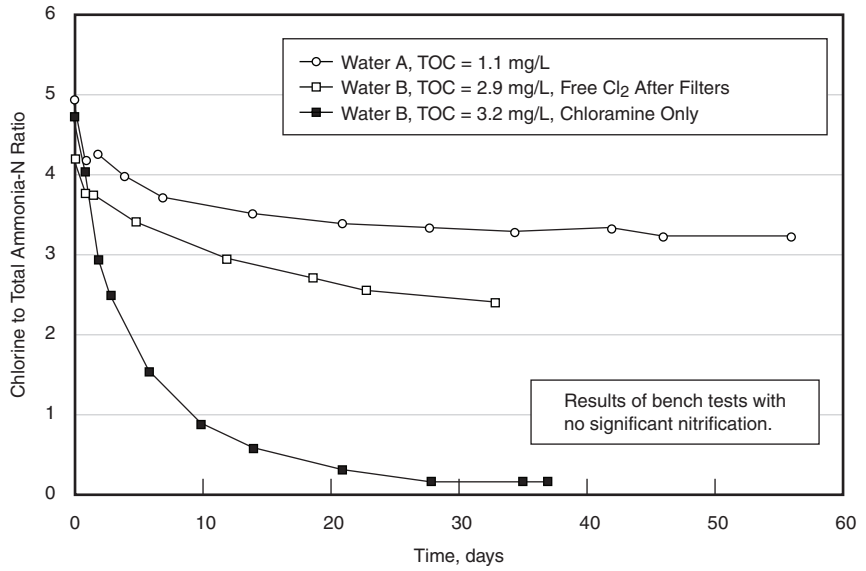


Figure 4-10 Total chlorine to total ammonia-N weight ratio resulting from chloramine demand/decay reactions in a California plant's effluent waters, pH >8.5, 20°C

In the water B service area, approximately 35% of the facilities maintained the residual when free chlorine was applied after the filters for a short period of time. All of these tanks in the water B service area lost residual and nitrified when chloramine leaving the treatment plant was unstable, as shown by the rapid demand/decay curve in Figure 4-8. This analysis underscores the need for stable chloramine leaving the

Table 4-5 Occurrence of nitrification in a California utility's distribution water storage reservoirs as a function of the source water and stability of chloramine*

Chloramine Stability	Number of Facilities	Percent Facilities With Stable Water Quality Without Symptoms of Nitrification
Very stable chloramine† Smaller reservoirs	105	70
Very stable chloramine† Large reservoirs (25–150 mil gal)	11	27
Moderately stable chloramine‡	26	35
Unstable chloramine§	26	0

* All reservoirs have common inlet/outlet, water elevation cycling used to promote turnover. Based on 2003 water quality data.
† Water A (refer to Figure 4-8).
‡ Water B. Free chlorine after the filters prior to chloramine formation (see Figure 4-8).
§ Water B. Chloramine only after the filters.

treatment plant. Allowable detention time and the need for operational and engineering improvements will depend, to a large extent, on this parameter.

CONCLUSIONS

The causes of nitrification can be divided into three major categories: (1) water quality conditions, (2) distribution system operations and maintenance conditions, and (3) distribution system design conditions. The relative impact of these causes may be interrelated and if some are addressed others may become less significant. Typically, nitrification would result from a combination of several factors, and all of these should be addressed in a chloraminated distribution system.

The root cause of nitrification is the availability of free ammonia as a substrate to nitrifying bacteria and long detention time in the distribution system, allowing for the otherwise slow-growing nitrifying bacteria to proliferate. Free ammonia is available either through ammonia feed overdose or through release of free ammonia from chloramine demand and decay. Understanding of chloramine demand and decay kinetics for a given water supply is key to nitrification prevention.

The fundamental basis of nitrification control is for the rate of AOB inactivation to exceed the rate of their growth. The reason that chloramine demand and decay become important is that the chloramine concentration dictates inactivation rate while free ammonia concentration dictates growth rate. Temperature and pH become important because they influence inactivation rate, growth rate, chloramine decay rate, and free ammonia release rate (pers. commun., G. Harrington, 2005). For example:

- Removal of chloramine-demanding substances leads to higher chloramine concentrations and lower free ammonia concentrations. Therefore, removal of chloramine-demanding substances will increase the rate of inactivation while decreasing the rate of growth.
- Higher temperature leads to faster inactivation rates and faster growth rates but it also leads to lower chloramine concentrations and higher free ammonia concentrations. Therefore, the net effect is that a temperature increase will increase growth rate to a more significant degree than the inactivation rate. (This has implications for summer versus winter and for thermally stratified reservoirs.)

- Sediments in pipe networks and in reservoirs will contain chloramine-demanding materials, which leads to lower chloramine concentrations and higher free ammonia concentrations. Therefore, sediments will lead to faster growth rates and slower inactivation rates, suggesting that sediment removal by flushing and reservoir cleaning will help prevent or delay the onset of nitrification.
- Longer residence times increase the extent of growth and the extent of inactivation but they also lead to lower chloramine concentrations and higher free ammonia concentrations. The net effect is to favor growth over inactivation as residence time increases.
- Chloramine booster stations increase the chloramine concentration and decrease the free ammonia concentration, thereby increasing the rate of inactivation and decreasing the rate of growth (pers. commun., G. Harrington, 2005).

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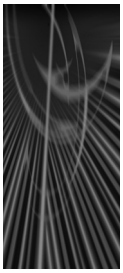


Chapter 5

Microbiology and Isolation of Nitrifying Bacteria

Hélène Baribeau

INTRODUCTION

This chapter presents the microbiology and fundamentals of nitrification. It is divided in two sections: (1) taxonomy and morphology of nitrifying bacteria and (2) isolation and enumeration techniques. The in-depth discussion of the current knowledge about the biology of nitrifying bacteria presented in this chapter can help water professionals better understand the nitrification-related phenomena that occur in drinking water distribution systems as discussed in this manual. Table 5-1 presents a brief summary of the information found in this chapter.

TAXONOMY AND MORPHOLOGY OF NITRIFYING BACTERIA

Taxonomy of Nitrifying Bacteria

Nitrification is carried out by two metabolically distinct groups of bacteria: ammonia-oxidizing bacteria (AOB) are responsible for the oxidation of ammonia to nitrite, which is subsequently converted to nitrate by nitrite-oxidizing bacteria (NOB). No single species yet found oxidizes ammonia to nitrate (Watson et al., 1989), although some organisms such as *Thiosphaera pantotropha* can convert ammonia into nitrogen gas without accumulation of intermediates such as nitrite (NO_2^-) and hydroxylamine (NH_2OH) (Robertson et al., 1988).

Based on their form and structure (i.e., morphology), nitrifiers were once classified in the family *Nitrobacteraceae* but have been reclassified based on 16S rRNA analysis in four separate subdivisions of the *Proteobacteria* division (α, β, γ, and δ), as well as other classes. The *Proteobacteria* division is one of the major lineages in the *Bacteria* kingdom and consists of a large and diverse group of Gram-negative, chemotrophic bacteria derived from a common ancestor. The names of genera of AOB have the prefix *Nitroso-*, whereas the names of genera of NOB have the prefix *Nitro-*. Although strains in a given species express similar or identical genes with regard to substrate transformation, they may vary in their genetic constitution. Serological

Table 5-1 Key points from chapter 5

Taxonomy and Morphology of Nitrifying Bacteria	• Nitrification is carried out by various bacteria that belong to several subdivisions of the *Proteobacteria*, as well as other classes. • AOB are responsible for the oxidation of ammonia into nitrite, while NOB are responsible for the oxidation of nitrite into nitrate. The first step, ammonia oxidation into nitrite, is often referred to as incomplete nitrification, whereas the combination of both steps, oxidation of ammonia into nitrate, is referred to as complete nitrification. • AOB and NOB are not physiologically related and NOB appear more sensitive to environmental conditions, which may explain why incomplete nitrification can happen and nitrite is often present in water distribution systems. No single species yet found oxidizes ammonia to nitrate. The names of genera of AOB have the prefix *Nitroso-*, whereas the names of genera of NOB have the prefix *Nitro-*. • Most nitrifiers are chemolithotrophs, although some heterotrophs can also be responsible for nitrification. • Nitrifiers are aerobic, although some may grow in low oxygen concentration, and others are facultative aerobes. For practical purposes, the growth of nitrifiers is not oxygen limited in the majority of the drinking water distribution systems that have dissolved oxygen concentrations well above 1 mg/L. • Nitrifiers are commonly found in a variety of environments including soil, fresh water, brackish water, seawater, and sewage. • *Nitrosomonas oligotropha* appears to be the dominant AOB in full-scale drinking water distribution systems receiving chloraminated water, and *Nitrosospira* seems to constitute a negligible fraction of the AOB community. *Nitrospira* (and particularly *Nitrospira moscoviensis*) appears to be the NOB detected in most of the samples collected from full-scale chloraminated drinking water distribution systems. • Many of the nitrifiers occur in cell aggregates (with slime layers) referred to as zoogloea or cysts. These slime layers protect nitrifiers from disinfectants. Zooglea may be the preferred mode of cell aggregation for drinking water nitrifiers. • Competition between heterotrophs and nitrifiers for dissolved oxygen, nitrogen, and space is significant. Both groups of microorganisms also benefit from interacting with each other. In extreme circumstances rapid growth of heterotrophic bacteria may actually prevent nitrification from occurring, although these conditions would be undesirable from a water quality point of view. • Denitrification is an important component of the nitrogen cycle and may happen in drinking water systems. It refers to the dissimilatory reduction, by facultative anaerobic bacteria, of nitrate and/or nitrite to nitric and nitrous oxides, which may themselves be further reduced to dinitrogen (N_2). Denitrification can conceivably happen in isolated cases of dead-end pipelines where oxygen is depleted with the net result of the loss of measurable nitrogen.

Table continued next page

diversity (i.e., diversity in serum or plasma constitution) was also observed within a nitrifying bacterial population (Belser and Schmidt, 1978b).

Autotrophic and Heterotrophic Nitrification

Most nitrifiers are obligate chemolithotrophs (i.e., microorganisms that fix carbon dioxide [CO_2] as a source of carbon for production of cell material and oxidize inorganic substrates such as ammonia and nitrite as electron donors), with the exception of the *Nitrobacter* species, which consist of facultative chemolithotroph microorganisms (i.e.,

Table 5-1 Key points from chapter 5 (continued)

Isolation and Enumeration Techniques	• The lack of simple, quantitative and rapid methods for nitrifier detection, identification, and enumeration increases the difficulty of resolving nitrification problems in a timely and cost-effective manner. For drinking water system operation, surrogate chemical indicators are used instead. • Nitrification in drinking water distribution systems is mainly monitored using indicator parameters such as nitrite, nitrate, ammonia, chlorine residual, and HPCs. • Though infrequently used, the most common method used by drinking water providers for nitrifier detection is a culturing technique requiring incubation in darkness, at 25–30°C for 21 to 28 days. Enumeration is usually performed using an MPN technique. Culturing techniques are, however, limited in their ability to recover all target microorganisms and, as such, underestimate the organisms present. • MPN levels for nitrifiers should be considered underestimated and used only as relative indicators due to poor recovery of the MPN technique. AOB and NOB enumeration is going to be questionable until more accurate and faster assay methods are developed. • Large serological diversity of nitrifiers and the co-existence of several serotypes in one ecosystem can limit the efficiency of serological techniques. • Molecular methods for the detection and identification of nitrifiers have gained interest in the drinking water industry. Several primers and probes specific to various nitrifiers or groups of nitrifiers are now available. However, molecular methods are still semi-quantitative only.

NOTE: AOB, ammonia-oxidizing bacteria; HPC, heterotrophic plate count; MPN, most probable number; NOB, nitrite-oxidizing bacteria.

microorganisms that can use CO_2 and organic substrates as carbon source) (Ford, 1980; Watson et al., 1989; Holt et al., 2000). They are generally autotrophic (use CO_2 as carbon source), but some can grow mixotrophically (use organic carbon sources and inorganic electron donors). Also, various groups of heterotrophic bacteria (i.e., microorganisms that fix organic nutrients as a source of carbon), such as *Alcaligenes faecalis*, *Pseudomonas*, and *Thiosphaera pantotropha*, fungi, and even some algae, can be responsible for nitrification, although at a much slower rate than chemolithotrophic organisms (Verstraete and Alexander, 1973, 1986; Focht and Verstraete, 1977; Watson et al., 1989; Killham, 1986; Bock et al., 1992). This process of heterotrophic nitrification is not associated with energy generation, as the growth of all heterotrophic nitrifiers is completely dependent on the oxidation of organic substrates (Focht and Verstraete, 1977). Nonetheless, heterotrophic nitrification (involving the use of organic compounds as a source of carbon) may be greater than autotrophic nitrification (involving carbon dioxide as the sole source of carbon) in some environments, such as forest soils (Schimel et al., 1984). Different pathways are involved in heterotrophic nitrification. Heterotrophic nitrifying organisms produce gaseous nitrogen oxides, and the final product of heterotrophic nitrification is often nitrite. This abundance of nitrite may explain why, in many environments, the number of NOB is much higher than the number of AOB.

Morphology of Nitrifying Bacteria

All strains of nitrifiers are aerobic, but some may be grown in low-oxygen concentrations (Watson et al., 1989; Holt et al., 2000). Nitrifiers present a wide variety of characteristics, as presented in Tables 5-2 and 5-3. Cells can be rod-shaped, ellipsoidal, spherical, spirillar, or lobular without endospores, as described below (Watson et al., 1989; Holt et al., 2000). Most but not all nitrifier species have a Gram-negative

Table 5-2 Characteristics of various AOB

Characteristic	*Nitrosomonas*	*Nitrosococcus*	*Nitrosospira*	*Nitrosolobus*	*Nitrosovibrio*
Cell shape:					
Straight rod	+	–	–	–	–
Coccus	–	+	–	–	–
Helical	–	–	+	–	–
Curved rod	–	–	–	–	+
Lobed	–	–	–	+	–
Cell size:					
Width (μm)	0.7–1.5	–	0.3–0.8	1.0–1.5	0.3–0.4
Length (μm)	1.0–2.4	–	1.0–8.0*	1.0–2.5	1.1–3.0
Diameter (μm)	–	1.5–2.2	–	–	1.0–1.2†
Motility	D	+	D	+	+
Cytomembranes present	+	+	–	+	–‡
Nature of cell membranes:					
Peripheral	+	D§	–	–	–
Randomly arranged	–	–	–	–	–
Central	–	D§	–	–	–
Tubular	–	–	–	–	–
Lamellar	+	D§	–	–	–
Internal, compartmentalizing the cell	–	–	–	+	–
Mol% G+C of DNA**	45–54	48–51	53–55	53–56	54

Adapted from Doetsch and Cook, 1973; Ford, 1980; Watson et al., 1989; Holt et al., 2000.

NOTES: –: 90% or more of strains are negative.
+: 90% or more of strains are positive.
D: Different reactions observed in different taxa.

* Amplitude of the turns. May contain up to 20 turns (average of 3 to 8 turns).
† Spherical form is present in the early stationary phase of growth.
‡ Occasional invagination of plasma membrane.
§ Occur as a centrally located parallel bundle or in a peripheral lamellar arrangement.
** Percent ratio of (G+C)/(A+T+G+C), where G, C, A, and T represent the relative molar amounts of guanine, cytosine, adenine, and thymine, respectively, in a given organism. The value varies according to genus and species, and provides a useful criterion in microbial taxonomy.

multilayered cell wall. However, the marine and some other strains of AOB may have additional cell wall layers composed of repeating subunits arranged in a geometric symmetrical array. Many but not all nitrifiers possess membranous structures within the cytoplasm, which may occur as flattened lamellae or randomly arranged tubes. Cells are nonmotile or motile, using flagella that can be polar, lateral, or distributed more or less uniformly over the cell surface.

Cell Membrane Fatty Acids

When grown under similar conditions, the fatty acids present in cell membranes of the same species or strains are consistent. As such, fatty acid composition can be used to

Table 5-3 Characteristics of various NOB

Characteristic	*Nitrobacter*	*Nitrospina*	*Nitrococcus*	*Nitrospira*
Cell shape:				
Straight rod	+	+	–	–
Coccus	–	–	+	–
Helical	–	–	–	+
Curved rod	–	–	–	–
Lobed	–	–	–	–
Cell size:				
Width (μm)	0.5–0.8	0.3–0.4	–	0.3–0.4
Length (μm)	1.0–2.0	1.7–6.6	–	0.8–1.0*
Diameter (μm)	–	–	1.5–1.8	–
Reproduction:				
Binary fission only	–	+	+	+
Budding (autotrophically); budding or binary fission (heterotrophically)	+	–	–	–
Motility	D	–	+	–
Cytomembranes present	+	–†	+	–
Nature of cell membranes:				
Peripheral	+‡	–	–	–
Randomly arranged	–	–	+	–
Central	–	–	–	–
Tubular	–	–	+	–
Lamellar	+	–	–	–
Internal, compartmentalizing the cell	–	–	–	–
Capable of facultative chemoheterotrophic growth	D	–	–	–
Mol% G+C of DNA§	60–62	58	51	50

Adapted from Doetsch and Cook, 1973; Ford, 1980; Watson et al., 1989; Holt et al., 2000.

NOTES: –: 90% or more of strains are negative.
+: 90% or more of strains are positive.
D: Different reactions observed in different taxa.

* Spiral amplitude.

† Only occasional bleb-like invaginations of the plasma membrane into cytoplasm.

‡ Only at polar region of cell.

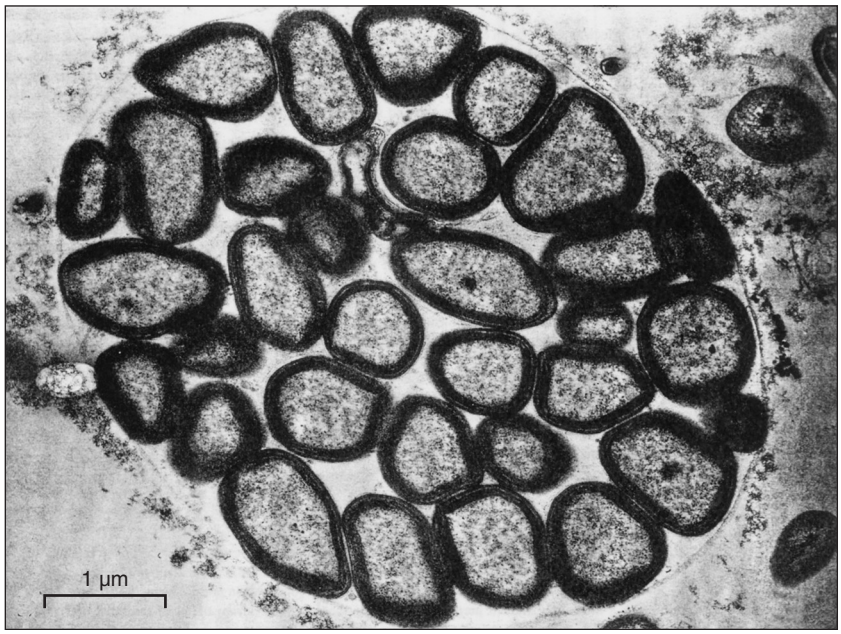
§ Percent ratio of (G+C)/(A+T+G+C), where G, C, A, and T represent the relative molar amounts of guanine, cytosine, adenine, and thymine, respectively, in a given organism. The value varies according to genus and species, and provides a useful criterion in microbial taxonomy.

identify microorganisms. It can also be used to indicate the organism viability, microbial activity, nutritional/physiological status, level of stress, and so forth. In the case of AOB and NOB, the fatty acid composition reflects some peculiarities in chemolithotrophic functions. Doetsch and Cook (1973) and Blumer and colleagues (1969) report that marine nitrifying bacteria appear to possess only a few fatty acids. In the marine AOB, two fatty acids, palmitic acid (hexadecanoic acid, 16:0 [16 carbon atoms

total:0 double bond]) and palmitoleic acid (16:1, 16 carbon atoms:1 double bond), account for 96 to 100% of the total fatty acid content. A wider spectrum of fatty acids is observed in the NOB; however, still only two to four fatty acids comprise more than 80% of the total fatty acids. In another study, Wilkinson (1988) reported that 16:0 and 16:1 are found in NOB, whereas 18:1 is found in AOB. These contradictory results may be explained by the fact that several factors influence lipid composition in microorganisms including, but not limited to, temperature, pH, quantity and quality of carbon and nitrogen nutrients, oxygen levels, and presence of trace metals.

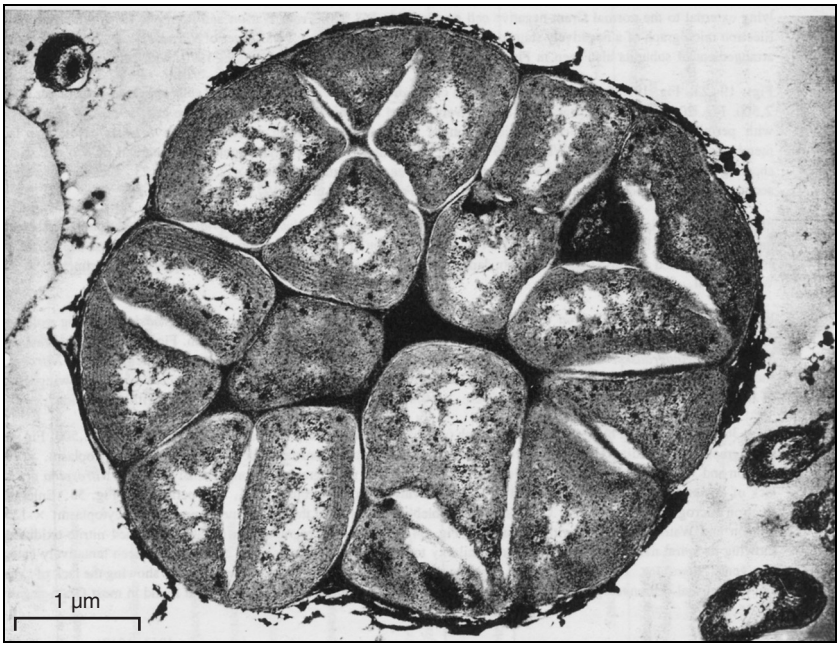
Aggregation of Nitrifier Cells

Nitrifier cells occur singly, in pairs, or, occasionally, in short chains. Many of the nitrifiers occur in cell aggregates referred to as zooglea or cysts. In the case of AOB, these zoogloea or cysts occur in nature and in enrichment cultures but not in pure cultures (Holt et al., 2000). Zoogloea are composed of loosely associated cells embedded in and surrounded by a soft slime layer of low electron density (Figure 5-1). In zooglea, there is no distortion or compression of cells. Conversely, cysts are comprised of closely packed cells (clusters) embedded in and surrounded by a firm slime layer of high electron density (Figure 5-2) (Watson et al., 1989; Holt et al., 2000). In cysts, the cells are tightly compressed and are often distorted and the cytomembranes are frequently localized in the outermost surface of the cells. These slime layers protect nitrifiers from disinfectants (Stewart and Lieu, 1997). In fact, results of Wolfe and colleagues (1990) and Stewart and Lieu (1997) suggested that AOB may be more densely concentrated in drinking water distribution system biofilms than in the water column. Earlier work conducted with nitrifiers isolated from a southern California drinking water



Source: Watson, S.W., F.W. Valois, and J.B. Waterbury. 1981. The Family Nitrobacteraceae. In *The Prokaryotes*. Starr, M.P. et al., ed. New York: Springer-Verlag. Copyright Springer-Verlag.

Figure 5-1 Nitrifying bacterial zooglea (loose aggregate of *Nitrosomonas europaea* cells); electron micrograph (bar, 1 µm)



Source: Watson, S.W., F.W. Valois, and J.B. Waterbury. 1981. The Family Nitrobacteraceae. In *The Prokaryotes*. Starr, M.P. et al., ed. New York: Springer-Verlag. Copyright Springer-Verlag.

Figure 5-2 Nitrifying bacterial cyst (compact aggregate of *Nitrosomonas europaea* cells); electron micrograph (bar, 1 µm)

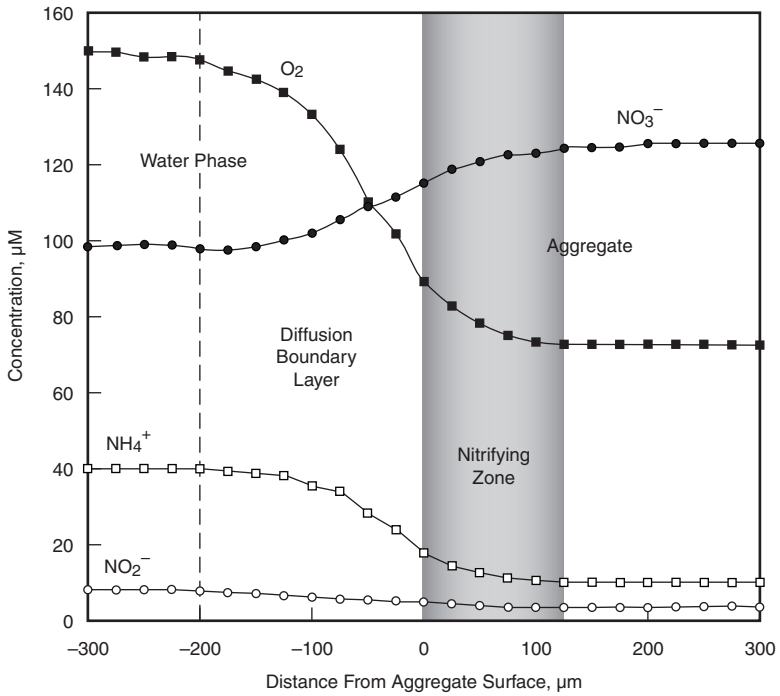
distribution system and grown on agar plates suggested that zooglea appeared to be the preferred mode of aggregation for drinking water nitrifiers.

Interactions Between Nitrifiers and Other Bacterial Communities

Several authors have reported the competition between heterotrophs and nitrifiers for dissolved oxygen, nitrogen, and space, as well as the benefits that may result from these interactions (Rittmann et al., 1994):

- Heterotrophs produce organic compounds that stimulate nitrifiers.
- Heterotrophs biodegrade organic compounds that are inhibitory to the nitrifiers.
- Heterotrophs produce extracellular polymers that improve aggregation of both heterotrophs and nitrifiers into flocs and biofilms.
- The faster-growing heterotrophs protect the slower-growing nitrifiers from detachment by predominating the outer layer of multispecies biofilms.
- Nitrifiers produce and release soluble microbial products (SMPs) that augment the heterotroph substrate supply.

Nogueira and colleagues (2002) explained that microbial community competition within a mixed-culture biofilm may result in stratification of the biofilm structure, with the faster-growing heterotrophs being placed in the outer layers and the slow-growing nitrifiers staying deeper inside the biofilm. This stratification may create a disadvantage to the nitrifiers when the bulk liquid oxygen concentration is low. However, the



Adapted from Schramm et al., 1998.

Figure 5-3 Typical microprofiles of oxygen, ammonium ion, nitrite, and nitrate concentrations in nitrifying aggregates. The gray area marks the zone with nitrifying activity; negative distance indicates water phase and positive distance represents the biofilm.

heterotrophic layer on the outside part of the biofilm may present an advantage to the nitrifiers by protecting them from detachment (Nogueira et al., 2002).

Schramm and colleagues (1996) examined nitrifying biofilms from trickling filters of an aquaculture water recirculation system. They observed that nitrification was restricted to a narrow zone of 50 µm on the very top of the film. *Nitrosomonas* formed a dense layer of cell clusters in the upper part of the biofilm, whereas *Nitrobacter* showed less-dense aggregates in close vicinity to the *Nitrosomonas* clusters. Both species were not restricted to the oxic zone of the biofilm but were also detected in substantially lower numbers in the anoxic layers and even occasionally at the bottom of the biofilm. In a subsequent study involving a nitrifying fluidized bed reactor operated with low ammonia concentrations to resemble a natural freshwater habitat, Schramm and colleagues (1998) demonstrated the occurrence of complete nitrification in the outer 125 µm of the aggregates (Figure 5-3). AOB were identified as members of the *Nitrosospira* group and NOB as *Nitrospira moscoviensis* using molecular methods. *Nitrosomonas* or *Nitrobacter* were not detected. Results showed that the dominant populations of AOB *Nitrosospira* spp. and NOB *Nitrospira* spp. formed separate, dense clusters that were in contact with each other and occurred throughout the aggregate. A second, smaller, morphologically and genetically different population of *Nitrospira* spp. was restricted to the outer nitrifying zones. Although these results provide important information regarding interactions of nitrifiers with other bacterial communities, they may not apply directly to drinking water systems where substrate concentrations are much lower and biofilms much thinner.

When conducting chemostat experiments with NOB *Nitrobacter* sp. and AOB *Nitrosomonas europaea*, Rittmann and colleagues (1994) demonstrated that both nitrifiers produce defined SMP that can support heterotrophic bacteria. The first evidence was the presence of significant concentrations of soluble chemical oxygen demand in the chemostat effluent, even though the influent was free of organic compounds. The second evidence was the maintenance of a small population of heterotrophic bacteria, apparently through utilization of the nitrifier-produced SMP. The hypothesis that nitrifiers create organic substrates is supported by the following facts (Rittmann et al., 1994):

- Being autotrophs, nitrifiers fix inorganic carbon for cell synthesis. Thus, the cells themselves are a potential source of organic carbon; and
- Aerobic, heterotrophic cells are known to produce SMP as part of their normal metabolism.

Kindaichi and colleagues (2004) studied interactions between nitrifying and heterotrophic bacteria in a carbon-limited nitrifying biofilm fed only with ammonium ion as an energy source. Since no external organic carbon was added in the experiment, SMP produced by nitrifiers provided the sole organic substrates for heterotrophic bacteria. Molecular methods (microautoradiography–fluorescence in-situ hybridization [FISH]) were used to determine the community structure and spatial organization in the biofilm. Results indicated that the biofilm was composed of 50% nitrifying bacteria (22% AOB and 28% *Nitrospira* phylum [NOB]) and 50% heterotrophic bacteria. Results also indicated that a pair of nitrifiers (AOB and NOB) supported a heterotrophic bacterium via production of SMP. The heterotrophic bacterial community was composed of bacteria that were physiologically and metabolically diverse and to some extent metabolically redundant, which ensured the stability of the ecosystem as a biofilm. Different groups of heterotrophs were responsible for mineralizing different low- and high-molecular-weight organic compounds produced or released by nitrifiers. Moreover, FISH results suggested that primary degraders directly colonize or occur around the nitrifying clusters that excrete SMP. These primary degraders recruit other species to form metabolically structured and functionally integrated biofilm communities that ensure maximum utilization of SMP produced by nitrifiers, and prevent buildup of metabolites or waste materials of nitrifiers to significant levels. Kindaichi and colleagues (2004) estimated that approximately 1.5 mg of chemical oxygen demand per liter of SMP could be produced from 3.6 mM NH_4^+ fed. Similar information in drinking water systems is not available. As such, extrapolation of these results to drinking water conditions needs to be done carefully.

Barker and Stuckey (1999) identified SMP as humic and fulvic acids, polysaccharides, proteins, amino acids, nucleic acids, and structural cell components.

Ammonia-Oxidizing Bacteria

Mechanism of ammonia oxidation. The first step of the nitrification process, oxidation of ammonia into nitrite, is often called incomplete nitrification when a buildup of nitrite is observed. In the literature, the reaction is often summarized by the following equation:

$$NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+ \quad (5\text{-}1)$$

However, earlier investigations indicate that ammonia (NH_3) rather than ammonium ion (NH_4^+) is the substrate of the energy-generating system (Suzuki et al., 1974). This finding was later confirmed by Kleiner (1985) who observed that cell membranes are highly permeable to NH_3 but not to NH_4^+.

The process may be characterized as a two-stage reaction (Prosser, 1989):

$$NH_3 + O_2 + 2H^+ + 2\ e^- \rightarrow NH_2OH + H_2O \quad (5\text{-}2)$$

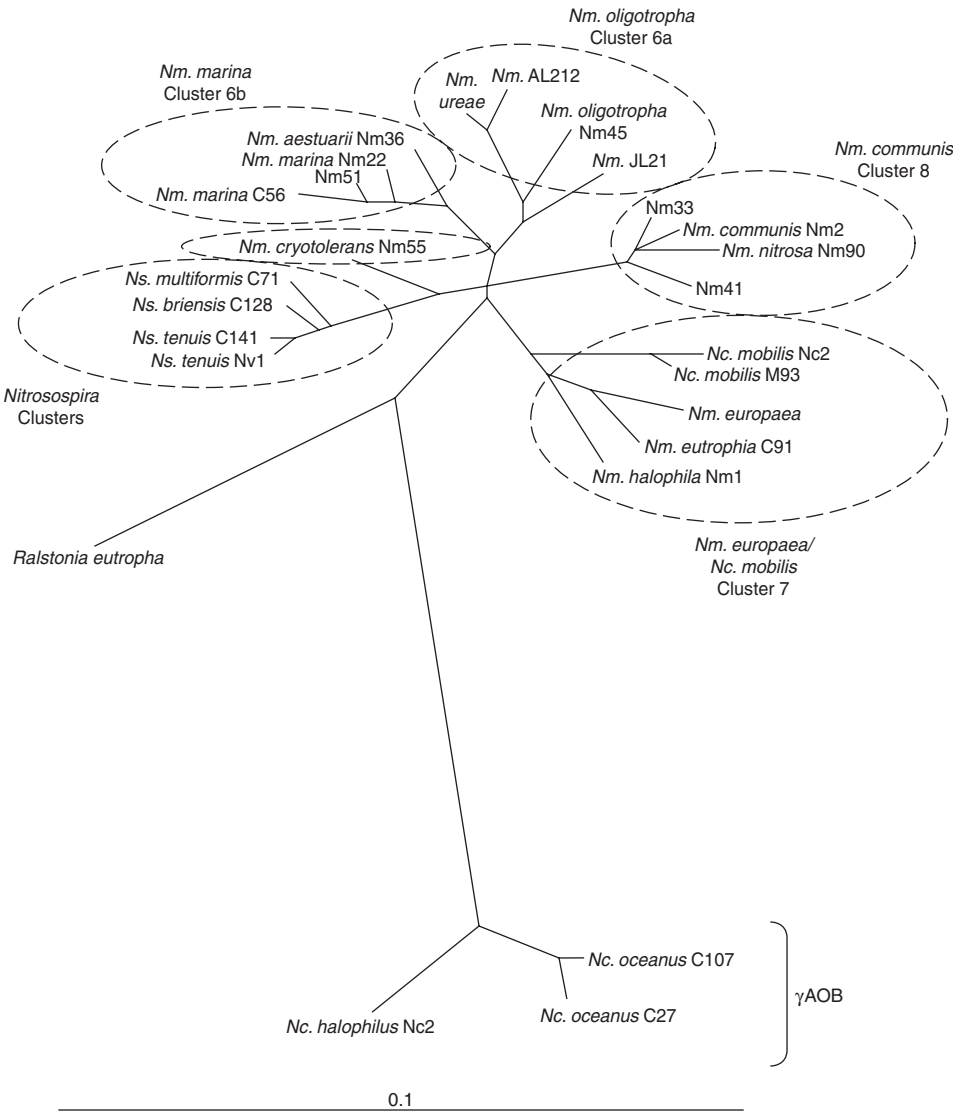
$$NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4\ e^- \quad (5\text{-}3)$$

The first reaction is carried out by a membrane-bound ammonia mono-oxygenase (AMO) enzyme. The reaction requires oxygen, supplied as molecular oxygen (O_2), which serves two purposes: direct incorporation into the substrate and as a terminal electron acceptor. The theoretical demand for biological oxidation of ammonia to nitrite is 3.43 g O_2 per g of ammonia oxidized (Ford, 1980) (further information about oxygen requirements is presented below). The second reaction is carried out by a soluble enzyme (hydroxylamine oxidoreductase) inside the membrane and generates energy and receives oxygen from water. Carbon dioxide serves as the primary carbon source for cellular carbon and is fixed via the Calvin cycle, a metabolic pathway in which carbon enters in the form of CO_2 and leaves in the form of sugar. For the lithotrophic AOB (AOB that use an inorganic substance as substrate in energy metabolism), ammonia is the primary substrate and nitrite is the primary nitrogenous end product of this reaction, with small amounts of nitrous oxide (N_2O) and nitric oxide (NO). The release of free energy by these reactions has been estimated at 58 to 84 kcal/mole NH_4^+ (McCarty, 1964; Painter, 1970).

The oxidation of ammonia to nitrite is thermodynamically favorable (Doetsch and Cook, 1973). However, it has been suggested that energy is required to initiate the oxidation of ammonia to NH_2OH, the principal reaction intermediate. Energy is then derived from the oxidation of NH_2OH (via NOH) to nitrite. Other intermediates of reaction were identified by Doetsch and Cook (1973) and Bock and colleagues (1992) and include NHOH and NO. Electron flow is assumed to proceed from NH_2OH to O_2 via specific enzymes (Doetsch and Cook, 1973). Energy, under the form of adenosine triphosphate (ATP), is generated during this electron flow by oxidative phosphorylation (Grady et al., 1999). Although NH_2OH is believed to be the real energy source, all attempts to grow AOB on NH_2OH in the absence of ammonia have failed (Bock et al., 1992). Focht and Verstraete (1977) add that NH_2OH is unstable and toxic.

Taxonomy of ammonia-oxidizing bacteria. Based on morphologic distinction (i.e., difference in form and structure), AOB were originally separated into five genera: *Nitrosomonas, Nitrosococcus, Nitrosospira, Nitrosovibrio,* and *Nitrosolobus*. More recently, the taxonomy of nitrifiers was re-assessed using sequence similarities of their 16S rDNA. As such, most chemolithotrophic AOB (and all AOB characterized in fresh water) now belong to the β-subdivision of the class *Proteobacteria*, which comprises the genera *Nitrosomonas* and *Nitrosospira* (which formerly included strains of *Nitrosolobus*, *Nitrosovibrio*, and *Nitrosospira* itself). The only AOB belonging to the γ-subdivision of *Proteobacteria* is *Nitrosococcus* (*N. oceanus* and *N. halophilus*), which are marine AOB (*Nitrosococcus mobilis* belongs to the β-subdivision of the *Proteobacteria*). These AOB are separated in clusters, as shown in Figure 5-4, which presents a phylogenetic tree, i.e., a graphical representation of the similarities of DNA sequences. The lengths of the branches reflect how closely the organisms differ from one another in the particular gene of interest. The tree presented in Figure 5-4 was generated using the neighbor-joining distance matrix method excluding positions with gaps. Results indicate that the *Nitrosomonas* strains and *Nitrosococcus mobilis* form a broad assemblage, while *Nitrosospira*, *Nitrosolobus*, and *Nitrosovibrio* comprise a very tight branch within the β-subclass. These results also suggest that *Nitrosospira* strains are very similar in 16S rDNA sequence, making them more difficult to discriminate from one another (Regan, 2001).

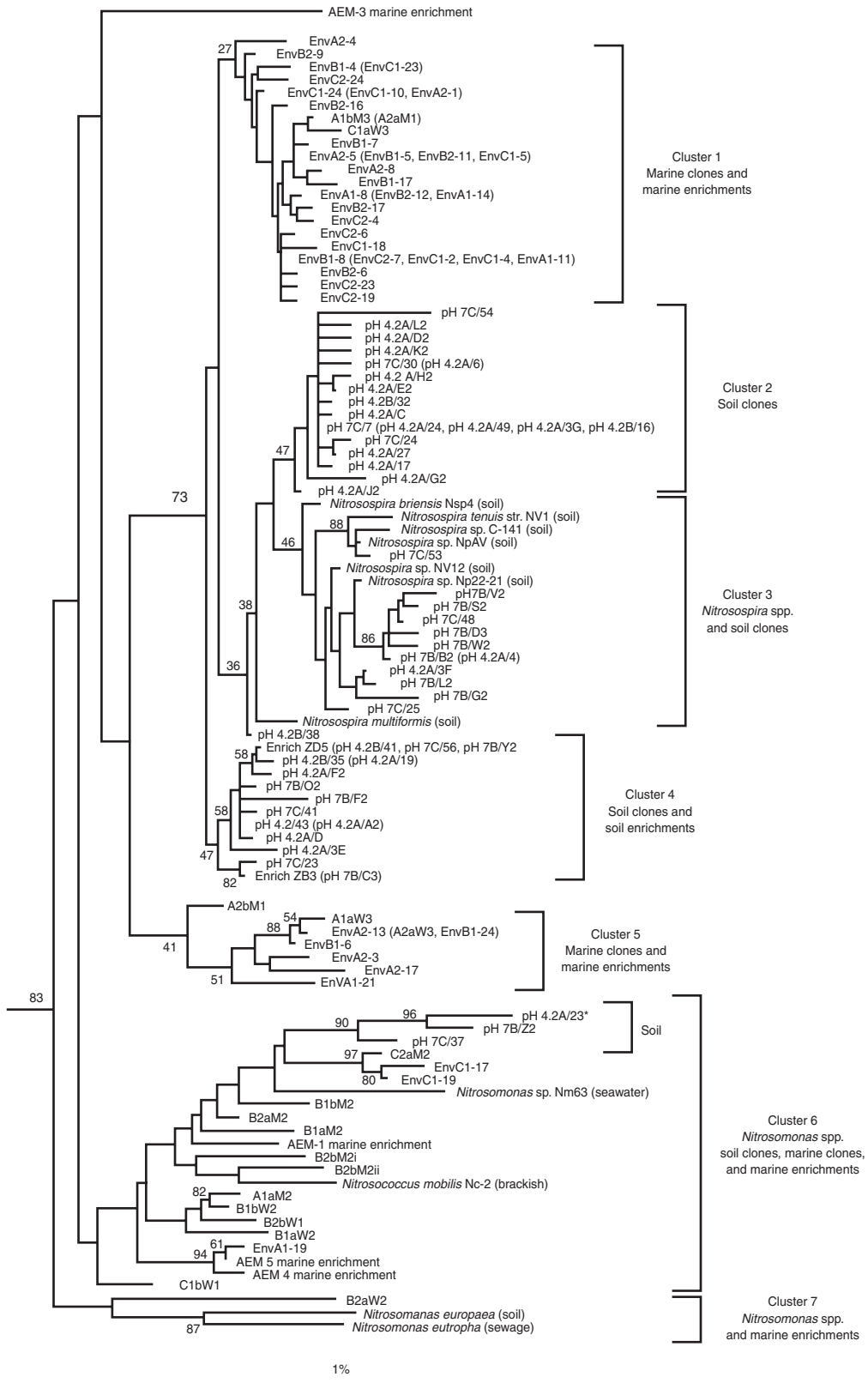
The diversity of AOB in the β-subclass *Proteobacteria* has been further differentiated into clusters based on the 16S rDNA sequence relationships by Stephen and colleagues (1996), using samples from acid and neutral soils and polluted and nonpolluted marine sediments. The grouping suggests seven clusters, as shown in Figure 5-5. In a subsequent study, Stephen and colleagues (1998) modified cluster 6 into cluster 6a, which contained soil clones, and cluster 6b, which included marine clones and enrichments. Other groupings have also been suggested by subsequent researchers, and it is likely that AOB classification will be revisited in the future.



Source: Regan, 2001.

Figure 5-4 Phylogenetic tree of AOB based on multiple alignment of 55 nearly full-length AOB 16S rDNA sequences. Abbreviations are Nm for *Nitrosomonas*, Nc for *Nitrosococcus*, and Ns for *Nitrosospira*. *R. eutropha* is a non-AOB member of the β-subclass *Proteobacteria*. Scale bar represents 10% sequence difference.

Speciation of ammonia-oxidizing bacteria in different environments and in water distribution systems. Historically, *Nitrosomonas* has been the most frequently mentioned genus associated with the first step of the nitrification process in drinking water, wastewater, and seawater. However, Feben (1935) isolated *Nitrosococcus* species from filter beds and tap water samples collected from a chloraminated system. According to Prosser (1989), *Nitrosolobus* species are the most common AOB in soils, whereas *Nitrosospira* species dominate in acid soils and *Nitrosococcus* species are important in marine environments. In soil samples collected from Waukegon silt loam (Apple Valley, Minnesota), Belser and Schmidt (1978a) observed that *Nitrosomonas*



Source: Stephen et al., 1996.

Figure 5-5 Relationships of environmental partial 16S rRNA sequences to partial sequences from reference AOB (neighbor-joining tree)

and *Nitrosospira* were the main genera detected using culturing techniques, with *Nitrosolobus* occasionally seen in soils treated with ammonium nitrate or sewage effluents. Belser and Schmidt (1978a) added that media selectivity and enumeration efficiency used during the culturing technique may have favored the recovery of *Nitrosomonas* over the other genera. Accordingly, results obtained from the recent introduction of molecular methods suggest that *Nitrosospira* types are the most common AOB in soils and fresh water, not *Nitrosomonas* types as was previously thought using culturing techniques.

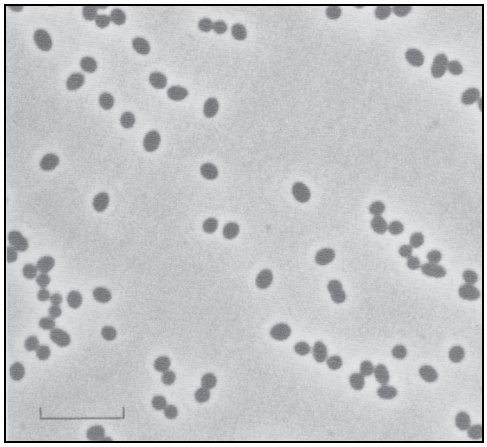
Conversely, when using molecular techniques, Regan and colleagues (2003) observed results with *Nitrosomonas* (and particularly strains from the *Nitrosomonas oligotropha* cluster) being ubiquitous in full-scale drinking water distribution systems receiving chloraminated water and *Nitrosospira* constituting a negligible fraction of the AOB community. Similarly, Regan and colleagues (2002) observed the presence of *Nitrosomonas oligotropha* and *Nitrosomonas ureae* in pilot-scale chloraminated drinking water distribution systems, with a considerably smaller presence of *Nitrosospira*-like AOB. Regan and colleagues (2002, 2003) explained that the predominance of *Nitrosomonas oligotropha* over other *Nitrosomonas* species could be associated with the low concentrations of free ammonia in the distribution systems studied (<0.20 mg/L NH_3-N). The reported half-saturation constant (or half-velocity coefficient, equivalent to the growth-limiting substrate concentration at half the maximum specific growth rate, K_s) for *Nitrosomonas oligotropha* strains is 0.42 to 1.05 mg/L N, which is approximately one order of magnitude lower than the K_s of other *Nitrosomonas* species.

When studying the nitrifying bacterial population occurring in nitrifying activated sludge of an industrial wastewater treatment plant receiving sewage with high ammonia concentrations using molecular methods, Juretschko and colleagues (1998) observed the dominance of *Nitrosococcus mobilis*.

In bench-scale biofilm reactors fed with nitrifiers collected from nitrifying circulating bed reactors, Nogueira and colleagues (2002) used molecular methods to identify the AOB present. Results showed that the AOB population was most likely affiliated with the *Nitrosomonas europaea/eutropha* group. No AOB belonging to the *Nitrosospira* cluster were detected and *Nitrosococcus mobilis* was also absent.

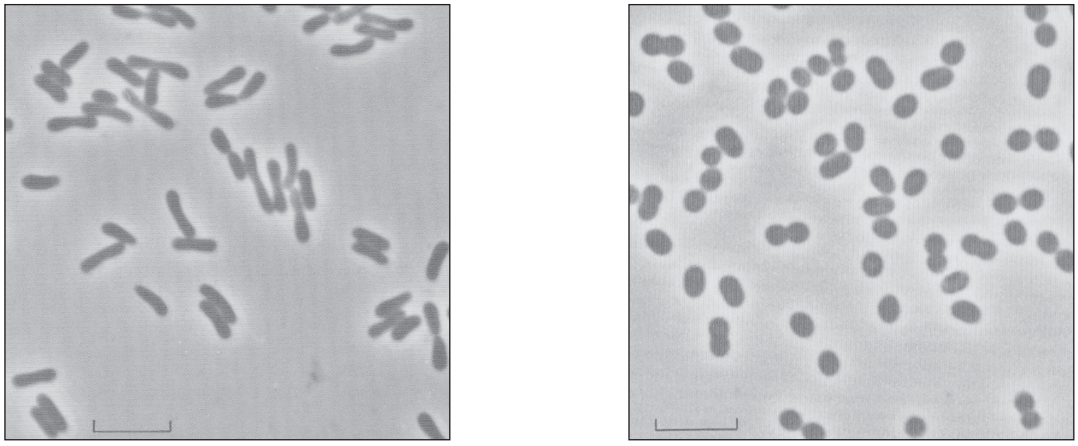
Lithotrophic nitrifying bacteria are thought to be the most important nitrifiers in nature. However, a group of various species of prokaryote and eukaryote heterotrophic nitrifiers can also oxidize ammonia without the ability of energy utilization (Bock et al., 1992). As an example, methane-oxidizing bacteria are able to oxidize ammonia to nitrite, although they cannot grow from this reaction (Bock et al., 1992). There are some similarities between the ammonia and the methane mono-oxygenase enzymes of the nitrifiers and the methanotrophs, respectively, and these similarities were discussed by Bedard and Knowles (1989). Interestingly, all attempts to grow AOB on methane or to grow methane oxidizers on ammonia as sole source have failed (O'Neil and Wilkinson, 1977; Jones and Morita, 1983).

When studying eutrophic freshwater lakes, Hastings and colleagues (1998) observed that the numbers of AOB in the lake water were small throughout the year, but sediments from littoral and profundal sites supported comparatively large populations. In enrichment cultures consisting of Watson and Mandel medium (Watson and Mandel, 1971) containing ammonium sulfate, lake water samples nitrified at low ammonium concentrations (0.67 mM or 12.1 mg/L NH_4^+-N) only, whereas sediment samples exhibited nitrification at low and high ammonium concentrations (0.67 and 12.5 mM, 12.1 and 225.5 mg/L NH_4^+-N). Results suggest that the AOB populations in the lake water and sediments were different. With only one exception, molecular methods enabled the detection of *Nitrosospira* in all samples, but *Nitrosomonas* (*Nitrosomonas europaea-eutropha* lineage) was never obtained. However, the possible presence of *Nitrosomonas* was detected using enrichment cultures (Hastings et al., 1998).



Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

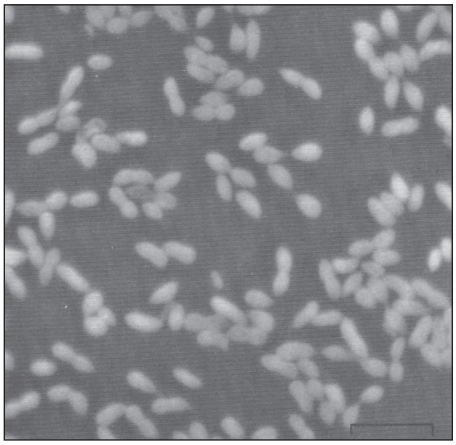
Figure 5-6 *Nitrosomonas europaea* ATCC 25978; phase-contrast photomicrograph (bar, 5 µm)



Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

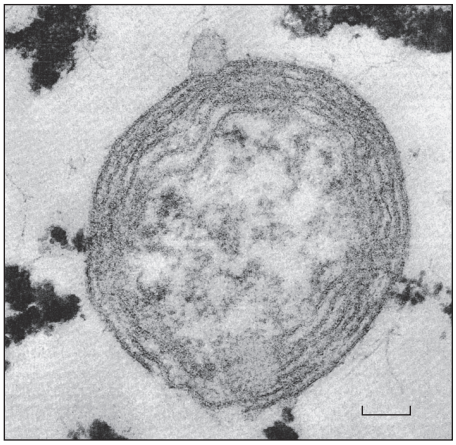
Figure 5-7 *Nitrosomonas* species terrestrial strains; phase-contrast photomicrograph (bar, 5 µm)

Morphology of ammonia-oxidizing bacteria. Table 5-2 summarizes various characteristics of AOB, and Figures 5-6 through 5-11 present various AOB isolated from different environments. All AOB studied as of this writing reproduce by binary fission only; none reproduce by budding. Watson and colleagues (1989) mention that cells of *Nitrosomonas* are rich in cytochrome C-type pigment, which imparts a yellowish to reddish color to cell suspensions. This pigment has an absorption peak at 415 nm, which means that exposure of *Nitrosomonas* cells to light at that particular wavelength may inhibit these organisms.



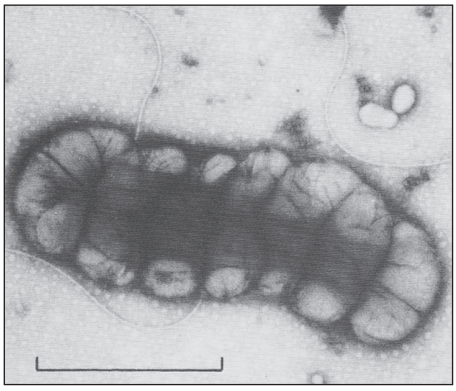
Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

Figure 5-8 *Nitrosomonas* species sewer strain; phase-contrast photomicrograph (bar, 5 µm)



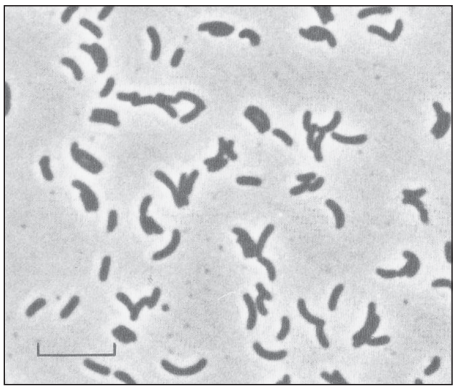
Source: Reprinted with permission from the American Society for Microbiology, Journals Department. Wolfe et al. 1990. 56(2): 451.

Figure 5-9 *Nitrosomonas* species isolated from a drinking water reservoir; transmission electron micrograph (bar, 0.1 µm)



Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

Figure 5-10 *Nitrosospira briensis* negatively stained cell; electron micrograph (bar, 1 µm)



Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

Figure 5-11 *Nitrosovibrio tenuis*; phase-contrast micrograph (bar, 5 µm)

Nitrite-Oxidizing Bacteria

Mechanism of nitrite oxidation. When the first step of nitrification (ammonia oxidation into nitrite) is followed by the second step (nitrite oxidation into nitrate), the combined process is often called complete nitrification. The second reaction is a single step without reaction intermediate and can be summarized by the following equation (Doetsch and Cook, 1973; Prosser, 1989; Bock et al., 1992):

$$NO_2^- + H_2O \leftrightarrow NO_3^- + 2H^+ + 2\ e^- \quad (5\text{-}4)$$

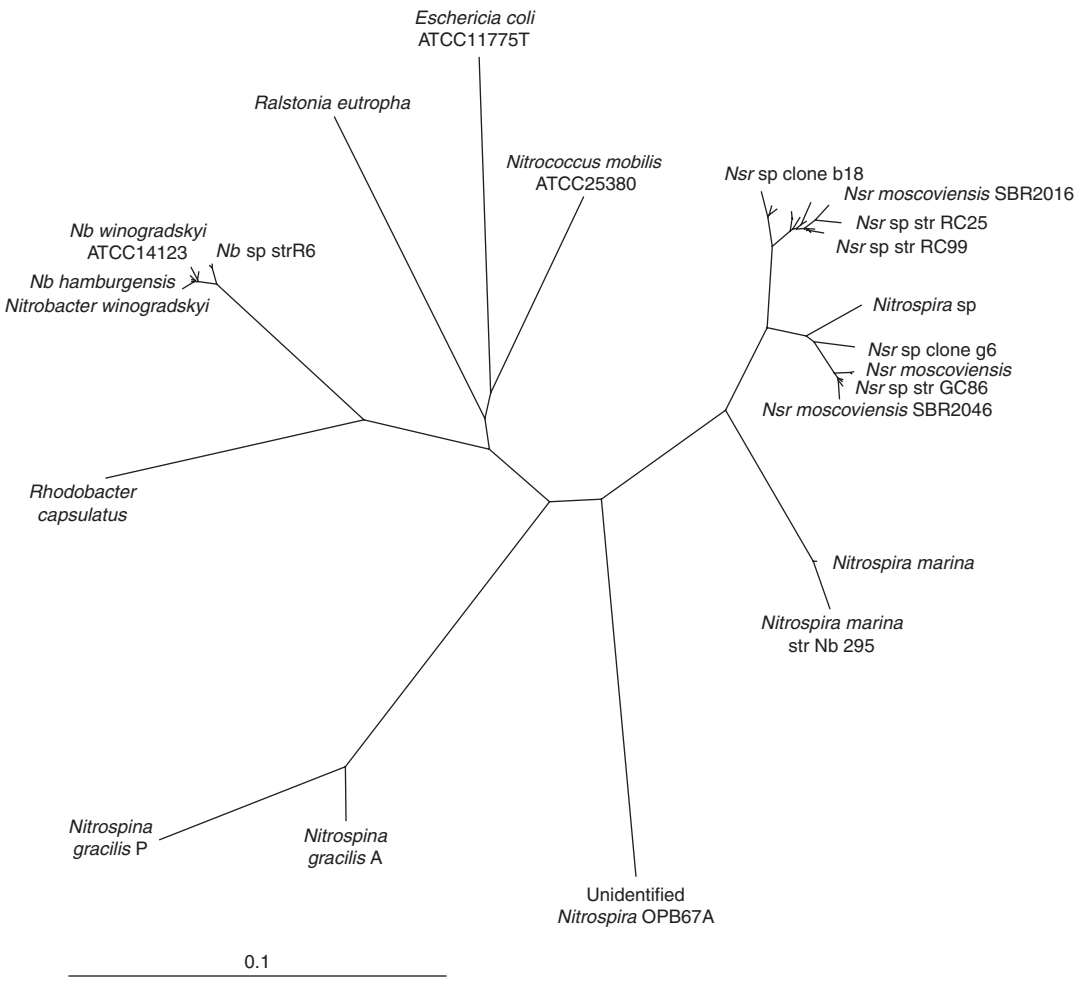
According to Prosser (1989) and Bock and colleagues (1992), nitrite oxidation is a reversible process. Note that H_2O is the source of oxygen during nitrite oxidation, which is carried out by the soluble enzyme nitrite oxidoreductase. In this oxidation process, electrons released from the substrate (nitrite) are transferred to the electron transport chain where ATP and reduced nicotinamide adenine dinucleotide (NADH) are generated by oxidative phosphorylation, without mediation of nonreduced nicotinamide adenine dinucleotide (NAD), as is the case for most chemolithotrophs (Doetsch and Cook, 1973; Watson et al., 1989). The reaction has been estimated to release 15.4 to 20.9 kcal/mole nitrite (McCarty, 1964).

Taxonomy of nitrite-oxidizing bacteria. NOB have been identified in various subdivisions of the class *Proteobacteria*. *Nitrobacter* (also includes *Nitrocystis*) is the most frequently mentioned genus associated with this second step of the nitrification process, although other genera, including *Nitrospina*, *Nitrococcus*, and *Nitrospira*, can also oxidize nitrite to nitrate. The genera *Nitrococcus*, *Nitrospira*, and *Nitrospina* are generally restricted to marine environments and grow optimally at high salt concentrations (Prosser, 1989). One exception is a *Nitrospira* strain isolated from soil by Bock and colleagues (1986). *Nitrobacter* form a tight cluster within the α-subclass of *Proteobacteria*, whereas *Nitrospina* are loosely related to the δ-subclass. *Nitrococcus mobilis* is a member of the γ-subclass, whereas *Nitrospira* constitute their own phylum in the *Bacteria* domain (Regan, 2001). Figure 5-12 presents the phylogenetic relatedness of NOB based on 16S rDNA sequences and illustrates the high sequence similarity of *Nitrobacter* strains and the diversity represented by *Nitrospira* strains. This tree was generated using the neighbor-joining distance matrix method excluding positions with gaps. Figure 5-13 presents another form of phylogenetic tree for NOB.

Speciation of nitrite-oxidizing bacteria in different environments and in water distribution systems. More recently, Hovanec and colleagues (1998) observed that *Nitrobacter winogradskyi* was not the dominant NOB isolated from fresh water using molecular methods, but *Nitrospira moscoviensis* and *Nitrospira marina* appeared to be the dominant species. In bench-scale biofilm reactors fed with nitrifiers collected from nitrifying circulating bed reactors, Nogueira and colleagues (2002) used molecular methods to identify the NOB present. Results showed that the NOB population present was affiliated with the genus *Nitrospira*. Members of the *Nitrobacter* genus were detected in the biofilm only under specific conditions (higher retention time of 5.0 hours and addition of acetate).

When studying the nitrifying bacterial population occurring in nitrifying activated sludge of an industrial wastewater treatment plant receiving sewage with high ammonia concentrations using molecular methods, Juretschko and colleagues (1998) observed that *Nitrospira*-like bacteria were present in significant numbers (9% of the total bacterial counts) and frequently occurred in co-aggregated microcolonies with *Nitrosoccocus mobilis*, an AOB.

Using molecular techniques, Regan and colleagues (2003) observed that *Nitrospira* (and particularly *Nitrospira moscoviensis*) were detected in most of the samples collected from full-scale chloraminated drinking water distribution systems, while *Nitrobacter* were detected in a few samples only. Similarly, Regan and colleagues



Source: Regan, 2001.

Figure 5-12 Phylogenetic tree of NOB based on a multiple alignment of 40 NOB 16S rDNA sequences. Abbreviations are Nb for *Nitrobacter* and Nsr for *Nitrospira*. *Rh. capsulatus* is in the α-subclass of the *Proteobacteria*, *R. eutropha* is in the β-subclass, and *E. coli* is in the γ-subclass of the *Proteobacteria*. Scale bar represents 10% sequence difference.

(2002) observed that the NOB communities of pilot-scale drinking water distribution systems were comprised primarily of *Nitrospira*, although *Nitrobacter* was detected in some samples. Regan and colleagues (2002, 2003) explained that the low-nitrite environment may have selected for *Nitrospira*, which has an estimated K_s of 0.14 mg/L NO_2^--N, approximately one to two orders of magnitude lower than the K_s calculated for *Nitrobacter* species.

Although nitrifying bacteria are obligate chemolithotrophs (they can only obtain energy by the metabolism of inorganic substrates), some *Nitrobacter* species are facultative chemolithotrophs (they can obtain energy by the metabolism of both inorganic and organic substrates). However, most strains of *Nitrobacter* cells grow much slower and heterotrophic growth (in the presence of organic substrate) is much less efficient than autotrophic growth (in the presence of inorganic substrate) (Ford, 1980; Watson et al., 1989). Although nitrifiers are obligate aerobic organisms, some strains

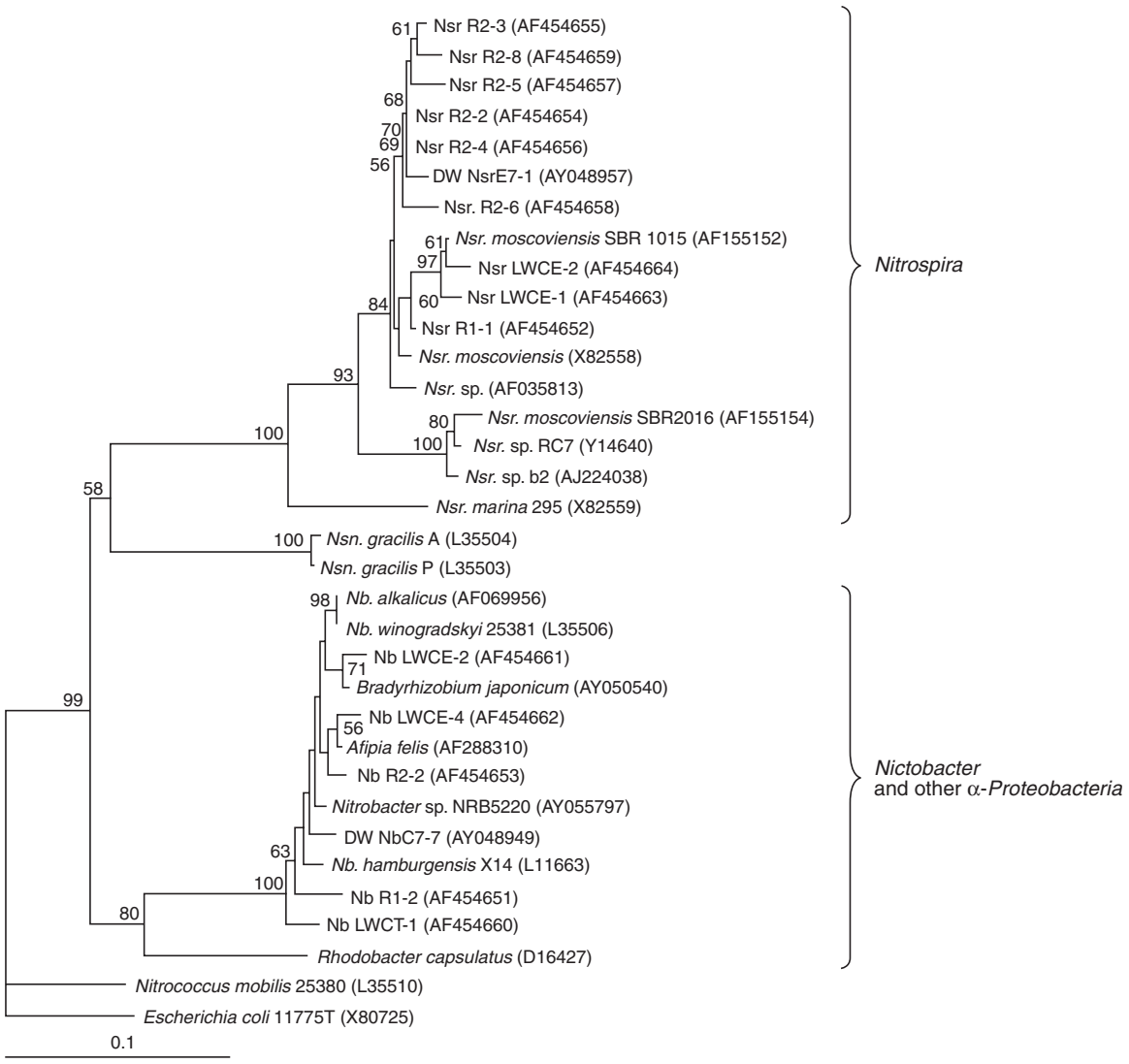


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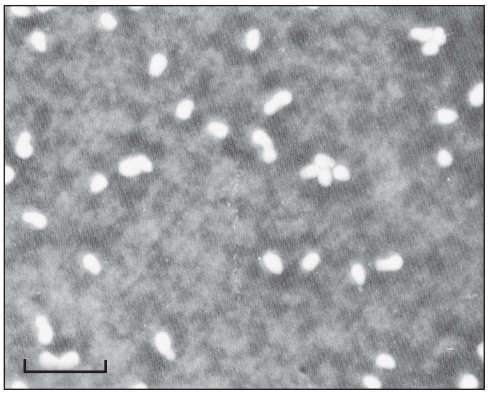
Figure 5-13 Neighbor-joining tree generated from an alignment of 168 rDNA sequences from NOB and other *Proteobacteria*. Abbreviations are Nb for *Nitrobacter*, Nsn for *Nitrospina*, Nsr for *Nitrospira*. Accession numbers are shown in parentheses. Scale bar represents 10% sequence difference.

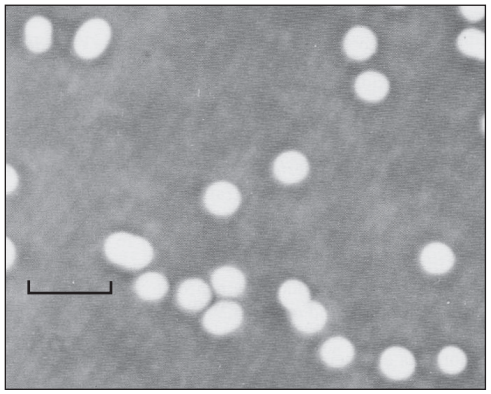
of *Nitrobacter* have been found to be facultative aerobes. In fact, Bock and colleagues (1988) mentioned that *Nitrobacter* cells are able to grow by denitrification in anaerobic environments.

Morphology of nitrite-oxidizing bacteria. Table 5-3 summarizes key characteristics of NOB, and Figures 5-14 to 5-16 show various NOB genera. Cell suspensions of *Nitrobacter* and *Nitrococcus* show characteristic absorption peaks at 420, 440, 550, 587, and 600 nm (Watson et al., 1989). *Nitrobacter* membranes impart a brownish color that is typical of NOB.



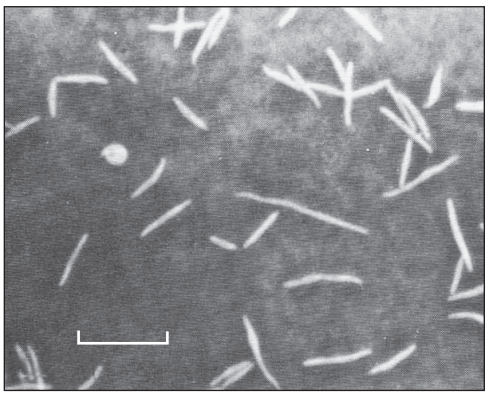
Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

Figure 5-14 *Nitrobacter winogradskyi*; phase-contrast photomicrograph (bar, 5 µm)



Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

Figure 5-15 *Nitrococcus mobilis*; phase-contrast photomicrograph (bar, 5 µm)



Source: Watson, S.W., E.E. Bock, H. Harms, H.P. Koops, and A.B. Hooper. 1989. Nitrifying Bacteria. In *Bergey's Manual of Systematic Bacteriology*, Vol. 3. Saley, J.T., M.P. Bryant, N. Pfennig, and J.G. Holt, eds. Baltimore, Md.: Williams and Wilkins. Copyright James Staley and Bergey's Manual Trust, Department of Microbiology and Molecular Genetics, Michigan State University, East Lansing, Michigan.

Figure 5-16 *Nitrospina gracilis*; phase-contrast photomicrograph (bar, 5 µm)

Denitrifying Bacteria

As presented in chapter 1, denitrification is an important component of the nitrogen cycle. Circumstantial evidence suggests that it may happen in drinking water systems, although it has not been studied nor identified as a major phenomenon. Likely, denitrification is a marginal process that may occur only in portions of the distribution system that are rarely used where conditions conducive to this process (lack of oxygen) develop. Samples with depleted nitrate level may be checked for dissolved

oxygen level to diagnose denitrification. The fundamentals and microbiology of denitrification are presented in this chapter.

Mechanism of denitrification. In the general literature, denitrification refers to the dissimilatory reduction, by facultative anaerobic bacteria, of one or both of the ionic nitrogen oxides (nitrate and nitrite) to the gaseous oxides (nitric oxide [NO] and nitrous oxide [N_2O]), which may themselves be further reduced to dinitrogen (N_2). The nitrogen oxides act as terminal electron acceptors in the absence of oxygen. However, if oxygen is present, it will be used preferentially over nitrate. The oxygen concentration at which denitrification stops has been reported to be 0.2 mg/L in pure cultures (Grau et al., 1982) and 0.3 to 1.5 mg/L in activated sludge systems (Henze, 1991) (similar values in drinking water systems are not available in the literature). A carbon source is generally used as electron donor, although some denitrifiers can grow lithotrophically using hydrogen gas (H_2) or CO_2 as electron donor. The process can be referred to as anaerobic respiration.

Zumft (1992) characterized denitrification as an optional assembly of three possible blocks of reactions: (1) nitrate respiration (involving a nitrate reductase enzyme, DNaR); (2) nitrite respiration (involving a nitrite reductase enzyme, NiR); and (3) nitrous oxide respiration (involving a nitrous oxide reductase enzyme, N_2OR). This author indicated that nitrate respiration, terminating at the nitrite level, is apparently the most widely distributed variant among the prokaryotes. However, studies on genetic organization of denitrifiers indicate that genes for nitrate respiration (*nar*) may be chromosomally coded, whereas genes for nitrite respiration (*nir*) are plasmid-borne (Schneider et al., 1988). Thus, horizontal genetic transfer of nitrite respiration among the prokaryotes is possible.

The denitrification process can be summarized as follows (Christensen and Harremoës, 1977, 1978; Doetsch and Cook, 1973):

Dissimilatory nitrate reduction (type A):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \tag{5-5}$$

Assimilatory nitrate reduction (type B):

$$NO_3^- \rightarrow NO_2^- \rightarrow X \rightarrow NH_2OH \rightarrow \text{Organic nitrogen bound in bacteria} \tag{5-6}$$

Possible electron transport system of the first step of denitrification:

$$\begin{aligned} e\text{-donor} \rightarrow \text{NAD} \rightarrow \text{FAD} \rightarrow \text{Quinone} \rightarrow \text{Cytochrome} \rightarrow \\ \text{Nitrate reductase} \rightarrow NO_3^- \end{aligned} \tag{5-7}$$

Dissimilatory nitrate reduction (i.e., energy-yielding metabolism during which nitrate is reduced to various compounds) is inhibited by oxygen, whereas assimilatory nitrate reduction (i.e., reduction of nitrate to ammonia, allowing the assimilation of ammonia as a source of nitrogen) is unaffected by oxygen. Any of the last three steps can be the final one, and pH determines the end product. Low pH values (<7.3) favor N_2O production, whereas higher pH values favor N_2 gas production (Christensen and Harremoës, 1977). Knowles (1982) mentioned that under anaerobic conditions, a dissimilatory reduction of nitrate and nitrite may occur, in which the major product is ammonia (NH_4^+).

Taxonomy of denitrifying bacteria in different environments. Denitrifying bacteria thrive in practically all habitats. They have been isolated from soil, fresh water, polluted habitats, oceans, plants, animals, and humans and from exotic sources such as boiled ox blood, honey bee larvae, medicinal leeches, and oil brine (Zumft, 1992).

The microorganisms involved in denitrification are distinctly different than those involved in the nitrification process. They are also biochemically and taxonomically very diverse. Denitrifiers are predominantly Gram-negative eubacteria (Zumft,

1992). According to Knowles (1982), most are heterotrophs, whereas others grow autotrophically on hydrogen and CO_2 or reduced sulfur compounds. Zumft (1992) surveyed known denitrifiers and reports an extensive list of 130 species within more than 50 genera. Half of the species identified by this author are members of only three genera: *Pseudomonas* (28 members), *Neisseria* (13 members), and *Bacillus* (12 members). Knowles (1982) also described various denitrifiers. Denitrifiers observed in sewage include *Acinetobacter*, *Alcaligenes*, *Micrococcus*, *Pseudomonas*, *Achromobacter*, and *Bacillus* (Christensen and Harremoës, 1977, 1978; Knowles, 1982).

Most denitrifiers are anaerobic, although some species such as *Paracoccus denitrificans* can denitrify under aerobic conditions (Zumft, 1992). Other organisms can denitrify under partial oxygen concentrations. Some organisms such as *Thiosphaera pantotropha* are capable of simultaneous heterotrophic nitrification and aerobic denitrification (Robertson et al., 1988). The large majority of denitrifiers are mesophilic (i.e., optimum growth temperature in the range of 15 to 45°C; Zumft, 1992).

Previous work indicates that AOB can also carry out denitrification by using nitrite as a terminal electron acceptor, but simultaneous oxidation of ammonia is required as a source of electrons. Poth and Focht (1985) suggest that the purpose of such behavior is to (1) conserve oxygen for use by the AMO; (2) reduce production of nitrite, which may accumulate to toxic levels; and (3) decrease competition for oxygen by NOB by denying them their source of substrate. Similarly, *Nitrobacter*, but not *Nitrospira*, can reduce nitrate to nitrite in the presence of an electron donor such as NADH or methylviologen/benzylviologen (Tanaka et al., 1983; Sundermeyer-Klinger et al., 1984).

ISOLATION AND ENUMERATION OF NITRIFYING BACTERIA

Methods for nitrifying bacteria detection and enumeration are available, although many of them are complex, time consuming, and/or do not allow enumeration of the organisms. The lack of simple, rapid, and adequate methods for nitrifier detection and identification increases the difficulty of resolving nitrification problems in a timely and cost-effective manner.

Because of this, nitrification in drinking water systems is often detected by monitoring for trends in other indicator parameters, such as a decrease in chloramine residual, decrease in ammonia concentration, increase in nitrite and possibly nitrate concentrations, decrease in dissolved oxygen concentration and pH, and increase in heterotrophic plate count (HPC), as discussed in Chapter 7 (Ike et al., 1988; Wolfe et al., 1990; Cunliffe, 1991; Kirmeyer et al., 1995; Odell et al., 1996; Wilczak et al., 1996). However, these indicators are the result of nitrification and occur once nitrification is already well underway. They do not predict the onset of nitrification. Also, these factors are system dependent and some of them may be observed during nitrification episodes in some systems and not in others.

The most commonly used methods for nitrifier detection and identification are presented here and are separated by type of technique: culturing, serological, and molecular.

Culturing Techniques

The traditional approach for identifying bacteria has involved culturing the bacteria on solid growth media, isolating individual colonies that develop, and evaluating attributes such as morphology, staining properties, and nutritional requirements of the colonies. In the case of nitrifiers, however, the energy yields from ammonia and nitrite oxidations are low, leading to small biomass yields and low maximum specific growth rates. Growth of visible colonies on solid media takes several months, and elimination of heterotrophic contaminants is difficult because of their higher growth

Table 5-4 Media composition for enrichment of AOB

	Terrestrial				Marine	Brackish
Chemicals	Soriano and Walker (1968)	Watson (1971)	Watson et al. (1971)	Matulewich et al. (1975)	Watson (1965)	Koops et al. (1976)
$(NH_4)_2SO_4$	500 mg	130 mg	2,000 mg	500 mg	1,320 mg	
NH_4Cl						500 mg
$MgSO_4 \cdot 7H_2O$	40 mg	200 mg	200 mg	50 mg	200 mg	
KH_2PO_4	200 mg					
K_2HPO_4		87 mg	15.9 mg	500 mg	114 mg	50 mg
$CaCl_2 \cdot 2H_2O$	40 mg	20 mg	20 mg	20 mg	20 mg	
Chelated Fe (sequestrene 138 Fe)	0.1 mg					
Chelated Fe (13% Geigy chemical)		1 mg	1 mg		130 mg	
$Na_2MoO_4 \cdot 2H_2O$		100 µg	100 µg	2.4 µg	1 µg	
$MnCl_2 \cdot 4H_2O$		200 µg	200 µg		2 µg	
$CoCl_2 \cdot 6H_2O$		2 µg	2 µg		2 µg	
$CuSO_4 \cdot 5H_2O$		20 µg	20 µg		20 µg	
$ZnSO_4 \cdot 7H_2O$		100 µg	100 µg		100 µg	
Trace metal mix No. 44				1 mL		
0.5% phenol red	1 drop					
NaCl				500 mg		
$KHCO_3$				20 mg		
$CaCO_3$						5,000 mg
Distilled water	1,000 mL	1,000 mL	1,000 mL	1,000 mL		600 mL
Sea water					1,000 mL	400 mL

Source: Watson et al., 1981.

rate. Thus, conventional microbiology involving culture on/in nutrient media is difficult and recovery efficiencies are low (0.1 to 1% for environmental samples) (Wolfe and Lieu, 2001). Also, it is recognized that culturing methods considerably underestimate organisms present because of the inability of any media to support all microorganisms, the presence of metabolically active but not culturable bacteria, the limited sample size that can be processed, possible cell aggregation in response to stress conditions, and the lack of immediate results (the incubation period for some organisms such as nitrifiers is 21 to 28 days). Nonetheless, culturing techniques have provided a large amount of important information throughout the years (e.g., see Table 6-5), despite their limitations.

Many media types and associated methods have been developed, and several of them are presented in Table 5-4 for AOB and Table 5-5 for NOB. For AOB, incubations are usually conducted in darkness, at 25 to 30°C for 1 to 4 months. Enumeration can be performed using a most-probable-number (MPN) technique. An agar medium can also be used for AOB isolation by plating techniques and should contain 1.0% agar, 0.05*M* HEPES, and inorganic salts, as listed in Table 5-4 (Watson et al., 1981). The medium should be adjusted to pH 7.8 to 8.0. Plates should be incubated in darkness at 25 to 30°C

Table 5-5 Media composition for enrichment of NOB

	Terrestrial	Marine
Chemicals	Aleem and Alexander (1958)	Watson and Waterbury (1971)
$NaNO_2$		69 mg
KNO_2	300 mg	
$MgSO_4 \cdot 7H_2O$	187.5 mg	100 mg
KH_2PO_4	500 mg	
K_2HPO_4	500 mg	1.74 mg
$CaCl_2 \cdot 2H_2O$	12.5 mg	6.0 mg
$FeSO_4 \cdot 7H_2O$	10 mg	
$KHCO_3$	1,500 mg	
Chelated Fe (13% Geigy chemical)		1.0 mg
$Na_2MoO_4 \cdot 2H_2O$		30 µg
$MnCl_2 \cdot 4H_2O$		66 µg
$CoCl_2 \cdot 6H_2O$		0.6 µg
$CuSO_4 \cdot 5H_2O$		6.0 µg
$ZnSO_4 \cdot 7H_2O$		30 µg
NaCl	187.5 mg	
Distilled water	1,000 mL	300 mL
Sea water		700 mL

Source: Watson et al., 1981.

in a moist chamber for 4 months. Microcolonies, tan-brown in color and visible with a microscope, may be observed after 1 week, but colonies visible to the naked eye may take 1 to 4 months to develop. Because AOB microcolonies have no distinguishable features, it is not possible to determine whether the colonies observed are from AOB or from microbial contaminants (Watson et al., 1981). Thus, confirmation by subcultures needs to be performed.

Suwa and colleagues (1994) enumerated 34 AOB isolates from various environments using different ammonium sulfate ($(NH_4)_2SO_4$) concentrations from 0.76 to 37.9 mM (100 to 5,000 mg/L) $(NH_4)_2SO_4$. They observed that MPN estimates varied depending on the isolates and growth conditions. Some isolates grew at low $(NH_4)_2SO_4$ concentration but not at high concentration. Suwa and colleagues (1994) also used different variations of growth media to select specific strains or study physiological and kinetic parameters.

Belser and Schmidt (1978a) examined several media, including the Soriano and Walker media (1968), the media from Matulewich and colleagues (1975), the Alexander and Clark media (1965), and the Watson media (1971). They observed that each medium was selective to particular strains and the media differed greatly in incubation times required to reach maximum counts. Nonetheless, they report that the Soriano and Walker (1968) media was superior to others for enrichment of AOB from soil for the following reasons: (1) it requires the shortest incubation time for MPN enumeration; (2) it is convenient to prepare; (3) it includes an indicator; and (4) precipitate does not form, which facilitates isolation (Belser and Schmidt, 1978a). This media has been used more extensively in the drinking water industry and particularly by

Ike et al. (1988), Wolfe et al. (1988), Lieu et al. (1993), and Baribeau et al. (2001). In this method, serial dilutions of sample are incubated in multiwell microplates containing the Soriano and Walker (1968) media (Table 5-4) in the dark at 28°C for approximately 24 days. AOB are enumerated using an MPN technique based on the production of nitrite, which is determined colorimetrically using sulfanilic acid and N,N-dimethyl-α-naphtylamine. Wells that exhibit a red color within 1 minute after reagent addition are determined positive for nitrite. Wells that develop a slight pink color or remain colorless after 1 minute are determined negative.

In the case of NOB, some microorganisms such as *Nitrospina gracilis* cannot tolerate more than 1 mM nitrite (Watson et al., 1981). When higher nitrite concentrations are used, *Nitrobacter winogradskyi* usually dominates the enrichment culture. Thus, it is important to use low as well as high concentrations of nitrite in enrichment cultures. Enrichment cultures are incubated at 25 to 30°C for 1 to 4 months and examined periodically for nitrite oxidation (Watson et al., 1981). Enumeration can be performed using an MPN technique.

When culturing techniques are used, nitrifiers can be categorized taxonomically by their shape, size, and membrane arrangement within their cytoplasm (Watson et al., 1981).

Serological and Microscopy Techniques

Serological reactions (involving serum or plasma), such as immunofluorescent antibody-based techniques, have been used to study the species composition of nitrifiers and relationships between groups of bacteria. These techniques eliminate the lengthy incubation period necessary when using culturing techniques. However, they also require initial isolation of pure cultures to raise antibodies for subsequent detection assays and may require confirmation for identification (Holt et al., 2000; Stephen et al., 1996). Also, the large serological diversity of nitrifiers and the co-existence of several serotypes in one ecosystem seriously limit the efficiency of serological techniques for environmental samples. Belser and Schmidt (1978b) examined the cross-reactivity of fluorescent antibodies prepared against 16 AOB strains. Results obtained indicate that AOB exhibit considerable serological diversity. As such, several antibodies are required to cover each genera of AOB.

Other techniques available involve epifluorescent microscopy using various fluorochromes or dyes, such as acridine orange, 4,6-diamidino-2-phenylindole (DAPI), or *Bac*Light (Molecular Probe Inc., Eugene, Ore.). Acridine orange reacts with double-stranded DNA (which fluoresces green) and single-stranded nucleic acid (which fluoresces orange-red) to allow estimation of cell viability. DAPI is a fluorochrome that leads to a bright blue fluorescence when complexed with DNA and a weak yellow fluorescence when complexed with non-DNA material (Porter and Feig, 1980). *Bac*Light is a commercial bacterial viability test kit that relies on SYTO9 and propidium iodide fluorochromes. Green fluorescing cells are considered alive, whereas red fluorescing cells are considered dead. Many other dyes are also available; however, these dyes are not specific to nitrifiers and detect all microorganisms present.

Molecular Methods

Molecular technologies have eliminated several of the limitations observed with culturing, serological, or microscopy techniques. The 16S rRNA gene is carried by all bacterial species and the precise sequence of a given 16S rRNA gene is indicative of the species from which it was derived. It is therefore becoming the target of choice for analysis of complex or unknown bacterial communities. Target nucleic acid amplification techniques, such as polymerase chain reaction (PCR), are often needed for detection of low copy number bacterial DNA such as observed in low-biomass environmental samples.

Table 5-6 Examples of PCR primers developed to identify AOB (16S rRNA region)

Organisms Targeted	Primer Name	Reference
AOB of the β-subclass of *Proteobacteria*	NIT-A and NIT-B	Voytek and Ward (1995)
AOB of the β-subclass of *Proteobacteria* (V-2 and V-3 variable domains)	CTO189f-GC and CTO654r	Kowalchuk et al. (1997)
amoA gene	amoA-1F and amoA-2R	Rotthauwe et al. (1997)
amoA gene	amo-F2 and amo-R2	Juretschko et al. (1998)
amoA gene	amoA-3F and amoA-4R	McTavish et al. (1993) and Alzerreca et al. (1999)
AOB of the β-subclass of *Proteobacteria*	βAMOf and βAMOr	McCaig et al. (1994)

Specific organisms can also be detected by genetic probe hybridization, with or without prior nucleic acid amplification. When hybridization follows nucleic acid amplification, it is used as a confirmation step in microorganism identifications. A variety of other molecular methods, such as denaturing gradient gel electrophoresis (DGGE), terminal restriction fragment length polymorphism (t-RFLP), fluorescent in-situ hybridization (FISH), cloning, and sequence analysis, are also available for microorganism detection and identification.

Several researchers have developed primers and probes specific to nitrifiers. Examples of PCR primers and hybridization probes are presented in Tables 5-6 and 5-7, respectively. Using molecular methods, Purkhold and colleagues (2000) were able to complete the 16S rDNA sequence data of 10 *Nitrosomonas* species and *Nitrosococcus mobilis* and determine the sequence for three *Nitrosomonas* sp. isolates and the γ-subclass proteobacterium *Nitrosococcus halophilus*. Phylogenetic analyses of the molecular isolates of 11 nitrifying wastewater treatment plants were also conducted. Numerous primers and probes were used to conduct this survey and are presented in Purkhold et al. (2000). This work establishes robust phylogenetic frameworks for molecular surveys of AOB and helps resolve several inconsistencies observed in the literature. Unfortunately, a sequence specific to all AOB or all NOB has not been identified yet. Thus, a combination of different primers is necessary to identify nitrifiers. In the case of AOB, the *amoA* gene is often used as a target gene (see Table 5-6).

There has been recent interest in using molecular biology tools to overcome the delay and bias inherent to the culturing assays for enumerating nitrifiers. One such strategy involves a PCR protocol, called *real-time PCR*, that provides quantitative data on the target organism. This method has been applied to AOB enumeration in soils (Hermansson and Lindgren, 2001), activated sludge (Araki et al., 2004), and chloraminated drinking water distribution systems (Regan et al., 2004). These reports add another dimension to the qualitative nitrifier speciation studies by providing AOB concentrations in these various systems.

CONCLUSIONS

Nitrification is carried out by two distinct groups of nitrifiers—AOB and NOB. Bacteria of these two groups are distinguished "operationally" by utilizing a different substrate—ammonia or nitrite. Within each group, nitrifiers belong to several subdivisions of the class *Proteobacteria* and, as such, may even be unrelated.

In drinking water distribution systems, AOB are of major operational concern because their activity produces nitrite, which contributes to the decomposition of chloramine residual. NOB require the presence of nitrite, which is produced by AOB, and their activity does not in itself contribute to instability of water quality since they

Table 5-7 Probes for hybridization of nitrifying bacteria

Organisms Targeted	Probe Name	Reference
Ammonia-oxidizing bacteria:		
AOB of the β-subclass of *Proteobacteria*	β-AO233	Stephen et al. (1998)
AOB of the β-subclass of *Proteobacteria*	NIT-C	Voytek and Ward (1995)
AOB of the β-subclass of *Proteobacteria*	Nso190	Mobarry et al. (1996)
AOB of the β-subclass of *Proteobacteria*	Nso1225	Mobarry et al. (1996)
Nitrosomonas Cluster	Nsm156	Mobarry et al. (1996)
Nitrosospira Cluster	Nsv443	Mobarry et al. (1996)
Nistrosococcus mobilis lineage	NmV	Pommerening-Röser et al. (1996)
Most halophilic and halotolerant AOB (*Nitrosomonas europaea, Nitrosomonas eutropha, Nitrosomonas cryotolerans, Nitrosomonas aestuarii, Nitrosomonas marina, Nitrosomonas halophila,* and *Nitrosococcus mobilis*)	NEU	Wagner et al. (1995)
All *Nitrosomonas*	Nmo254 and Nmo254a	Stephen et al. (1998)
Nitrosomonas Cluster 6a	NmoCL6a_205	Stephen et al. (1998)
Nitrosomonas Cluster 6b	NmoCL6b_376	Stephen et al. (1998)
Nitrosomonas Cluster 7	NmoCL7_439	Stephen et al. (1998)
All *Nitrosospira*	Nsp436	Stephen et al. (1998)
Nitrosospira Cluster 1	NspCL1_249	Stephen et al. (1998)
Nitrosospira Cluster 2	NspCL2_458	Stephen et al. (1998)
Nitrosospira Cluster 3	NspCL3_454	Stephen et al. (1998)
Nitrosospira Cluster 4	NspCL4_446	Stephen et al. (1998)
Nitrite-oxidizing bacteria:		
Nitrobacter spp.	Nb1000	Mobarry et al. (1996)
Nitrobacter	NIT2 and NIT3	Wagner et al. (1996)
Nitrospira	Ntspa0685 M	Hovanec et al. (1998)
Freshwater *Nitrospira* spp.	Nsr826	Schramm et al. (1998)
Freshwater *Nitrospira* spp.	Nsr1156	Schramm et al. (1998)
Nitrospira moscoviensis	Ntspa1026	Kane et al. (1993)

convert nitrite to stable, fully oxidized nitrate. AOB and NOB growing in drinking water distribution systems are selected for their affinity to the low levels of substrates present and are selected to withstand environmental stresses. To do so, they can grow in clumps (cell aggregates) and are primarily concentrated in protective layers of the biofilm and sediments.

Because nitrifiers belong to diverse groups, serological and molecular methods cannot capture them all in a single assay. Because of their slow growth rate, conventional culturing techniques require long incubation periods (3 to 4 weeks). Culturing techniques are also not species specific. As a result, the detection, identification, and enumeration of nitrifiers are complex and limited by available analytical methods. This may explain why information is still lacking regarding the presence and speciation of nitrifiers in the environment, particularly in drinking water.

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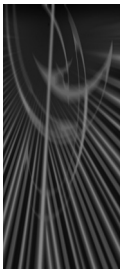


Chapter 6

Growth and Inactivation of Nitrifying Bacteria

Hélène Baribeau

INTRODUCTION

This chapter presents the growth characteristics of nitrifiers and denitrifiers. It also discusses available information on the inactivation of nitrifying bacteria by the most common drinking water disinfectants. Information on this subject in the literature is relatively limited, sometimes conflicting, and only future, better enumeration techniques for ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) will allow for more precise evaluation of the effect of disinfectants on nitrifiers. Table 6-1 presents a brief summary of the information found in this chapter.

OPTIMUM GROWTH CONDITIONS FOR AMMONIA- AND NITRITE-OXIDIZING BACTERIA

This section presents the general growth conditions of nitrifiers. Large species-level differences have been observed. The phenotypic diversity of AOB and NOB is also not well understood. Nonetheless, Table 6-2 presents typical growth characteristics of representative genera of nitrifiers, and further characteristics are presented in the paragraphs below. Typical of most chemolithotrophs, nitrifiers grow slowly. Table 6-2 suggests that the growth rate of AOB is faster than the growth rate of NOB, which may explain the accumulation of nitrite in some environments. As such in drinking water distribution systems, authors have seen nitrite concentrations reaching 1.0 mg/L NO_2^--N (Skadsen, 1993; Wilczak et al., 1996; Odell et al., 1996; McGuire et al., 1999; Harrington et al., 2002).

Bacterial growth rate is typically expressed using two parameters: maximum specific growth rate and half-saturation constant (i.e., concentration at which bacteria grow at half of their maximum growth rate). Prosser (1989) listed maximum specific growth rates of pure cultures of several species of nitrifiers. Specific growth rates usually range between 0.014 and 0.064 hr^{-1}, which is the equivalent to doubling times (time needed for the biomass or population to double in numbers) of 50 to 11 hr. These specific growth rates are limited by the low energy gain obtained from ammonia or nitrite oxidation (Prosser, 1989). In fact, Kelly (1978) estimates that 80%

Table 6-1 Key points from chapter 6

Growth Conditions	• Many factors affect the growth of nitrifiers including substrate concentration, temperature, pH, oxygen concentration, alkalinity, light intensity, microbial community composition, and presence of inhibitory substances.
	• Ammonia (NH_3) rather than ammonium ion (NH_4^+) is the substrate of the AOB energy generating system. Cell membranes are highly permeable to NH_3 but not to NH_4^+. Nitrite offers NOB approximately a third of the electrons that are provided to AOB by ammonia.
	• The optimum temperature for nitrifier growth ranges between 20 and 30°C, and the optimum pH between 7.5 and 8.0. Each reduction in pH value of one unit decreases the concentration of free ammonia by one order of magnitude. This explains the sharp decrease in AOB specific growth rates observed with decreasing pH values, within the pH range where AOB can survive.
	• Theoretical oxygen requirement for biological oxidation of ammonia to nitrite is 3.22 g O_2 per g NH_4^+-N, and 1.11 g O_2 per g NO_2^--N for oxidation of nitrite to nitrate. Thus the total theoretical oxygen requirement is 4.33 g O_2 to oxidize NH_4^+-N into NO_3^--N.
	• Nitrifiers can be inhibited by light, but are not fully inactivated by it. It also appears that nitrifiers have the ability to recover from inhibition during dark periods.
	• Growth rates for nitrifiers are considerably less than those for the heterotrophic bacteria due to more restricted energy yielding metabolism and the fact that they must synthesize all cell components from carbon dioxide. Doubling times for nitrifiers may be estimated at 11 to 50 hours.
Inactivation of Nitrifiers	• The reported rates of nitrifier inactivation depend on the enumeration method used.
	• Disinfectant stability is affected by various parameters, including incubation time, water matrix, temperature, pH, turbidity, NOM concentration and composition, and disinfectant dosage. In turn, disinfectant stability affects inactivation rates.
	• Bacteria grown in tap water may have higher disinfectant resistance than bacteria grown in laboratory water.
	• The ability of nitrifiers to grow in tight clusters of cells surrounded by a slime layer and to attach to surfaces, sediments, and other debris renders them resistant to disinfection.
	• Nitrifiers are much more sensitive to free chlorine than to chloramines; therefore, free chlorine is a superior disinfectant for inactivation of nitrifiers. Monochloramine is not as effective as free chlorine against AOB. Inactivation by chloramines appears to be due to dichloramine rather than monochloramine.
	• Chlorite, the main by-product of chlorine dioxide, is very effective at inactivating nitrifiers.

NOTE: AOB, ammonia-oxidizing bacteria; NOB, nitrite-oxidizing bacteria; NOM, natural organic matter.

of the energy generated by autotrophs is used to fix carbon dioxide (CO_2), while Glover (1985) determined that the thermodynamic efficiencies for growth of AOB and NOB are in the range of 4.4 to 21.3%. In chemolithotrophically grown cells of *Nitrobacter*, only 2 to 11% of the free energy generated from the oxidation of nitrite is used for cell growth. Grady and colleagues (1999) mentioned that the maximum specific growth rate coefficients for the autotrophic bacteria are considerably less than those for the heterotrophic bacteria, reflecting their more restricted energy-yielding metabolism and the fact that they must synthesize all cell components from carbon dioxide.

Table 6-2 Growth characteristics of nitrifying bacteria

Characteristic	*Nitrosomonas* (AOB)	*Nitrobacter* (NOB)
Generation time (hours)	8 to 36	12 to 59
Observed yield coefficient (g cell/g N oxidized)	0.04 to 0.13	0.02 to 0.07
Specific growth rate coefficient (day^{-1})	0.33 to 2.2*	0.14 to 1.39
	0.34 to 2.21†	
Half-saturation constant, or half-velocity coefficient	1.0 mg/L at 20°C*†	1.3 to 8.4 mg/L
	10 mg/L at 30°C*	
	0.06 to 5.6 mg/L N (sum of NH_3 and NH_4^+)†	

Source: Painter, 1970; Ford, 1980; Grady et al., 1999.
* Ford (1980).
† Grady et al. (1999).

It is tempting here to present specific growth rate and half-saturation coefficients for heterotrophic bacteria for comparison purposes. However, Grady and colleagues (1999) warned that these coefficients are very dependent on the microorganism and substrate employed. As a result, it is very difficult to generalize the parameter values and care should be exercised in the use of values considered to be typical. As an example, the specific growth rate and half-saturation coefficients of heterotrophic bacteria in domestic wastewater (a complex substrate) range from 0.12 to 0.55 hr^{-1} and 10 to 180 mg/L chemical oxygen demand, respectively (Grady et al., 1999).

Prosser (1989) lists yield and maintenance coefficients calculated from steady-state continuous cultures for various species of nitrifiers. These values indicate that at low ammonium concentration (1 µg/L NH_4^+-N), the specific growth rate of *Nitrosomonas* strains is 21% of the maximum specific growth rate and 76% of the substrate is consumed for maintenance (Prosser, 1989). Similarly, the specific growth rate for *Nitrobacter* is reduced to 26% of its maximum value at low nitrite concentration (1 µg/L NO_2^--N), with 81% of nitrite oxidized for maintenance (Prosser, 1989). These results suggest that the specific growth rates for AOB and NOB decrease significantly at low substrate concentrations, such as in drinking water distribution systems.

As for the saturation constants for enzyme activity and the saturation constants for growth, Prosser (1989) reported that the values obtained from the literature vary greatly: from 0.018 to 14 mM NH_4^+ (0.12 to 10 mM, or 1.68 to 140.1 mg/L N, for the sum of NH_4^+ and NH_3) for *Nitrosomonas* species and from 0.039 to 3.6 mM NO_2^- (0.55 to 50 mg/L N) for *Nitrobacter* species.

The growth kinetics of AOB and NOB are related to their substrate concentration and can be generally modeled using the empirical Monod equation. However, Suwa and colleagues (1994) observed that some AOB strains sensitive to ammonia inhibition may not be adequately modeled using this equation; the Haldane equation better described the results obtained. Also, kinetic parameter estimation is difficult due to the generally low growth rates and yields of these organisms. An additional complication in the estimation of the kinetic parameters is the fact that NH_3 and not NH_4^+ is considered to be the substrate for AOB. However, the Monod equation usually considers the sum of both NH_3 and NH_4^+. Figure 6-1 shows a conceptual graph of Monod kinetics and below is the Monod equation.

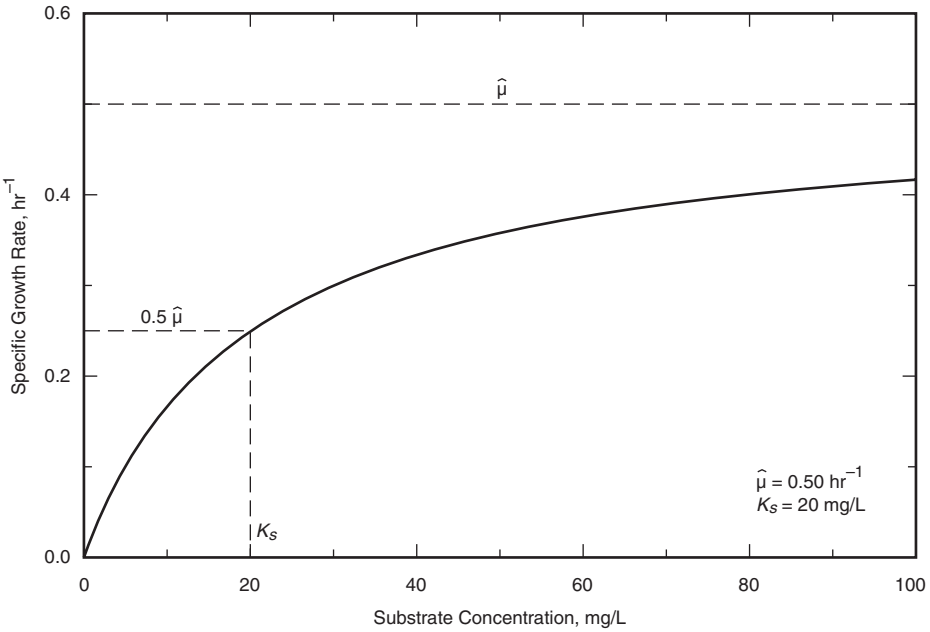


Figure 6-1 Generalized graph of Monod kinetics showing the relationship between the specific growth rate ($\hat{\mu}$) and half saturation coefficients (K_s) for a single limiting substrate concentration

$$\mu = \hat{\mu} \frac{S_s}{K_s + S_s} \tag{6-1}$$

Where: μ is the growth rate of *Nitrosomonas* (days^{-1})
$\hat{\mu}$ is the maximum nonammonia limited growth rate of AOB (days^{-1})
S_s is the ammonia concentration (mg/L NH_3-N)
K_s is the half-saturation coefficient (mg/L)

Information could not be found regarding oxidation rates of ammonia and nitrite in drinking water. However, using batch experiments with enriched acclimated cultures isolated from an oxidation ditch treating poultry wastes (substrate concentration ranging from 100 to 1,200 mg/L N), Wong-Chong and Loehr (1975) observed that both the oxidation of ammonia and the oxidation of nitrite were characterized by zero-order reactions (i.e., the specific growth rate is independent of the substrate concentration) at such high substrate concentrations, which led to much higher S_s than K_s values. Wong-Chong and Loehr (1975) also determined the nitrification rate of the same enriched acclimated cultures isolated from the oxidation ditch (at pH of 7.0 to 7.5) and observed that it was characterized by an equation similar to the Michaelis-Menten equation as opposed to the Monod equation (the Michaelis-Menton equation considers the rates of chemical reactions catalyzed by enzymes and has a mechanistic basis, whereas the Monod equation is strictly empirical):

$$k_2^* = \frac{k_{2\max}^* k_2 S a_m}{k_{2\max}^* + k_2 S a_m} \tag{6-2}$$

Table 6-3 Optimum growth conditions for AOB genera

Conditions	*Nitrosomonas*	*Nitrosococcus*	*Nitrosospira*	*Nitrosolobus*	*Nitrosovibrio*
Temperature	25–30°C	25–30°C	20–35°C	25–30°C	25–30°C
pH	7.5–8.0	7.5–8.0	7.5–8.0	7.5	7.5–7.8
Media	Chemolithotroph (can grow mixotrophically, but not heterotrophically)	Chemolithotroph (can grow mixotrophically, but not heterotrophically)	Obligate chemolithotroph	Chemolithotroph (can grow mixotrophically)	Chemolithotroph (can grow mixotrophically, but not heterotrophically)

Adapted from Watson et al., 1989; Holt et al., 2000.

Table 6-4 Optimum growth conditions for NOB genera

Conditions	*Nitrobacter*	*Nitrospina*	*Nitrococcus*	*Nitrospira*
Temperature	5–37°C	20–30°C	25–30°C	20–30°C
pH	6.5–8.5	7.0–8.0	7.5–8.0	7.6–8.0
Media	Facultative chemolithotroph (can grow mixotrophically)	Obligate chemolithotroph	Obligate chemolithotroph	Chemolithotroph (can grow mixotrophically)

Adapted from Watson et al., 1989; Holt et al., 2000.

Where: k_2^* is the oxidation rate (mg N l^{-1} hr^{-1})

$k_{2\max}^*$ is the maximum reaction rate (mg N l^{-1} hr^{-1})

k_2 is the reaction rate of the reacting entities (substrate and enzyme) (hr^{-1})

Sa_m is the amount of reacting enzyme (mg/L)

Many factors affect the growth rate of nitrifiers, including substrate concentration, temperature, pH, light intensity, oxygen concentration, and microbial community composition. The critical factors are detailed below. The optimum growth conditions for various AOB and NOB genera are summarized in Tables 6-3 and 6-4, respectively.

Growth Substrates

Inorganic nitrogen. Most strains of AOB and NOB grow optimally at ammonia and nitrite substrate concentrations of 2 to 10 mM (28 to 140 mg/L N) and 2 to 30 mM (28 to 420 mg/L N), respectively (Watson et al., 1989). According to Prosser (1989), liquid cultures of nitrifiers require ammonia concentrations in the order of 50 to 2,000 µg/L NH_4^+-N and nitrite concentrations in the order of 50 to 200 µg/L NO_2^--N. These ranges of concentrations are similar to the conditions found in drinking water distribution systems. Using continuously fed reactors of municipal wastewater, Princic and colleagues (1998) observed maximum nitrifying biomass in the reactor fed with the highest concentration of ammonia, 3,000 mg/L NH_4^+-N (pH was maintained between 7.0 and 8.0). These conditions also selected for a nitrifier population unidentified prior to this study. The other reactors were fed with ammonia concentrations ranging from 50 to 1,000 mg/L NH_4^+-N. When enumerating AOB isolates from various environments,

Suwa and colleagues (1994) also observed strain selection by $(NH_4)_2SO_4$ concentration (0.76 versus 37.9 mM, 100 versus 5,000 mg/L $(NH_4)_2SO_4$), although these concentrations are outside those encountered in drinking water systems.

Nitrifiers are subject to both substrate (ammonia and nitrite) and product (nitrite and nitrate) inhibition. If the concentration of either the substrate or the product is too high, the rate of nitrification decreases (Focht and Verstraete, 1977). Studies involving pure cultures of these organisms have shown that excess concentration of free ammonia slows the rate of nitrification more than excess concentration of total ammonia and nitrite (Aleem and Alexander, 1958; Boon and Laudelot, 1962). Most of these studies suggest that substrate and product concentrations need to be much higher than those found in drinking water systems to inhibit nitrifier growth, as presented in the following paragraphs.

Stein and Arp (1998) observed that *Nitrosomonas europaea* lost an increasing amount of ammonia oxidation activity over a 24-hr period when nitrite concentration was high, as confirmed by decreasing rate of NH_4^+-dependent oxygen consumption. The loss of ammonia oxidation activity via nitrite occurred under both aerobic and anaerobic conditions, and more activity was lost under alkaline (pH 8) than under acidic conditions (pH of 5.5 to 6), except in the presence of large concentrations of nitrite (20 mM, 260 mg/L N).

Ford (1980) reported that free ammonia inhibits *Nitrosomonas* at concentrations of 10 to 150 mg/L and inhibits *Nitrobacter* at concentrations of 0.1 to 1.0 mg/L. Because the NH_4^+/NH_3 ratio depends on pH, the toxicity of ammonia also depends on environmental pH. Prosser (1989) reported that *Nitrospina gracilis* cannot grow at nitrite concentrations greater than 1 mM (14 mg/L N). Bock and colleagues (1992) also reported that nitrate at concentrations between 30 and 65 mM (420 and 910 mg/L N) is inhibitory to NOB. Free nitrous oxide (N_2O) also inhibits both *Nitrosomonas* and *Nitrobacter* at concentrations varying between 0.2 and 2.8 mg/L (Ford, 1980), and free nitrous acid (HNO_2) inhibits at concentrations ranging between 0.22 and 2.8 mg/L.

Alexander and Clark (1965) observed that 35 and 100 atoms of nitrogen are oxidized by *Nitrosomonas* and *Nitrobacter*, respectively, for the fixation of one molecule of CO_2. This can be explained by the fact that nitrite offers NOB approximately a third of the electrons that are provided to AOB by ammonia. As such, the difference in free energy for the oxidation of ammonia is –66 kcal/mol and –17.5 kcal/mol for nitrite (Focht and Verstraete, 1977).

Organic matter. Most nitrifiers (and all AOB) are obligate chemolithotrophs. As such, nitrifiers oxidize inorganic substrates, such as ammonia and nitrite, as sole sources of energy and do not require organic carbon. Some strains of AOB can incorporate organic compounds (pyruvate, formate, acetate, glucose, peptone), which may exhibit various results in AOB, from no effect, to stimulation, to inhibition (Focht and Verstraete, 1977). In any case, heterotrophic growth of AOB (use of organic carbon for both carbon and energy sources) has never been observed (Watson et al., 1989; Prosser, 1989).

Some *Nitrobacter* species are facultative chemolithotrophs, as they can use organic substrates as a carbon source (Ford, 1980; Watson et al., 1989; Holt et al., 2000). As such, the incorporation of organic carbon (acetate, casein hydrolysate, glycerol, pyruvate) may increase NOB growth rates and cell yields (Focht and Verstraete, 1977; Prosser, 1989; Watson et al., 1989). However, an inorganic source is the preferred medium, and heterotrophic growth of *Nitrobacter* species is slower than growth on nitrite and slower than the growth of other heterotrophs.

As mentioned above, various groups of organisms, including heterotrophic bacteria, fungi, and algae, can also be responsible for nitrification, although at a much slower rate than chemolithotrophic nitrifying bacteria. An elaborated discussion of these organisms is outside the intent of this document.

Several authors suggest that removal of natural organic material (NOM) may prevent nitrification by enhancing the biological stability of the water. However, because AOB use CO_2 as a carbon source, NOM is not the source of biological instability from the AOB perspective (Harrington et al., 2002, 2003). Instead, ammonia is the source of biological instability and NOM enhances this instability by reacting with chloramines to release ammonia, which promotes AOB growth. A discussion on chloramine demand and decay is presented in chapter 4.

Phosphorus. Earlier work suggested that nitrification is favored by the presence of calcium and phosphate (Doetsch and Cook, 1973). This was confirmed by van der Aa and colleagues (2000) who observed that low-temperature water should contain at least 10 µg/L PO_4^{3-}-P to maintain sufficient nitrification. These authors dosed phosphoric acid (30 µg/L PO_4^{3-}-P) in a drinking water treatment plant in the winter to stimulate growth and re-established ammonia removal within the plant. These results suggest that phosphorus limitation may inhibit the growth of nitrifiers in drinking water systems.

Effect of Temperature on Growth of Nitrifying Bacteria

Nitrifiers can be found at temperatures ranging from 4 to 60°C. The optimum growth temperature has been reported in the range of 20 to 30°C (Tables 6-3 and 6-4), although optimum temperature for nitrite oxidation may be lower. Generally, the optimum growth temperature reported in the literature is 30°C for AOB and 28°C for NOB (Holt et al., 2000). Between 5 and 30°C, temperature affects nitrifier growth according to an Arrhenius relation (i.e., biological activity doubles with every 10°C water temperature increase) (Wong-Chong and Loehr, 1975). Maximum specific growth rates of AOB at 10, 20, and 30°C are 0.3, 0.65, and 1.2 d^{-1}, respectively (USEPA, 1993).

Kirmeyer and colleagues (1995) presented a laboratory study during which AOB were incubated in dechlorinated treated drinking water. Results show that AOB grew at all temperatures tested, 10, 15, and 25°C, although growth took 3 to 4 weeks longer at 10°C than at the other temperatures. In the presence of chloramine, nitrification occurred earlier at 25°C than at 15°C (Odell et al., 1996).

Lieu and colleagues (1993) conducted extensive inactivation studies using AOB cultures inoculated in drinking water samples in the presence of different monochloramine concentrations (1.7, 2.0, and 2.5 mg/L) and chlorine to ammonia-N weight ratios (3:1, 4:1, and 5:1). Results show that all chloramine conditions tested prevented the growth of AOB (<0.2 most probable number [MPN]/mL) at 10°C and AOB did not recover (Table 6-5). At 15°C, AOB were able to recover at different rates following exposure to 1.7 and 2.0 mg/L chloramines but not following exposure to 2.5 mg/L chloramines. Contact time and chloramine dosage controlled the growth of AOB at 15°C, and the chlorine to ammonia-N ratio did not have a significant effect. At 25°C, only the AOB exposed to 1.7 mg/L chloramines were able to recover following two logs of inactivation and regrowth. Nitrification was controlled by chloramine dosage, contact time, and chlorine to ammonia-N ratio at 25°C. The rate of inactivation and regrowth was faster at 25°C than at 15°C (Lieu et al., 1993). Based on the results of this study, this utility increased chloramine residual in their large storage reservoirs from 1.7 to 2.5 mg/L Cl_2 and discontinued the practice of 1-month annual free chlorine burn. Further information regarding the control of nitrifiers using chloramines can be found later in this chapter.

Using bench-scale distribution system simulators, Pintar and colleagues (2000) showed that nitrification occurred at 12°C at a chloramine residual of 0.05 to 0.6 mg/L and a chlorine to ammonia-N weight ratio of 3:1. When the bench-scale system temperature was decreased to 6°C, nitrite production was also observed following a period of acclimation, showing that AOB are capable of metabolic activity at low

Table 6-5 Regrowth of AOB (MPN/mL) following exposure to chloramines

Temperature (°C)	Contact time (days)	Recovery controls* (days)	Chloramine dose of 1.7 mg/L			Chloramine dose of 2.0 mg/L			Chloramine dose of 2.5 mg/L		
			Chlorine-to-ammonia-N ratio			Chlorine-to-ammonia-N ratio			Chlorine-to-ammonia-N ratio		
			3:1	4:1	5:1	3:1	4:1	5:1	3:1	4:1	5:1
10	2		†	†	†	†	†	†	‡	‡	‡
	8		‡	‡	‡	‡	‡	‡	‡	‡	‡
	Non-neutralized§		‡	‡	‡	‡	‡	‡	‡	‡	‡
		2	**	**	**	**	**	**	**	**	**
		8	**	**	**	**	**	**	‡	‡	‡
15	2		**	**	**	**	**	**	**	**	**
	8		**	**	**	**	**	**	‡	‡	‡
	Non-neutralized§		‡	‡	‡	‡	‡	‡	‡	‡	‡
		2	**	**	**	**	**	**	**	**	**
		8	**	**	**	**	**	**	‡	‡	‡
25	2		**	**	**	**	**	**	**	‡	‡
	8		**	**	**	**	‡	‡	‡	‡	‡
	Non-neutralized§		**	**	**	**	‡	‡	‡	‡	‡

Adapted from Lieu et al., 1993.

* Recovery controls: AOB exposed for 2 to 8 days and recovered at 25°C.

† AOB regrowth of ≤10 MPN/mL during a 6-week period.

‡ No AOB regrowth within a 6-week period and no nitrite detected.

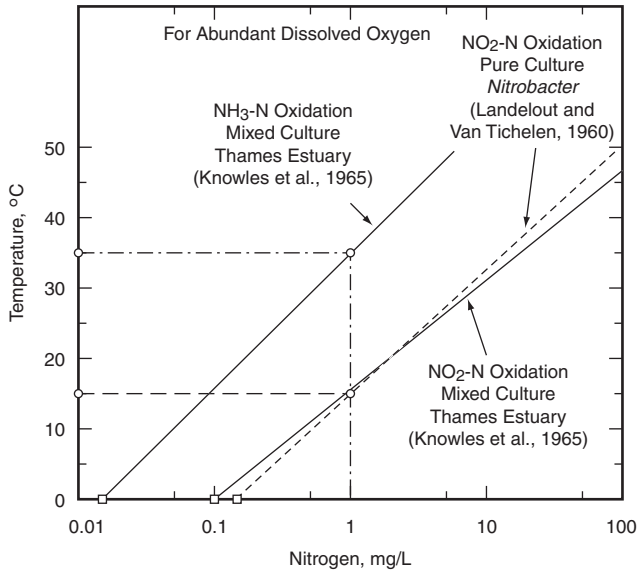
§ Samples with extended exposure to disinfectant.

** AOB regrowth to a level of ≥100 MPN/mL within a 6-week period.

temperature. Pintar and colleagues (2000) observed that at lower temperature, a lag or acclimation period occurs prior to nitrite production.

Quinlan (1980) examined the effects of temperature and substrate concentrations on the rate of ammonia and nitrite oxidation by mixed and pure cultures of AOB and NOB. Results show that the maximum rate of substrate oxidation increases with temperature and substrate concentration (Figures 6-2 and 6-3). Thus, the determination of optimum temperature for AOB and NOB growth needs to consider substrate concentrations as well. These results also suggest that for substrate concentrations in the range of 0.5 to 10 mg/L N, the optimum temperature for nitrite production (i.e., oxidation of ammonia to nitrite) is between 29 and 55°C, while the optimum temperature for nitrite consumption (i.e., oxidation of nitrite to nitrate) is between 10 and 33°C (Quinlan, 1980). As a result, thermal enrichment of a nitrifying system should generally favor the production of nitrite over nitrate, with accumulation of nitrite.

Finally, it is important to distinguish between short-term temperature dependence (i.e., shock temperature response) and long-term temperature dependence (Christensen and Harremoës, 1978). The short-term temperature dependence reflects the immediate ability of microorganisms to change reaction rates. The long-term temperature dependence is a combination of adaptation by organisms originally present and selection of organisms favored by the new temperature conditions.



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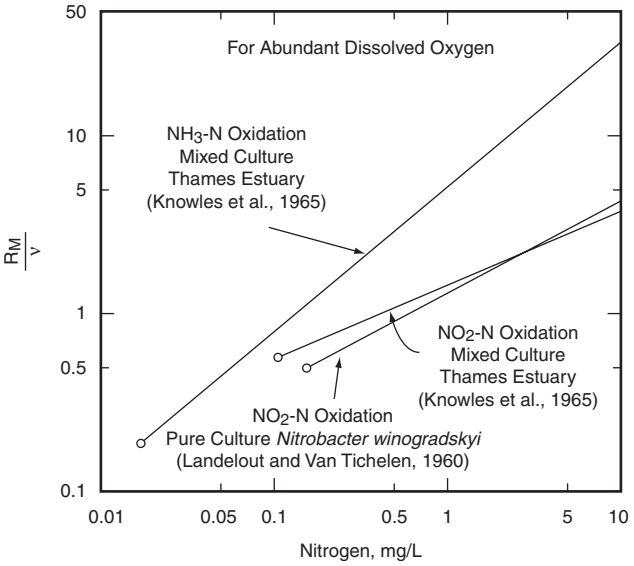
NOTE: The circles indicate the optimum temperatures corresponding to a substrate concentration of 1 mg/L N.

Figure 6-2 Optimum temperature as a function of substrate concentration



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NOTE: The circle on each line indicates the concentration of nitrogen substrate and maximum rate of oxidation for which the optimum temperature equals 0°C.

Figure 6-3 Maximum rate of oxidation as a function of substrate concentration

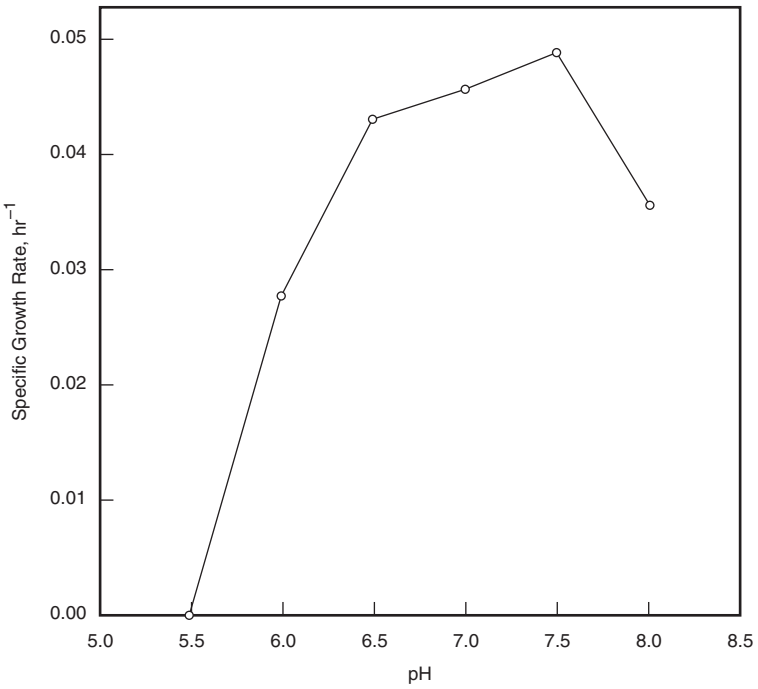

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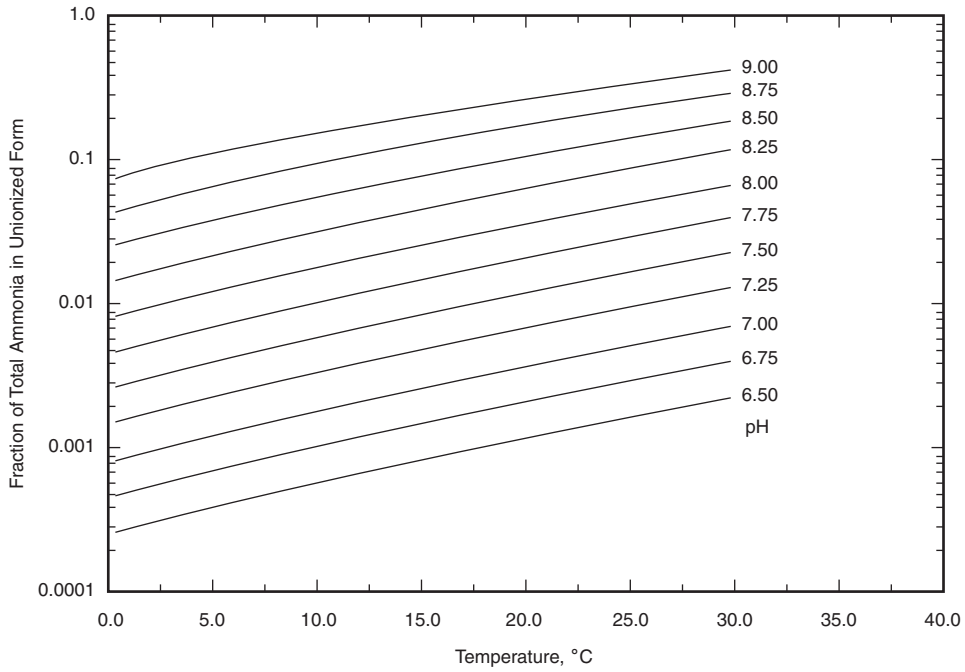
Figure 6-4 Effect of pH on maximum specific growth rate of *Nitrobacter* species

Effect of pH on Growth of Nitrifying Bacteria

Nitrifying bacteria are very sensitive to pH, as seen in Figures 6-4 and 6-5. Optimal pH values for most AOB and NOB range between 7.5 and 8.0 (Tables 6-3 and 6-4). Generally, the optimum pH reported in the literature is 7.5 to 8.0 for AOB and 7.6 to 7.8 for NOB. Growth can be observed within a pH range of approximately 2 pH units and is inhibited at acidic pH. The maximum specific growth rate of *Nitrosomonas europaea* is observed at pH 8.0, but a 54% reduction in growth rate is observed at pH 7 and growth stops at pH 6.5 (Keen and Prosser, 1987).

The effect of pH on AOB can be explained by the equilibrium NH_4^+/NH_3, which possesses a pK value of 9.26 at 20°C. As presented earlier, NH_3 and not NH_4^+ is the substrate for ammonia oxidation, and each reduction in pH value of one unit decreases the concentration of free ammonia by one order of magnitude. This explains the sharp decrease in specific growth rates observed with decreasing pH values within the pH range where AOB can survive. This also implies that the optimum pH value for growth also depends on ammonia concentration.

Despite the neutrophilic/alkalophilic growth of pure cultures of AOB and NOB, nitrification did occur in enrichment cultures within a pH range of 6.5 to nearly 9.0 or in soil at pH values below 4.0. Prosser (1989) reports four possible explanations for this phenomenon: (1) the existence of acidophilic strains of AOB and NOB, (2) surface growth, (3) the existence of microenvironments of neutral pH value, and (4) heterotrophic nitrification. An additional explanation may include long detention times that favor the slow nitrification process. Although drinking water systems contain levels of substrates that are much lower than those used in the enrichment cultures used to draw these conclusions, some of the explanations presented above could also apply to drinking water systems.



Source: USEPA, 1985.

Figure 6-5 Effect of temperature and pH on un-ionized ammonia (NH_3)

Using continuously fed reactors of municipal wastewater, Princic and colleagues (1998) observed nitrifying activity and growth of nitrifiers at pH extremes (6.0 and 8.2), although these conditions somewhat altered the microbial community. The community was not altered at intermediate pH incubation conditions.

Quinlan (1984) studied the effect of ambient total ammonia concentration on optimum pH to maximize the rate of the first step of nitrification (i.e., oxidation of ammonia to nitrite). Figure 6-6 shows the effect of pH on the maximum rate of oxidation. Figure 6-7 describes the pH dependence of the rate of ammonia oxidation by *Nitrosomonas europaea* and presents the decrease in optimum pH (i.e., the pH that produces the maximum rate of oxidation) with increasing total ammonia concentration (Quinlan, 1984). Even though the shift in optimum pH with increasing ammonia concentration is small (approximately 0.8 pH units between 1 and 50 mg/L total ammonia-N), the consequences for nitrification control are important. For each mole of ammonia-N oxidized, 2 moles of hydrogen ion are produced. Thus, as ammonia is consumed, the pH should decrease and the growth rate of nitrifiers should decrease. However, this tendency is contrary to the shift in optimum pH; as ammonia concentrations decrease, the optimum pH increases. Consequently, a constant set point for pH will not achieve process optimization. Instead, the set point must be varied to optimize the rate of ammonia oxidation (Quinlan, 1984).

Siegrist and Gujer (1987) used bench-scale nitrifying trickling filters to evaluate the effect of pH on a nitrifying biofilm. These authors observed that as the pH decreases, ammonia oxidation decreases due to the decreasing ammonia uptake rate and the increasing Monod constant for ammonia. Also, a decrease in pH leads to an increase in nitrite oxidation due to the decreasing Monod constant for nitrite. As a result, the concentration of nitrite is significantly reduced as pH decreases. Siegrist

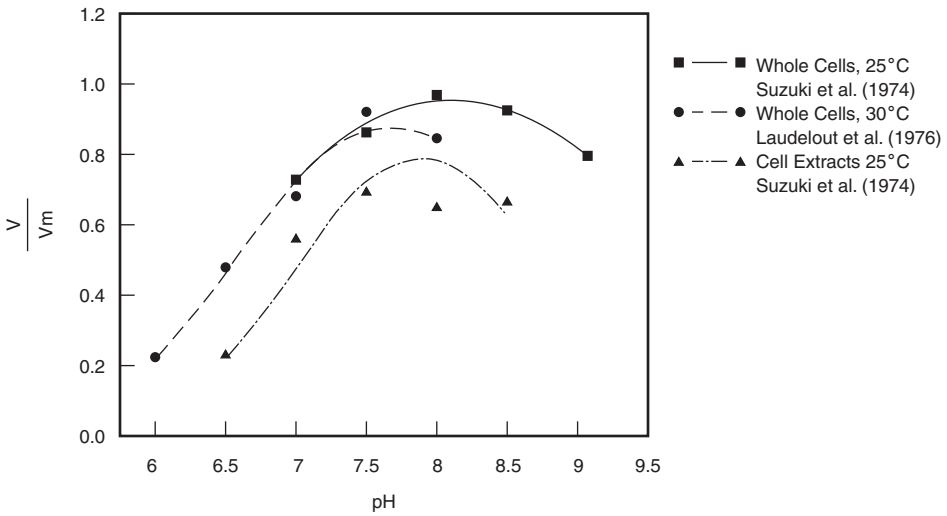


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Figure 6-6 The pH dependence of the maximum-velocity coefficient for the first step of nitrification

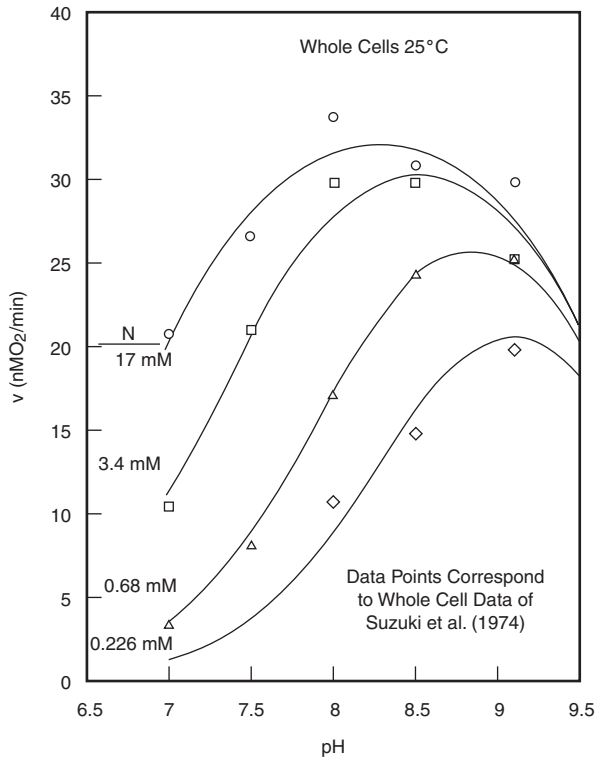

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Figure 6-7 The pH dependence of the oxidation rate of the first step of nitrification

and Gujer (1987) also proposed the following model to represent the effect of pH on uptake rate of ammonia between pH 6 and 8:

$$r = \frac{r_m}{1 + 10^{(6.5 - \mathrm{pH})}} \tag{6-3}$$

Where: r is the volumetric uptake rate of ammonia
r_m is the maximum volumetric uptake rate of ammonia

The slime layer in which nitrifiers are embedded may protect them against unfavorable conditions. Killham (1987) reported that cells of nitrifiers attached to glass beads have been shown to nitrify under acid conditions in which unattached cells did not survive.

As explained above for the temperature dependence, it is also appropriate to distinguish between short- and long-term pH effects (Christensen and Harremoës, 1978). Most investigations have focused on short-term pH changes. Acclimation of nitrifiers to nonoptimum pH conditions may allow their survival and growth under conditions that would not permit their development otherwise (USEPA, 1993).

Effect of Alkalinity on Growth of Nitrifying Bacteria

Ford (1980) reports that approximately 7.07 mg alkalinity as $CaCO_3$ is destroyed per mg NH_3-N oxidized. Grady and colleagues (1999) report that 8.62 mg HCO_3^- is required to remove 1 mg NH_4^+-N in wastewater. In any case, nitrification reduces alkalinity, and this reduction in alkalinity may lead to a significant decrease in pH, as observed by DiGiano and colleagues (2002). However, in a water quality survey of 10 drinking water distribution systems, Wilczak and colleagues (1996) did not observe any correlation between alkalinity and the occurrence of nitrification. The authors explained this observation by the fact that in drinking water, only small changes in alkalinity would result from nitrification, which may not have been detected during the survey.

Effect of Dissolved Oxygen on Growth of Nitrifying Bacteria

Nitrification is described as an aerobic process with molecular oxygen required for oxidation of ammonia and for respiration of both AOB and NOB. Ford (1980) reported that the theoretical demand for biological oxidation of ammonia to nitrite is 3.43 g O_2 per g of ammonia oxidized in wastewater nitrification. The subsequent demand for nitrite oxidation to nitrate is calculated at 1.14 g O_2 per g nitrite oxidized. Thus, the total theoretical oxygen requirement is 4.57 g O_2 to oxidize ammonia into nitrate. Grady and colleagues (1999) as well as laboratory experiments conducted by Ford (1980) showed slightly lower nitrification oxygen demands (3.22 mg/L O_2 for NH_4^+-N oxidation into NO_2^--N and 1.11 mg/L O_2 for NO_2^--N oxidation into NO_3^--N), probably attributable to the fact that some of the reduced nitrogen is assimilated as cellular material in the CO_2 fixation process. In any case, approximately 4 mg/L of oxygen are consumed during complete nitrification of 1 mg/L of NH_4^+-N in a chloraminated water system. This may explain why several authors report that dissolved oxygen concentrations below 0.5 to 2.5 mg/L O_2 may inhibit nitrification (2.0 mg/L is recognized in practice) (USEPA, 1993). These data also suggest that oxygen requirements for nitrifiers are fufilled in most drinking water systems.

In addition, earlier observations indicated that the oxidation of ammonia by *Nitrosomonas* under low oxygen concentrations is accompanied by production of N_2O or NO (Watson et al., 1989). Goreau and colleagues (1980) observed enhanced yield of

N_2O and lower production of NO_2^- at low oxygen concentrations. As the oxygen concentration decreased from 7 to 0.18 mg/L, the production of N_2O increased from 0.002 to nearly 0.1 mol N_2O-N per mol NO_2^-, at the expense of the production of NO_2^-. The growth rate varied only slightly (approximately 30%) over the entire oxygen range. On the other hand, Poth and Focht (1985) rejected the hypothesis that N_2O is produced directly from nitrification using isotope tracer experiments. They concluded that *Nitrosomonas europaea* is a nitrifier and a denitrifier that, under conditions of oxygen stress, uses nitrite as a terminal electron acceptor and produces N_2O. In any case, N_2O was not produced by well-aerated growing cells (Poth and Focht, 1985).

The effect of oxygen on nitrifying bacteria can be described by a Monod relationship, with a K_s value of approximately 1 mg/L O_2. The K_s values for O_2 for pure cultures of AOB and NOB are in the range of 0.25 to 2.5 mg/L O_2 (Painter, 1986), with similar values reported for mixed cultures activated sludge systems.

$$\mu = \mu_m \frac{C_{O_2}}{K_{s,O_2} + C_{O_2}} \tag{6-4}$$

Where: μ is the growth rate
μ_m is the maximum growth rate
C_{O_2} is the oxygen concentration (mg/L O_2)
K_{s,O_2} is the saturation constant for oxygen (mg/L)

Work conducted by Helder and de Vries (1983) suggests that AOB have greater K_s values for O_2 than NOB. These authors indicate that ammonium oxidation is inhibited below 30 µmol/L O_2 (0.96 mg/L O_2), whereas nitrite oxidation is inhibited below 125 µmol/L O_2 (4.0 mg/L O_2). These differences may lead to spatial separation of these two groups of nitrifiers when attached in biofilms limited by oxygen diffusion.

In a document addressing nitrification and denitrification in sequencing batch reactors for wastewater treatment, Irvine and colleagues (1979) reported that AOB do not oxidize ammonia if the dissolved oxygen concentration is less than approximately 1 mg/L O_2. However, in a study of nitrification followed by denitrification for wastewater treatment, Mechalas and colleagues (1970) observed that nitrifiers (AOB and NOB) do not appear to undergo major physiological damage with anaerobic periods as long as 70 hours. This was evidenced by the absence of large protein molecules and a relatively low level of amino acids in the process effluent, which indicated that massive cell lysis had not occurred.

High concentrations of oxygen may also inhibit nitrification. Gunderson (1966) observed that growth was optimal at a partial pressure of 10% of the partial pressure of air. Oxygen inhibition is of practical significance in activated sludge systems supplied with pure O_2 rather than with air, but it is likely not occurring in drinking water systems. Jones and Paskins (1982) found that nitrifiers can become acclimatized to high concentrations of oxygen but not to sudden increases in oxygen concentrations.

Studies conducted by Ward (1987) indicated that the effect of oxygen on the marine nitrifier *Nitrosococcus oceanus* varies with ammonia concentration. Results suggest that in environments where substrate concentration is low, ammonia oxidation may be enhanced by reduced oxygen concentrations. Similarly, Hart and colleagues (1986) mention that aeration specifications for nitrification in activated sludge are also a function of ammonia concentration, temperature, and organic loading rate.

Effect of Light on Growth of Nitrifying Bacteria

Although the effect of light is minimal in drinking water distribution systems (except in open storage reservoirs), it can be significant in water treatment plants. Nitrifiers

possibly present in source water can pass through treatment processes. Their possible survival following light exposure can affect their presence in distribution systems.

Growth of *Nitrosomonas* can be inhibited by sunlight (380 to 415 nm) and ultraviolet light (Hooper and Terry, 1974; Alleman et al., 1987; Watson et al., 1989; Wolfe and Lieu, 2001) but does not seem to be fully inactivated or limited by them (Odell et al., 1996). Olson (1981) observed 50% inhibition of AOB and NOB at light intensities approximately three orders of magnitude lower than the intensity of full sunlight. Schon and Engel (1962; reported by Prosser, 1989) and Bock (1965; reported by Prosser, 1989) found that strains of *Nitrobacter* were much more sensitive to light than strains of *Nitrosomonas* and suggested that photo-oxidation of cytochrome C was the mechanism of inhibition by light. Yoshioka and Saijo (1985) also observed differences in sensitivity between AOB and NOB, with the latter being more sensitive during short-term experiments.

Hooper and Terry (1974) observed reduced sensitivity to photo-inhibition in the absence of oxygen and in the presence of high concentrations of ammonia or NH_2OH. The ability to recover from inhibition during dark periods is also important. Several authors such as Hooper and Terry (1974) reported recovery of AOB from photo-inhibition within hours of exposure. Wolfe and Lieu (2001) reported that nitrifiers have an excision repair mechanism for DNA; therefore, low levels of nitrifiers may be recovered from partially shaded environments. Yoshioka and Saijo (1985) also observed that an extended exposure to light in the absence of ammonia extended the recovery period significantly.

Alleman and colleagues (1987) observed that *Nitrosomonas* cells collected from an activated sludge system and maintained under aerobic conditions without an external ammonium source were fully inhibited within 10 minutes under ambient light (i.e., fluorescent and indirect natural light). These cells were, however, protected against this inhibitive phenomenon during active respiration periods and during anoxic exposure conditions. Recovery from light-induced inhibition was initiated after a "dark contact period" of approximately 2.5 to 3 hours without the presence of external ammonium (Alleman et al., 1987). After 4 hours of "dark exposure," *Nitrosomonas* had recovered 40% of their pre-inhibition maximal oxygen uptake rate.

According to Prosser (1989), the extent of photo-inhibition and length of recovery period depend on the intensity of the illumination, the attenuation properties of the water, and the circulation of the water in the case of natural environments.

Inhibitory Substances

Ford (1980) and USEPA (1993) report that nitrifiers are extremely sensitive microorganisms that may experience severe upsets in the presence of very small concentrations of inhibitory substances. According to Ford (1980), these inhibitory substances include heavy metals, cyanides, halogenated compounds (e.g., perchlorate, chloroform), phenols, mercaptans, and thiourea. Watson and colleagues (1989) also reported that the oxidation of ammonia to nitrite is sensitive to inhibition by many compounds at low concentrations (such as copper-binding agents, acetylene), whereas the oxidation of NH_2OH to nitrite is unaffected or much less susceptible. Metal ions such as copper, nickel, or chromium can also inhibit nitrification (Ford, 1980). The complete or substantial inhibition of oxygen uptake by *Nitrosomonas* occurs at 0.01*M* of iron, aluminum, copper, zinc, lead, and manganese and at 0.0002*M* of nickel (Painter, 1970).

GROWTH OF DENITRIFYING BACTERIA

As stated above, denitrifying bacteria are facultative anaerobic microorganisms and play an important role in the nitrogen cycle. Knowles (1982) mentioned that in marine and freshwater systems, the depletion of oxygen below about 0.2 mg/L favors the

occurrence of denitrification, which proceeds until the nitrate and nitrite concentrations are very low. An increase in oxygen concentration tends to increase the proportion of N_2O in the products (Knowles, 1982). A distinction needs to be made between the oxygen concentrations in the macro-environment versus the micro-environment. Denitrification requires very small concentrations of oxygen adjacent to the bacterial cells, corresponding to a redox potential in the order of –200 mV. Such conditions may prevail in the interior of flocs and biofilms in spite of high concentrations of oxygen in the bulk fluid. Thus, denitrification may occur inside flocs and biofilms, even in aerobic macro-environments.

Denitrifiers need an exogenous carbon source to drive the oxidation–reduction reaction, although some denitrifiers can grow lithotrophically, using hydrogen gas (H_2) or CO_2 as an electron donor. The type of carbon source has a significant influence on denitrifying activity, and numerous organic compounds can serve as organic substrates. In wastewater treatment, methanol is often used for this purpose, particularly at lower temperatures. Internal carbon (raw sewage carbon and endogenous carbon) is the second most important carbon source. No information is available regarding carbon source for denitrifiers that can possibly be present in drinking water systems. The denitrification rate is higher (2 to 3 mg NO_3^--N per g of volatile suspended solids [VSS] per hour at 20°C) when raw sewage carbon is used as the electron donor than when endogenous carbon is the sole source of carbon (around 0.2 to 0.3 mg NO_3^--N/g VSS/hr at 20°C) (Christensen and Harremoës, 1978). Other organic substrates for denitrification include organics present in municipal and industrial wastewaters, ethanol, and acetic acid (USEPA, 1993).

Many authors report that nitrate concentration has little influence on denitrifying activity in suspended cultures. Most cases can be treated as a zero-order reaction. For attached cultures, the reaction rate is half-order with respect to nitrate concentration within the practical range of concentrations found in domestic wastewaters (Christensen and Harremoës, 1977). Knowles (1982) reported that low concentrations of nitrate controls the denitrification reaction rate with first-order kinetics (denitrification rate is first order with respect to nitrate concentration), although this author admitted that the effect of nitrate may not be direct in all systems.

In denitrification, Moore and Schroeder (1970, 1971) concluded that the specific nitrogen removal rate, r_0, followed the Monod equation in systems where nitrate was limiting. Using a bench-scale chemostat system with cell recycle, Engberg and Schroeder (1975) developed an equation for the specific nitrate removal rate when both nitrogen and organic substrate concentrations are rate limiting.

Mechalas and colleagues (1970) conducted batch denitrification experiments using nitrified primary effluents from a municipal wastewater treatment plant and calculated the rate of nitrate removal and ammonia buildup as a function of temperature between 18 and 29°C; the rate of nitrite removal was insignificant:

$$R(NO_3^-)\,(T) = -0.40 + 0.035\ T\ (\text{mg/min } NO_3^-\text{-N}) \quad (6\text{-}5)$$

$$R(NH_3)\,(T) = -0.062 + 0.0073\ T\ (\text{mg/min } NH_3\text{-N}) \quad (6\text{-}6)$$

$$R(\text{Total})\,(T) = R(NO_3^-)\,(T) + R(NH_3)\,(T) = -0.34 + 0.028\ T\ (\text{mg/min N}) \quad (6\text{-}7)$$

Temperature dependency on denitrification is pronounced. Reaction rates in suspended cultures increase by a factor of four for each 10°C change in temperature. The temperature dependence of attached cultures is considerably lower (Christensen and Harremoës, 1977). As an example, denitrification activity in lake sediments is reported not to vary with temperature in the range of 5 to 23°C (Anderson, 1977). Anderson (1977) suggested that this may be due to denitrifying activity being limited by nitrate concentration and diffusion rather than by biochemical reactions.

Christensen and Harremoës (1977) stated that the optimum pH for denitrification varies between 8.0 and 8.5, although Knowles (1982) reported an optimum pH in

the range of 7.0 to 8.0. At low pH values, the nitrogen oxide reductases are progressively inhibited such that at pH 4.0, N_2O may be the major product. The theoretical stoichiometry of the bicarbonate alkalinity production is 3.57 mg alkalinity $CaCO_3$ produced per mg NO_3^--N reduced to nitrogen gas (USEPA, 1993).

Zumft (1992) mentions that copper is required during nitrite and nitrous oxide respirations. Molybdenum metal uptake has also been observed by denitrifiers (Zumft, 1992). On the other hand, Knowles (1982) listed various inhibitors and mentioned that sulfide appears to inhibit the reduction of NO and N_2O. In general, denitrifiers are much less sensitive to inhibitory compounds than are nitrifiers (USEPA, 1993).

INACTIVATION BY DISINFECTANTS

The ability of selected disinfectants to inactivate nitrifiers is presented in this section. Throughout this discussion, readers need to keep in mind the following observations:

1. Inactivation rates depend on the method used to enumerate microorganism viability. This is particularly important in the case of nitrifiers. When conducting bench-scale inactivation experiments of *Nitrosomonas europaea* with chloramines, Harrington and colleagues (2003) observed that the culturing technique (MPN method) showed significantly higher rates of inactivation (approximately 3 orders of magnitude) than the culture-independent *Bac*Light (Molecular Probe Inc., Eugene, Ore.) staining/microscopy method. Also, the *Bac*Light method appeared to yield inactivation rates that were more consistent with those observed in a distribution system undergoing nitrification (Oldenburg et al., 2002; Harrington et al., 2003). Such a difference is not surprising as numerous researchers have observed differences in viability when different analytical techniques were used, depending on the basis of the test (measurement of metabolic function, membrane integrity, activity as measured by substrate uptake or oxygen utilization).
2. Disinfectant stability is affected by various parameters, including incubation time, water matrix, temperature, pH, turbidity, NOM concentration and composition, and disinfectant dosage. In turn, disinfectant stability affects inactivation rates.
3. Nitrifying bacteria can grow in tight clusters of cells surrounded by a slime layer. These microorganisms also tend to attach to surfaces, sediments, and other debris. These biofilms may be very resistant to disinfection. The metabolic status of the microorganisms, which is linked to their growth conditions, may also be responsible for the formation of cell aggregates.

Inactivation by Chloramines

Based on reported CTs (disinfectant concentration, C, multiplied by disinfectant contact time, T), the inactivation of 99% of AOB at a typical chloramine residual of 1.5 to 2 mg/L Cl_2 should be achieved in less than 30 minutes (Regan, 2001), which is much shorter than the average time that chloraminated water stays in reservoirs and distribution systems. Nonetheless, nitrification episodes are common in these systems, even in the presence of high chloramine residuals. There are a number of possible explanations for the observed growth and persistence of nitrifiers in chloraminated systems, such as the association of nitrifiers with biofilms imparting some degree of protection from the disinfectant and the limitation of the MPN detection methods, which may overpredict the disinfectant efficacy. It may also be possible that the presence of the disinfectant causes selection or adaptation of strains more resistant to chloramines. Only a few inactivation studies on *Nitrosomonas* or *Nitrospira* (prevalent AOB and

Table 6-6 CT_{99} values for AOB inactivation by chloramines

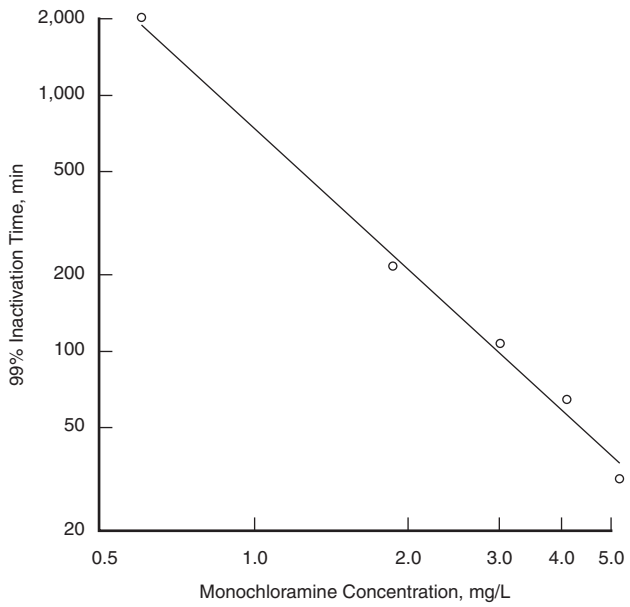
Temperature (°C)	pH	CT_{99} (mg·min/L Cl_2)	Enumeration Method	Chlorine-to-Ammonia-N Ratio (mg Cl_2:mg NH_3-N)	Reference
23	8.2	3	MPN–Soriano and Walker media*	3:1	Wolfe et al. (1990)
23	8.2	33	MPN–Soriano and Walker media*	3:1	Wolfe et al. (1990)
30	8.0	760	MPN–Skinner and Walker media†	(*not specified*)	Cunliffe (1991)
15	8.0	9,800	MPN–Soriano and Walker media‡	3:1, 4:1, and 5:1	Lieu et al. (1993)
20	8.6	14	MPN–Soriano and Walker media*	4:1	Harrington et al. (2003)
20	9.0	22	MPN–Soriano and Walker media*	4:1	Harrington et al. (2003)
20	7.0	1,900	*Bac*Light§	4:1	Harrington et al. (2003)
20	8.0	3,900	*Bac*Light§	4:1	Harrington et al. (2003)
20	9.0	19,000	*Bac*Light§	4:1	Harrington et al. (2003)
21	7.0	0.39	MPN–Soriano and Walker media**	5:1	Baribeau et al. (2005)
21	8.0	5.0 to 9.3	MPN–Soriano and Walker media**	5:1	Baribeau et al. (2005)

Adapted from Harrington et al., 2003.

* Incubation at 28°C for 21 days.
† Incubation at 30°C for 28 days.
‡ Incubation at 28°C for 23 days.
§ Cell membrane integrity as an indicator of viability.
** Incubation at 26°C for 25–30 days.

NOB species, respectively, in drinking water distribution systems) have been reported. Wolfe and Lieu (2001) suggested that NOB were more susceptible than AOB to disinfection by chloramines because the oxidation of nitrite to nitrate was observed to occur when the chloramine residual was lower than that for ammonia oxidation.

Table 6-6 summarizes CT_{99} values (time required to inactivate 99% of the microorganisms with a concentration of 1 mg/L Cl_2) for AOB inactivation by chloramines. The CT_{99} value of 3 mg·min/L Cl_2 (Wolfe et al., 1990, but calculated by Harrington et al., 2003) was obtained from inactivation experiments conducted on AOB isolated from a treated drinking water reservoir and grown in modified Soriano and Walker medium. The CT_{99} value of 33 mg·min/L Cl_2 was obtained from similar inactivation experiments, but using AOB grown in dechlorinated tap water (ammonium sulfate, $(NH_4)_2SO_4$, was used as a dechlorinating agent). Thus, AOB cultures grown in chlorine-neutralized tap water were approximately 11 times more resistant than AOB grown in culture medium (Wolfe et al., 1990). Cunliffe (1991) studied the resistance of a mixed population of nitrifiers collected from a drinking water reservoir to monochloramine, up to 5.2 mg/L (no distinction was made between AOB and NOB)



Reprinted with permission from the American Society for Microbiology, Journals Department. Cunliffe, D.A. 1991. 57(11): 3399–3402.

NOTE: The line of best fit was determined by regression analysis.

Figure 6-8 Inactivation of nitrifying bacteria by monochloramine

(Figure 6-8). As shown in Table 6-6, the CT_{99} value measured was much higher than that obtained by Wolfe and colleagues (1990). Differences in experimental design could explain the disparity between the various sets of laboratory results. As an example, several researchers have shown that bacteria grown in tap water may have higher disinfectant resistance than bacteria grown in culturing media (Wolfe and Olson, 1985; Ridgway and Olson, 1982).

Lieu and colleagues (1993) conducted extensive inactivation studies using AOB cultures inoculated in drinking water samples. At 10°C, regrowth occurred in all samples except when the AOB were exposed to 2.5 mg/L monochloramine for 8 days (Table 6-5). The chlorine to ammonia-N weight ratios (3:1, 4:1, and 5:1) did not affect survival or regrowth at any of the chloramine dosages (1.7, 2.0, and 2.5 mg/L) or contact times (up to 5 to 6 weeks). At 15°C, contact time and chloramine dosage controlled AOB regrowth, but the chlorine to ammonia-N ratio had no effect. Basically, increasing the contact time allowed regrowth when AOB were exposed to higher chloramine concentrations (Lieu et al., 1993). At 25°C, AOB regrowth was controlled by the chloramine dosage, contact time, and chlorine to ammonia ratio. AOB regrowth occurred in 77% of the samples following exposure to 1.7 mg/L monochloramine, regardless of the chlorine to ammonia-N ratio or contact time. When AOB were exposed to 2.0 mg/L monochloramine, regrowth appeared in 67% of the samples and recovery depended on both the chlorine to ammonia-N ratio and contact time. Regrowth did not occur in any of the samples exposed to 2.5 mg/L monochloramine, except when the chlorine to ammonia-N ratio was 3:1 and the contact time only 2 days, representing 26% of the samples (Lieu et al., 1993). This study indicates that AOB are inactivated better at higher monochloramine residuals, even if the effectiveness of monochloramine is questioned at higher concentrations.

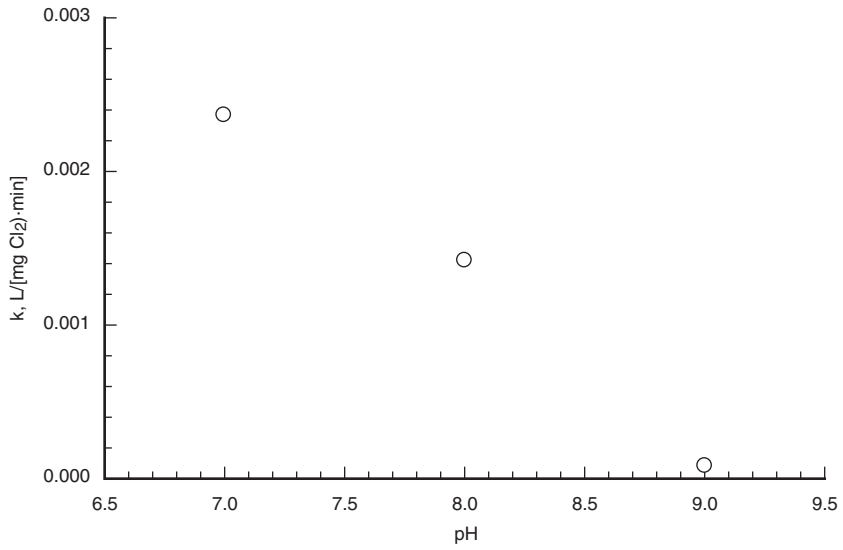
In bench-scale experiments, Harrington and colleagues (2003) observed that the rate of *Nitrosomonas europaea* inactivation by monochloramine decreases with increasing pH from 7.0 to 9.0. This suggests that chloramines may better control nitrification at lower pH and that inactivation was due to dichloramine, which is virtually nonexistent at pH 9.0 (5% of total chlorine as dichloramine at pH 9.0, 21% at pH 8.0, and 58% at pH 7.0). However, the rate of ammonia release from chloramine decay decreases with increasing pH (Harrington et al., 2003; Valentine et al., 1998). As a result, the amount of substrate available for AOB growth decreases with increasing pH, suggesting that increasing pH may control nitrification. Therefore, these pH effects are opposite to each other.

Nitrification has also been observed in drinking water distribution systems in the presence of chloramine residuals exceeding 2 mg/L. Feben (1935) observed that AOB could survive a chloramine residual of 2 mg/L Cl_2 for 60 minutes. Wolfe and colleagues (1988, 1990) indicated that AOB were not only capable of surviving in the presence of 1.2 to 1.5 mg/L monochloramine residual and a chlorine to ammonia-N ratio of 3:1 (water temperature of approximately 25°C and pH of about 8.2) but were also capable of growing in the presence of these disinfectant concentrations. Cunliffe (1991) examined 1,184 samples collected from five chloraminated drinking water supplies for the presence of nitrifiers. Nitrifiers were detected in 64% of all samples and in 21% of samples with more than 5.0 mg/L monochloramine. In a water quality survey of 10 drinking water distribution systems, Wilczak and colleagues (1996) observed that even at high chloramine concentrations in finished water (3 to 6 mg/L Cl_2), increases in nitrite and nitrate concentrations above 50 µg/L N occurred in the distribution systems.

Kirmeyer et al. (1995), Odell et al. (1996), and Harrington et al. (2002) observed that a chloramine dose above 2.0 mg/L may prevent the onset of nitrification. However, once a population of nitrifiers was established, a similar chloramine concentration did not inhibit the growth of nitrifiers.

Harrington and colleagues (2003) stated that if ammonia is present at a concentration where the rate of AOB growth exceeds the rate of AOB inactivation, then net AOB growth can theoretically occur in the presence of a chloramine residual. This phenomenon of AOB growth in the presence of chloramine residual is indeed typically seen in bulk waters at the onset of a nitrification episode, especially at total chlorine residuals below 1 mg/L Cl_2. Similarly, Kirmeyer and colleagues (1995) suggest that the resistance of established populations to high chloramine doses may be due to a higher rate of chloramine degradation and ammonia production, resulting in additional substrate for AOB and/or mass transfer limitation of the disinfectant in clusters, biofilms, and sediments, which harbor nitrifiers. Regan (2001) also hypothesized mechanisms that may explain the additional protection offered by biofilms: (1) the development of a chloramine concentration profile within the biofilm due to mass transport limitation of the disinfectant within the biofilm matrix, allowing a layer of microorganisms within the biofilm that is not exposed to disinfectant; (2) a gradient of growth physiologies within the biofilm producing a gradient of chloramine resistance; and (3) biofilm growth inducing the expression of genes that result in an increased resistance to chloramines that is not expressed in suspended-growth cultures. Ridgway and Olson (1982) have already demonstrated the selection or adaptation of more resistant strains to chloramines. Interestingly, the chloramine concentrations profile is also accompanied by a free ammonia concentration profile. The consumption of chloramine at the surface of the biofilm can release ammonia for nitrifiers that are located inside the biofilm.

When conducting bench-scale inactivation experiments using chloramines and a culture-independent enumeration technique (*Bac*Light) for AOB, Harrington and colleagues (2003) observed that the first-order Chick–Watson equation was adequate to model the inactivation kinetics of *Nitrosomonas europaea* over a 6-hr period. The



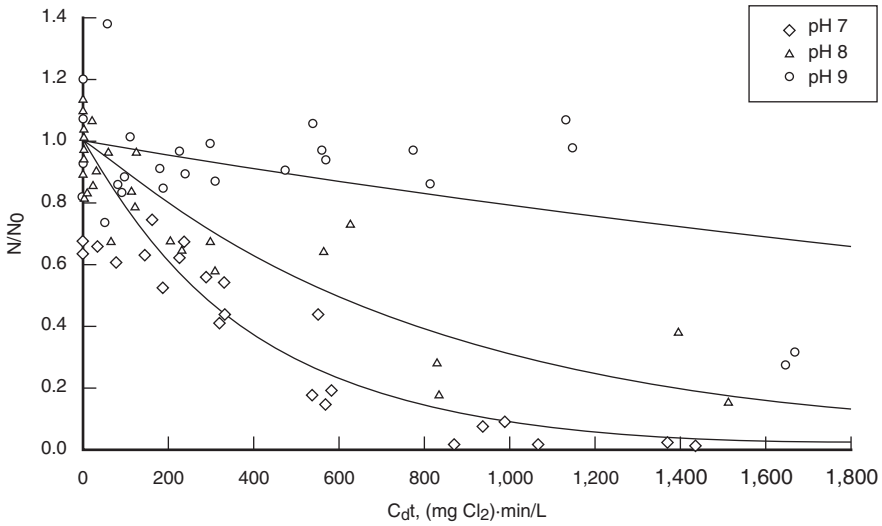
Source: Harrington et al., 2003.

Figure 6-9 Relationship between the first-order inactivation rate constant and pH

magnitude of the first-order inactivation rate constant decreased from $2.36 \times 10^{-3} \pm 1.10 \times 10^{-3}$ to $0.076 \times 10^{-3} \pm 0.039 \times 10^{-3}$ L/(mg·min Cl_2) as pH increased from 7 to 9 (Figure 6-9). Data obtained also showed a clear relationship between the inactivation rate constant and pH (Figure 6-10). Similar trends were observed when using a culture-dependent enumeration method (MPN), although the values of inactivation rate constant were different, as explained at the beginning of this section. Harrington and colleagues (2003) explained these trends (decreasing inactivation rate constants with increasing pH) by the following factors:

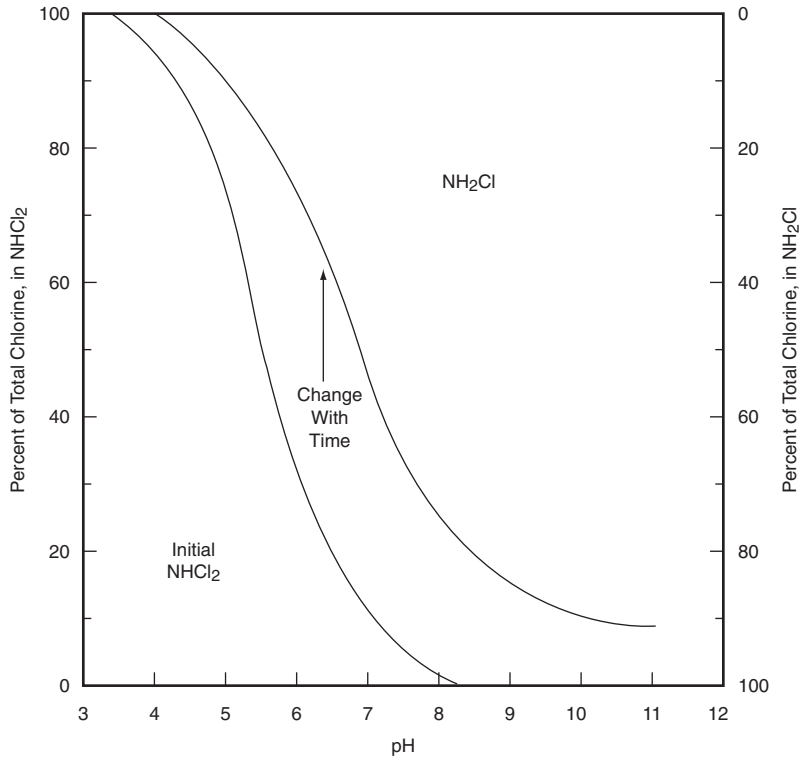
- Change in chloramine speciation from monochloramine to dichloramine as pH changes (Figure 6-11). As pH increases, the concentration of dichloramine decreases. Dichloramine may be a stronger disinfectant than monochloramine but its usage is discouraged in the drinking water industry because of the taste and odor associated with dichloramine.
- Equilibrium chemistry between monochloramine and free chlorine (which can dissociate) with pH. Free chlorine is a stronger disinfectant than monochloramine and the concentration of free chlorine is at a minimum near pH 8.3. As pH increases above 8.3, the concentration of free chlorine (primarily as hypochlorite ion, OCl^-) increases (Figure 6-12). As pH decreases below 8.3, the free chlorine concentration also increases, as a combination of OCl^- and hypochlorous acid (HOCl). Below pH 7.4, free chlorine is predominantly in the form of HOCl, which is considered a stronger disinfectant than OCl^-.

In natural and treated waters, organic nitrogen may also affect disinfection efficacy of inorganic chloramines by converting them into organic chloramines (Feng, 1966; Wolfe et al., 1985). Isaac and Morris (1983) have seen a 50% conversion of monochloramine to organic chloramines in 1 to 2 days. It was demonstrated that the preferential binding of amino acids and peptides with chlorine could greatly reduce the disinfection efficacy of inorganic chloramine (Wolfe et al., 1985). In addition, organochloramines are nongermicidal and interfere with the conventional methods to measure chloramine residuals, such as amperometric and *N,N*-diethyl-*p*-phenylenediamine (DPD) methods (Wolfe et al., 1985; White, 1999).



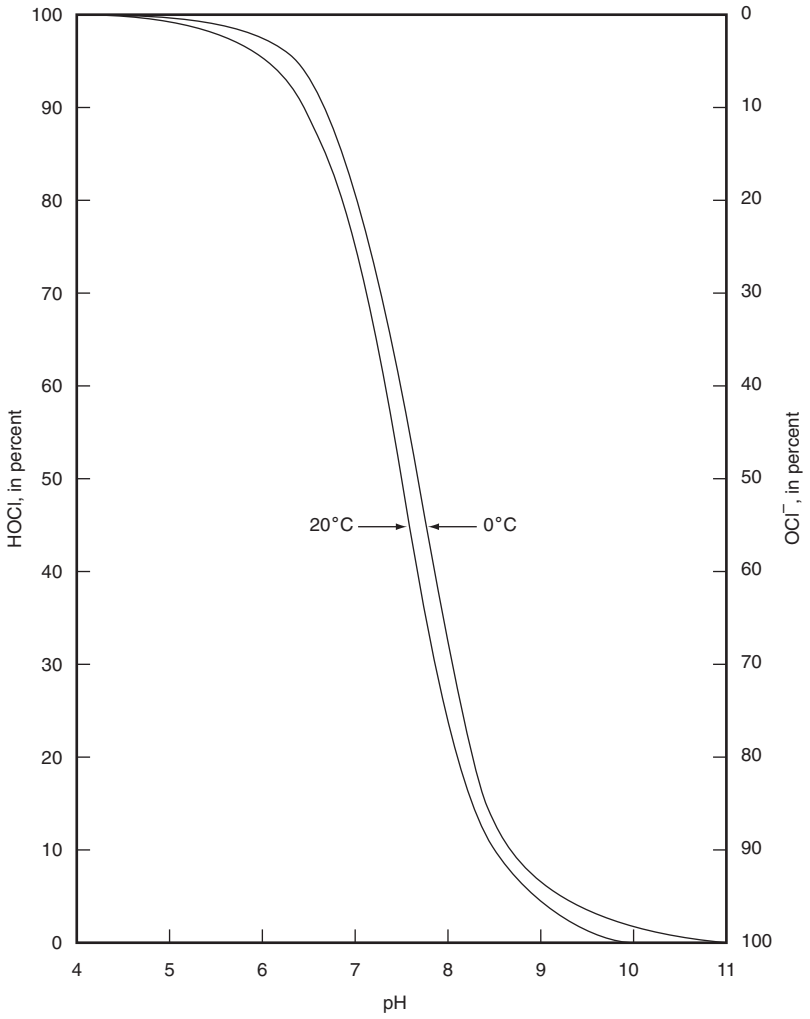
Source: Harrington et al., 2003.

Figure 6-10 Data and fitted regression plots for *Bac*Light based *Nitrosomonas europaea* inactivation experiments using the Chick–Watson model (n = 1)



Source: Connell, 1996.

Figure 6-11 Distribution of mono- and dichloramine as a function of pH



Source: Connell, 1996.

Figure 6-12 Distribution of hypochlorous acid and hypochlorite ion as a function of pH

Inactivation by Free Chlorine

In drinking water, nitrification occurs in chloraminated distribution systems. Some chloraminated systems, however, practice periodic free chlorination in an effort to limit nitrification (chapter 9). In fact, Wolfe and colleagues (1990) reported that free chlorine was 13 times more effective than monochloramine for inactivating suspended AOB. These authors measured a 99% inactivation of an AOB culture after 2 to 3 minutes of exposure to 1.0 mg/L free chlorine at 23°C and pH 8.2.

Skadsen (1993) reported that the only effective method against the severe nitrification episodes observed in their drinking water distribution system was the intermittent use of free chlorine as final disinfectant. A residual of 0.7 to 1.8 mg/L controlled and prevented further nitrification. However, in the distribution system studied by DiGiano et al. (2002), Kirmeyer et al. (1995), and Odell et al. (1996), the return to chloramination following a free chlorination period led to subsequent nitrification within a short period of time. These conflicting results suggest that the chlorination

treatment needs to be done properly to assure its effectiveness. Important issues to consider include development of a consistent free chlorine residual throughout the affected section of the distribution system and free chlorination during a sufficient period.

When examining the effect of free chlorine on nitrifiers and nitrification, the influence of nitrite needs to be considered. Nitrite exerts a significant free chlorine demand, according to the following equation (White, 1999):

$$HOCl + NO_2^- \rightarrow NO_3^- + HCl \quad (6\text{-}8)$$

Each milligram of nitrite requires 5 mg of chlorine (White, 1999).

Inactivation by Chlorine Dioxide

Information is lacking on the efficacy of chlorine dioxide to inactivate nitrifiers. Although chlorine dioxide may oxidize nitrite to nitrate (Narkis and Kott, 1992), chlorite and chlorate (the main by-products of chlorine dioxide oxidation) may block oxidation of nitrite into nitrate. Belser and Mays (1980) observed that 10 mM sodium chlorate (1.06 g/L $NaClO_3$) inhibits the oxidation of NO_2^- to NO_3^- by *Nitrobacter* spp. but does not affect the oxidation of NH_4^+ to NO_2^- by *Nitrosomonas europaea*. Hynes and Knowles (1983) demonstrated that the oxidation of NH_4^+ by *N. europaea* was insensitive to 10 mM (1.06 g/L) $NaClO_3$ but was strongly inhibited by sodium chlorite ($NaClO_2$; K_i of 2.0 µM, 181 µg/L). The oxidation of NO_2^- by *Nitrobacter winogradskyi* was inhibited by both chlorate and chlorite (K_i for chlorite was 100 µM, 674 mg/L). *N. winogradskyi* reduced chlorate to chlorite under both aerobic and anaerobic conditions. In mixed *N. europaea–N. winogradskyi* cell suspensions, the oxidation of both NH_4^+ and NO_2^- was inhibited in the presence of 10 mM (835 mg/L) ClO_3^- after a 2-hr lag period. Hynes and Knowles (1983) concluded that in mixed culture, NH_4^+ oxidation is inhibited by chlorite produced by reduction of chlorate by the NOB.

Also, chlorite was shown to inhibit nitrifiers. Using laboratory experiments with a mixed culture of AOB collected from a drinking water distribution system, McGuire and colleagues (1999) examined the effect of chlorite in AOB inactivation. Results showed a 2- to 3-log inactivation of AOB after 30 minutes of contact time to 1 mg/L chlorite. Even at a low chlorite concentration (0.05 mg/L), AOB inactivation of 4 to 5 log was observed after 24 hr of contact time. These trends were confirmed during field investigations in five drinking water distribution systems. Results showed more stable chloramine residual and ammonia concentration and thus less nitrification in the systems in which chlorite was present (McGuire et al., 1999).

McGuire and colleagues (1999) proposed the following mechanism to explain the effect of chlorite on AOB. The oxidation of ammonia has been shown to take place on the membrane structures of AOB rather than within the cell wall (Murray and Watson, 1965). As mentioned above, pH decreases when ammonia is degraded by AOB. Thus, if ammonia oxidation produces more hydrogen ion than can diffuse out of the cell, an acid pH may exist on AOB internal membrane structure. In acidic conditions, chlorite will react to produce chlorine dioxide according to the following equation (McGuire et al., 1999):

$$5NaClO_2 + 5HCl \leftrightarrow 4ClO_2 + 5NaCl + HCl + 2H_2O \quad (6\text{-}9)$$

McGuire and colleagues (1999) suggested that small, localized concentrations of chlorine dioxide inside the cell could affect AOB in several ways, including (1) alteration of the cell membrane permeability, (2) impairment of the cell's enzyme and protein functions, and (3) damage to the nucleic acids (Stewart and Olson, 1996).

CONCLUSIONS

Limiting the growth of nitrifiers in chloraminated distribution systems will depend on many factors that can be summarized as: environmental factors (distribution system operation and maintenance practices; presence of disinfectants; presence of protective biofilms and deposits; high water turnover rate, which would minimize nitrifier growth and proliferation in the bulk water) and growth rate factors (temperature, pH, substrates, microelements, etc.). Factors that affect the growth and inactivation of nitrifiers are at times consistent or opposed to each other at other times. Examples of factors that are consistent with each other include:

- Nitrifier specific growth rate decreases with decreasing substrate concentration (ammonia for AOB or nitrite for NOB). This is consistent with observations suggesting that nitrification is limited at low ammonia residuals in drinking water distribution systems.
- The maximum specific growth rate of AOB increases with increasing pH (up to pH ~8.0), within the pH range where AOB can survive, and the effect of pH on these nitrifiers is significant. This effect can be explained by the fact that NH_3 and not NH_4^+ is the substrate for ammonia oxidation, and NH_3 concentration increases with increasing pH.

Factors that are opposed to each other include:

- Under drinking water distribution conditions, an increase in water temperature increases the growth of nitrifiers but also increases inactivation kinetics. As a result, there is a certain temperature specific to each water where inactivation is maximum.
- Ammonia oxidation reaction indicates that pH decreases as ammonia is consumed. However, optimum pH for nitrifier growth increases as ammonia concentration decreases. Consequently, the set point to optimize the rate of ammonia oxidation varies. Typically, however, a pH decrease due to nitrification would not be substantial enough to get far away from optimum growth conditions.
- The rate of nitrifier inactivation by monochloramine decreases with increasing pH (under typical drinking water conditions), suggesting that chloramines may better control nitrification at lower pH. However, the rate of ammonia released from chloramine decay decreases with increasing pH. These opposing trends and some practical observations suggest that increasing pH may better control nitrification.
- Higher chloramine concentrations improve nitrifier disinfection efficacy (limiting nitrification) but also provide higher concentrations of ammonia following chloramine decay (enhancing nitrification). Therefore, increasing chloramine residual entering the distribution system is effective only if chloramine is stable and a high residual reaches the affected areas.

Factors that need to be considered when examining nitrifier inactivation by disinfectants include:

- Inactivation rates depend on the method used to enumerate microorganism viability.
- Nitrifiers can grow in biofilms that may be very resistant to disinfectants.
- Bacteria grown in water carrying a disinfectant residual may have higher disinfectant resistance than bacteria grown in culturing media without a disinfectant residual.

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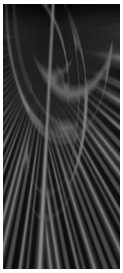


Chapter 7

Monitoring for Nitrification Prevention and Control

Charlotte D. Smith

INTRODUCTION

This chapter contains a discussion of the parameters, frequencies, and locations that should be included in nitrification monitoring or control plans. A single set of parameters is not recommended for the entire water system since various parameters take on more or less significance depending on their sampling location. The treatment plant, transmission and distribution systems, and storage facilities all require monitoring for specific parameters. For example, total or dissolved organic carbon (TOC or DOC) is more important as source water or treatment plant parameters than as distribution system parameters. Source water or plant effluent TOC or DOC can help explain total chlorine residual values (based on chlorine demand exerted by the organic matter). More important, something *can be done* with this data at the treatment plant; the treatment process can be adjusted to reduce TOC and the plant effluent values can aid in the prediction of disinfectant demand of water entering the system. In this chapter, the question, How will the data be used?, guides the recommendations for monitoring. Table 7-1 summarizes the key points from this chapter.

MONITORING PROGRAM GOALS AND PARAMETERS

A variety of parameters can be included in a monitoring program for nitrification. The number of parameters, frequency of monitoring, and selection of monitoring sites should overlap or complement the utility's regulatory compliance monitoring program. Locating distribution sample stations for regulatory compliance must consider requirements of the rules that may appear to conflict with each other or with the goals of a nitrification monitoring plan. For example, Total Coliform Rule (TCR) compliance locations are generally distributed to represent pressure zones and/or population distributions within a system. Monitoring of storage facilities or low-flow pipes is not required for compliance. However, storage facilities and low-flow areas should be considered for nitrification control monitoring since nitrification generally occurs first at these locations.

Table 7-1 Key points from chapter 7

Characteristics of Nitrification Monitoring Program	• Selection of monitoring sites for nitrification should overlap or complement the utility's regulatory compliance monitoring program. • Storage facilities and low-flow areas should be considered for nitrification control monitoring since nitrification generally occurs first at these locations. • System-wide averaging is required for regulatory compliance for most rules. However, an assessment of water quality at individual locations in the distribution system is essential for proper interpretation of data developed under a nitrification prevention and control program. • Monitoring sites should represent variations in pipe materials, water age, and various system pressures. Mixed zones—areas influenced by more than one source of water or areas where a blend of final disinfectants (free chlorine and chloramine) may be observed—should be included as well. Consideration of water age should be incorporated. • Because monitoring for nitrifying bacteria is not practical, water utilities must rely on chemical surrogates to characterize their water and interpret the extent of nitrification in the system. • The usefulness of any parameter is related to the accuracy of measurement, timeliness of results, and consistency of analysis. • The monitoring program should be reviewed annually and adjustments made based on historical data trends, changes in water use patterns, possible changes in treatment processes, or plant or distribution system operation. • The monitoring program may vary with sampling locations (e.g., plant effluent vs. distribution system samples vs. samples collected from storage reservoirs), and with seasons or time of year (some utilities increase monitoring during the warmer months).
Monitoring Parameters and Data Interpretation	• Total chlorine, free ammonia, nitrite, temperature, and pH are the most useful parameters to monitor for nitrification in the distribution system. If the background nitrate concentration is stable, nitrate is also very useful. The highest priority is monitoring total chlorine and nitrite. Utilities may monitor some parameters when triggered by other parameters (e.g. nitrite when total chlorine is below target; free ammonia or nitrate when total chlorine and nitrite exceed targets, etc.) • Although the DPD spectrophotometric total chlorine method suffers from organochloramine interference, it is a method of choice for field applications due to ease of measurement and on-site results. • Free ammonia is a more explicit parameter than total ammonia for chloramine formation and nitrification control. Total ammonia is used to calculate breakpoint chlorine dose and sometimes for monitoring to calculate free ammonia. • The presence of nitrite indicates nitrification is occurring and is essential for a "real-time" measure of nitrification. A system practicing chloramination should monitor nitrite on a weekly basis in the distribution system. • Temperature and pH are typically not used as indicators of nitrification, but elevated temperature and decreased pH may coincide with a nitrification episode. Increased water temperature may be used as a warning that nitrification is more likely to occur. • HPC using R2A agar should be monitored at least monthly under most conditions. • Proper interpretation of nitrification monitoring parameters relies on trend graphs. • Data should be archived and accessible for analysis and interpretation. Software programs that allow for the trending of data over time are especially beneficial to a utility that wishes to prevent nitrification rather than respond to its effects.

NOTE: DPD, N, N-diethyl-p-phenylenediamine; HPC, heterotropic plate count.

As described in chapter 1, most utilities have nondetectable nitrite levels; therefore, the presence of nitrite is a good surrogate for the presence of ammonia-oxidizing bacteria (AOB). Unlike monitoring for heterotrophic bacteria such as coliform bacteria, monitoring for AOB is not practical. Current methods that rely on culturing the organisms take several weeks and are difficult to perform. Molecular methods have an advantage in that results can be obtained in 1 day; however, they require sophisticated equipment and skills and are still not widely used by water utilities (a detailed discussion of AOB methods is presented in chapter 5). Currently, water utilities must rely on chemical surrogates to characterize the water and interpret the extent of nitrification in the system.

RELATIVE USEFULNESS OF MONITORING PARAMETERS

Various parameters included in a nitrification monitoring plan can be evaluated to determine the extent of nitrification and can be categorized as:

- *Very useful*—provides data that can be used to make a decision. These parameters are affected only or mainly by nitrification.
- *Useful*—aids in the interpretation of data.
- *Limited usefulness*—can support the conclusions derived from monitoring data results. These parameters may be influenced by factors other than nitrification.

The usefulness of any parameter is also related to the accuracy of measurement and timeliness of the results. If analytical methods are not applicable to field measurements and the turnaround time in the laboratory is long, the usefulness of the parameter is diminished.

Proper interpretation of nitrification monitoring parameters relies on trend graphs since there can be many causes for a loss of chlorine residual not related to nitrification (e.g., a cross-connection or other contamination event). However, trend graphs are only informative when monitoring is frequent and consistent. Parameters categorized as "very useful" should be monitored more frequently than other parameters. Nitrification is a biological phenomenon and can occur very rapidly (within a few days), but it does not occur instantaneously, the way a chemical contamination event would.

The remainder of this chapter describes the monitoring parameters frequently included in nitrification prevention and control plans. Tables 7-2 and 7-3 list the parameters described in this chapter to be monitored either at the treatment plant effluent/distribution system entry point or in the distribution system, respectively. Note that the designations related to the usefulness of the parameter only relate to nitrification prevention and control. Some parameters, such as pH, would be characterized much differently if the discussion were about coagulation or another water quality issue.

DESCRIPTION OF MONITORING PARAMETERS

Total Chlorine Residual

Description. Total chlorine includes all species of chloramine (mono-, di-, tri-, and organo-) and free chlorine. The breakpoint curve (see Figure 9-6 in chapter 9) describes the concentration of the inorganic species in relation to the amount and ratio of ammonia and chlorine present. According to the breakpoint curve, as chlorine is added to water containing ammonia, chloramines are formed. At a weight ratio of approximately 5:1, the chlorine and ammonia added to the water will exist as monochloramine. At weight ratios below 5:1, excess ammonia will be present. At

Table 7-2 Usefulness of water quality parameters at a treatment plant for nitrification monitoring

Parameter/Usefulness		
Very Useful	Useful	Limited Usefulness
Free chlorine	TOC	Hardness
Total chlorine	Chloramine decay	Alkalinity
Free ammonia-N		Nitrate-N*
pH		Nitrite-N*
Temperature		Total ammonia-N

NOTE: TOC, total organic carbon.
* Very useful as background or baseline.

Table 7-3 Usefulness of water quality parameters for distribution system nitrification monitoring

Parameter/Usefulness		
Very Useful	Useful	Limited Usefulness
Total chlorine	Nitrate-N*	Dissolved oxygen
Nitrite-N	Total ammonia-N	TOC
Free ammonia-N	HPC-R2A	Hardness
Temperature	pH	Alkalinity
Free chlorine†		AOB‡

NOTE: AOB, ammonia-oxidizing bacteria; TOC, total organic carbon.
* Very useful if background nitrate-N level is consistent.
† Very useful during breakpoint chlorination (not for routine monitoring).
‡ Limited usefulness until rapid inexpensive enumeration methods are available.

weight ratios greater than 5:1 (up to about 7.6:1), most of the chloramine will still be as monochloramine, but dichloramine will increase. Most of the excess chorine will react with monochloramine and yield nitrate, dinitrogen, and chloride. At higher chlorine-to-ammonia ratios, trichloramine may form, depending on pH. At about a 7.6 or above weight ratio, the chloramine species will be oxidized and the additional chlorine added will be free chlorine. Trace amounts of nitrogen trichloride (trichloramine) and dinitrogen will be present as well. These theoretical ratios generally apply to the mixing of chlorine and ammonia in distilled water or other laboratory-grade waters, but will vary in natural waters. Ratios as high as 12:1 have been reported to be necessary to achieve breakpoint and obtain a free chlorine residual in field samples. Furthermore, it should be noted that the breakpoint curve is time dependent. Until the reactants (chlorine and ammonia) and products (e.g., monochloramine) have reached equilibrium, various concentrations of reactants and products can occur simultaneously. This explains why free chlorine, ammonia, and monochloramine are observed when chlorine and ammonia are first mixed together.

When chlorine and ammonia first mix, the total chlorine residual may consist of monochloramine, dichloramine, and/or trichloramine (nitrogen trichloride), depending on the chlorine and ammonia concentrations, pH, and time. In addition to inorganic

chloramine compounds, organic nitrogen molecules can combine with chloramines in water to form organochloramines; this is typically observed at the ends of a distribution system where water age is highest. The total chlorine residual in a system that does not add ammonia or have a background ammonia concentration consists entirely of free chlorine and a small fraction of organic chloramines.

At chlorine-to-ammonia-N (Cl_2:NH_3-N) weight ratios of 5:1 or less, the predominant species will be monochloramine. This species has the lowest taste and odor threshold of the chloramine species, is the most stable, and usually predominates at the pH values found in drinking water systems.

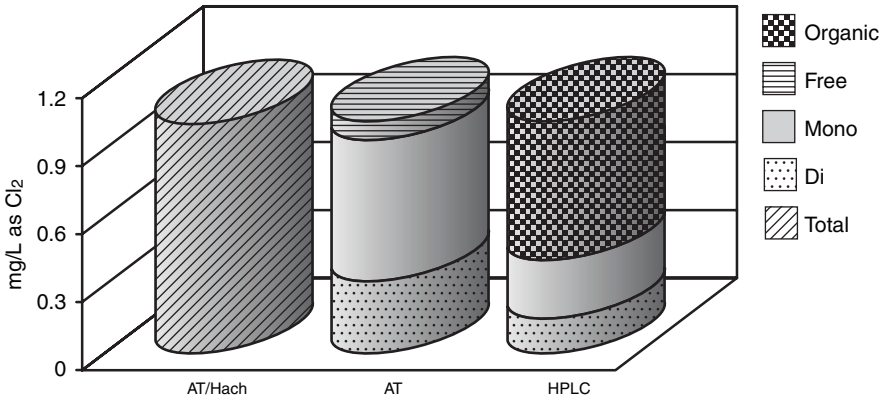
Chlorine residual regulatory issues. The Surface Water Treatment Rule (SWTR) requires utilities to maintain at least a 0.2-mg/L disinfectant residual at the entry point and a detectable disinfectant residual in 95% of the distribution samples analyzed each month. If a detectable residual is not found, a heterotrophic plate count (HPC) value of less than 500 colony forming units (cfu)/mL (using standard plate count agar) serves as the equivalent to a detectable residual for regulatory purposes. Generally, the disinfectant residual is monitored at the same locations as the TCR samples and is based on system population. Some states have chosen to set a definition for "detectable residual," such as 0.2 mg/L for chlorinated water and 0.6 mg/L for chloraminated water in Florida or 0.2 mg/L for chlorinated water and 0.5 mg/L for chloraminated water in Texas.

There are no regulatory requirements to monitor at dead-ends or finished water storage facilities for total chlorine. The regulation avoids requirements to monitor dead-ends or storage facilities because the US Environmental Protection Agency (USEPA) received comments during the rule-making process stating that the water at those locations does not represent water consumed by customers. However, from a "best management practices" point of view, it is prudent to monitor these sites for process and operation control since water age is an integral component to the loss of the chlorine residual. If possible, the total chlorine residual measured within or at the outlet to a storage facility should be correlated to operational data at the time of sampling, such as whether the tank or reservoir was filling or draining, supply flows and blends, season, temperature, etc. The data can be used to determine how much to fluctuate the water level to achieve adequate water turnover in the storage facility, thus maintaining desired total chlorine levels in the tank effluent during the drain cycle. If possible, the water quality data should also be correlated to the rate at which the reservoir or tank is filling.

Chlorine residual methods. Various tests are available to measure chlorinated species, including amperometric titration (AT), spectrophotometry, and high-performance liquid chromatography (HPLC).

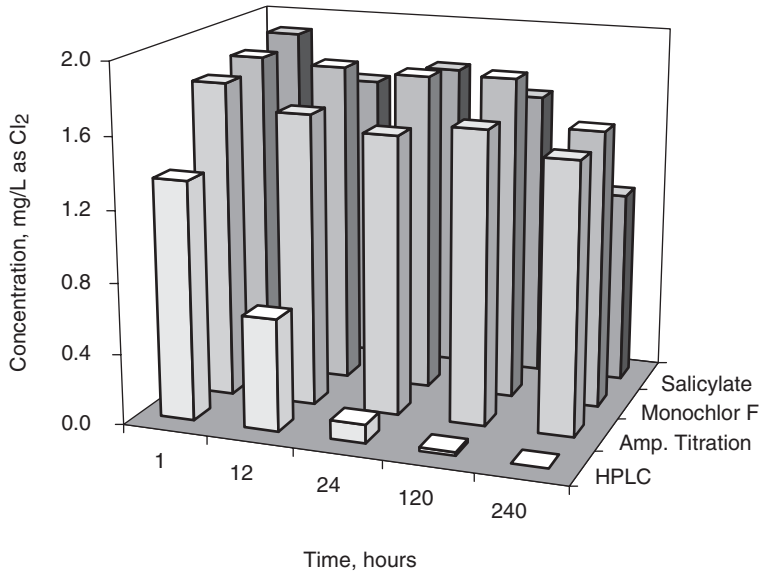
Andrews et al. (1999) described a method to determine organochloramines by subtraction. The method relies on subtracting accurate values of monochloramine and dichloramine from the total chlorine measurement (Figure 7-1). The results in Figure 7-1 show that AT and spectrophotometry indicated predominance of monochloramine in the water sample collected from a chloraminated distribution system. Conversely, HPLC measurement showed that a significant fraction of total chlorine in the same sample was not mono- or dichloramine but rather some unknown organospecies.

Studies performed for the San Francisco (California) Public Utilities Commission confirmed this finding. Monochloramine concentrations determined by AT, Hach's N,N-diethyl-p-phenylenediamine (DPD) spectrophotometric method (Monochlor F; Hach Company, Loveland, Colo.), and the standard salicylate method were found to be stable and consistent with each other, whereas HPLC-derived monochloramine concentrations (indicating the true monochloramine value) were less stable, indicating likely organochloramine interference will affect all methods tested except HPLC (Figure 7-2).



Source: Andrews, S.A., 2001.

Figure 7-1 Organochloramine determination by subtraction



Adapted from Andrews and Moffat, 2002.

Figure 7-2 Monochloramine concentrations by various methods

An evaluation of the Hach Method 10200 Monochloramine/Free Ammonia-N (Smith 2005) indicated that in some systems monochloramine values with this method were often higher than total chlorine values measured by DPD. For most systems studied, the free ammonia-N values matched the Ammonia Selective Electrode Method for ammonia-N (4500-NH_3; APHA et al., latest edition), but this is not the case for all systems. Therefore, it is recommended that utilities perform their own comparison between field methods and reference methods (i.e., *Standard Methods*) before adopting new methods for their monitoring program.

Standard Methods for the Examination of Water and Wastewater (APHA et al., latest edition) refers to AT as the "standard of comparison." Theoretically, AT should yield the most accurate and precise results. ATs are not affected by oxidizing agents,

Table 7-4 Examples of usefulness and levels of total chlorine

Location	Plant Effluent/ Distribution Entry Point	Transmission System	Distribution System Pipes	Storage Facilities
Usefulness	Very useful	Very useful	Very useful	Very useful
Typical concentration	1.5–3.5	1.5–3.5	1–3.0	1–2
Alert level*	Based on CT	1.8–2.2	1.8	1.8
Action level*	Based on CT	1.6–2.0	1.6	1.6

NOTE: CT = Concentration × contact time.

*Values shown assume an entry point value of 2.0 mg/L.

temperature, or turbidity of the sample and allow dissociation of the chloramine species. However, this method requires higher skill levels, is more time consuming than spectrophotometric methods, and is also prone to organochloramine interference. The cleanliness and condition of the electrodes or loss of residual during stirring may impact this method's accuracy and precision (APHA et al., latest edition). The water tested by AT should be between 0.2 mg/L and 2.0 mg/L. Alternatively, sample dilution using laboratory-grade water can be made to measure higher concentrations. AT is a laboratory measurement not adapted to field applications.

By contrast, methods using DPD are easier to perform and require simple and inexpensive equipment. DPD can be used in a titration to determine the chlorine concentration or used in the spectrophotometric method. The more common spectrophotometric method relies on the appearance of a red color (which absorbs light at 515-nm wavelength) to indicate the concentration of chlorine in the sample. *Standard Methods* lists the range for this method under ideal conditions as 0.010 to 2.0 mg/L (APHA et al., latest edition). However, another USEPA-approved reference lists the range as 0.02 to 2.00 mg/L (Hach, 2002). Samples above 2.0 mg/L should be diluted with chlorine demand-free water, or a sample cell with a reduced path length can be used. Two types of analysis blanks should always be determined: a reagent blank and a matrix blank. The reagent blank is prepared by adding the reagents to distilled water and then measured; this test shows whether or not the reagents cause a positive interference to the test. The matrix blank is a sample measured without the reagents added. The result from the matrix blank identifies whether there is a compound present in the sample that absorbs 515-nm light.

The use of the reagent blank allows for the subtraction of the color imparted by the reagent and improves accuracy of the test. This is especially important in dechlorination applications where the operator must determine if they have adequately removed chlorine from the water. Although equipment exists with preset calibration curves so that a calibration curve does not need to be generated by the analyst, verifying equipment with standards (as specified in *Standard Methods*) is still very important.

DPD methods are not well suited to development of breakpoint curves because nitrogen trichloride (trichloramine) reacts as free chlorine and confounds the results. Additional disadvantages of this method are discussed in the following section on free chlorine analyses.

Table 7-4 characterizes the usefulness of total chlorine as a monitoring parameter for nitrification control within the utility. The alert and action levels in this table and those that follow are provided to show the general concept and perhaps a starting point for utilities that have no historic data on which to base a monitoring plan. Ideally, alert and action levels should be set based on the historic data and are system specific. Ideally, the utility would determine summer and winter targets, alert, and

Table 7-5 Examples of usefulness and levels of free chlorine

Location	Plant Effluent	Transmission System	Distribution System Pipes	Storage Facilities
Usefulness	Very useful (to define chemical feed problem)	N/A*	N/A	N/A (unless when breakpoint chlorinating)
Typical concentration	0 (unless chemical feed problem)	0	0	0.5 to 1.5 (when breakpoint chlorinating)
Alert level	>0	N/A	N/A	N/A
Action level	>0	N/A	N/A	N/A

*NA, not applicable.

action levels. Generally, alert levels trigger increased monitoring and action levels trigger an operational response, such as increased turnover or flushing.

Free chlorine residual. According to the breakpoint curve, free chlorine and monochloramine do not co-exist. However, as mentioned earlier, the breakpoint curve represents a condition in which the reactants and products have reached equilibrium. Before equilibrium is reached (e.g., when preparing a breakpoint curve at a plant to determine the optimum ratio for formation of monochloramine or breakpoint chlorinating a storage facility), both free chlorine and monochloramine will be present until equilibrium is reached. As a routine practice, utilities practicing chloramination do not need to monitor for free chlorine in the distribution system. At the plant, the measurement of free chlorine immediately upstream of the point of ammonia addition is critical to proper dosing of ammonia. Also, if ammonia is significantly underfed, or chlorine overfed, the presence of a free chlorine residual will alert the operator to the problem. Since monochloramine interferes with the DPD reagent, it may appear that free chlorine is present when it is not.

When performing the free chlorine test in a chloraminated distribution system, it is important to note that common elements such as manganese and bromide interfere with the DPD measurement for free chlorine and can give false readings at parts-per-trillion levels. Monochloramine also interferes with this test and often is mistaken for free chlorine by the analyst. This mistake can be avoided by looking for a pink color in the sample vial immediately after the DPD powder is added to the vial. Do not shake the vial, look at the reagent in the vial *before* putting it into the instrument. If the sample is transparent and not red instantaneously (against a white piece of paper background), there is no free chlorine and the pink color that develops over time represents interference. This is sometimes referred to as a "flash test" (pers. commun., D. Foust, 2000). Table 7-5 characterizes the usefulness of free chlorine as a monitoring parameter for nitrification control within the utility.

Ammonia, Free and Total

Description. Free ammonia ($NH_3 + NH_4^+$) is present in a chloraminated distribution system as a result of three factors:

1. Source water ammonia.
2. Excess ammonia added at the treatment plant during formation of chloramine.
3. Liberated free ammonia from the decomposition of chloramine.

Total ammonia (free ammonia + $NH_2Cl + NHCl_2 + NCl_3$) is of little practical use as a distribution system nitrification control or response parameter since it represents both the ammonia combined with chlorine in the chloramine molecules and free ammonia, which is the energy source for nitrifying bacteria. When nitrification occurs,

the total ammonia concentration will decrease since part of the total ammonia is the free ammonia (used by AOB during nitrification). Therefore, total chlorine and free ammonia are more practical measures than total ammonia.

Total ammonia can be used for calculation of breakpoint chlorine dose, but free ammonia should be checked to verify breakpoint results or can be used as a back-up parameter at the treatment plant. For example, total ammonia is "useful" at the plant effluent because an operator can use it to determine if there is a chemical feed problem or to calculate the amount of free ammonia entering the transmission/distribution system. An accurate calculation of free ammonia depends on how well the water matches the theoretical 5:1 chlorine to ammonia-N ratio for maximum monochloramine formation. Inorganic and organic matter in the water can skew the breakpoint curve, requiring a ratio other than 5:1 in the water to achieve both no free ammonia and no dichloramine. If such data is available, the calculation to predict the free ammonia concentration should use the experimentally derived ratio, not the theoretical 5:1 ratio. In the distribution system, total ammonia is characterized as having limited usefulness because it supports conclusions drawn from the trending of other parameters (total chlorine and nitrite), but free ammonia rather than total ammonia should be used if the system is going to perform booster chloramination.

Free ammonia is a more explicit parameter to gauge process control at a treatment plant and nitrification in the distribution system. Free ammonia at the plant effluent is considered a very useful parameter because it gives the free ammonia result explicitly without assumptions or calculations. Unfortunately, free ammonia in plant effluent is a difficult parameter to measure because the aim of chloramine formation is to have very low resulting free ammonia concentrations, at or below 0.05 mg/L N, very near the detection limit of many methods.

Since ammonia is the food source for AOB, this parameter is used for process control to limit nitrification potential, as a warning that nitrification may occur, and to aid in the interpretation of distribution system data. In the Bangor, Maine, system, free ammonia has been observed to decrease before an increase in nitrite is observed (pers. commun., K. Moriarty, 2004). Therefore, free ammonia-N may be a useful parameter to predict the onset of nitrification in some systems. Other utilities use total ammonia for the same purpose. Alternatively, an increase in free ammonia concentration indicates overdosing at the plant or chloramine decay and suggests that nitrification could possibly occur.

In the plant effluent, the free ammonia concentration may be calculated from the free chlorine residual at the point of ammonia addition and a known ratio of chlorine to ammonia-N. Generally, the exact ratio is not known precisely, so the theoretical ratio is used according to the following formula:

$$\text{free ammonia} - N = \frac{Cl_2\ (free)}{Cl{:}N\ (ratio)} - \frac{Cl_2\ (free)}{5} \tag{7-1}$$

Where $Cl_2\ (free)$ is the free chlorine residual at the point of ammonia addition and 5 represents the 5:1 target ratio.

The chlorine to ammonia ratio is based on the dose of each chemical. Two common mistakes operators make when performing this calculation are to use the total chlorine residual instead of free chlorine residual and to use ammonia rather than ammonia as nitrogen. If either the total chlorine residual value or ammonia instead of ammonia-N are used, the free ammonia concentration will be overpredicted.* The

*An Internet search for on-line interactive spreadsheets that can be used to determine this ratio based on water quality parameters yielded one source (at the time of the search). It is available at: http://www.charlottesmith.us/documents.html#ExcelSpreadsheets. You will need to request a username and password. This can be done by sending an e-mail to smith.csa@earthlink.net.

Table 7-6 Examples of usefulness and levels of free ammonia-N

Location	Plant Effluent	Transmission System/Distribution System Entry Point	Distribution System Pipes	Storage Facilities
Usefulness	Very useful	Very useful	Very useful with Cl_2 and NO_2	Very useful with Cl_2 and NO_2
Typical concentration	0.01–0.05	0.01–0.05	0.01–0.05	0.05–0.15
Alert level	>0.05	0.05	N/A*	> 0.1
Action level	>0.05	0.10	N/A	> 0.2

*NA, not applicable.

Table 7-7 Examples of usefulness and levels of total ammonia-N

Location	Plant Effluent	Transmission System/Distribution System Entry Point	Distribution System Pipes	Storage Facilities
Usefulness	Useful	Useful	Useful with Cl_2 and NO_2	Useful with Cl_2 and NO_2
Typical concentration	0.4–1.0	0.4–1.0	0.4–1.0	0.4–1.0
Alert level*	*	*	*	*
Action level*	*	*	*	*

*Depends on the total chlorine levels.

spreadsheet allows for quick determination of the free ammonia-N concentration when the free chlorine residual concentration and chlorine to ammonia ratio are known. If a breakpoint curve has not been established for the water, the theoretical 5:1 ratio should be used. If a breakpoint curve has been established, the ratio at which no free ammonia is present should be used instead of 5.

Since the chlorine to ammonia ratio may fluctuate at the plant, it would be inappropriate to apply Eq. 7-1 to the distribution system. The equation is useful for the plant operator to predict the free ammonia-N value entering the transmission/distribution system. Operators should target a free ammonia-N concentration less than 0.05 mg/L to be in the area of maximum monochloramine formation (left of the hump in the breakpoint curve) but still minimizing free ammonia in the system.

Table 7-6 characterizes free ammonia-N as a monitoring parameter for nitrification control within the utility. Table 7-7 characterizes the usefulness of total ammonia-N as a monitoring parameter for nitrification control within the utility.

Ammonia regulatory issues. There are no regulatory requirements associated with either free or total ammonia.

Methods for ammonia-N. Total ammonia-N can be determined spectrophotometrically (Hach, 2002) or with an ammonia-selective electrode (APHA et al., latest edition), generally referred to as an ion-selective electrode (ISE). The free ammonia-N concentration can also be determined with an ammonia-selective electrode or spectrophotometer. The ammonia-selective electrode method is not practical for field measurements due to the lack of sensitivity of the electrode and the fact that the calibration standards should be the same temperature as the sample. Some analysts

add a known concentration of ammonia to the sample to improve the accuracy of the ammonia-selective electrode method if the ammonia concentration is below 0.1 mg/L. The range of the ISE method is 0.03 to 1,400 mg/L. Less common methods for ammonia are the manual or automated phenate method (APHA et al., latest edition).

Hach method 10200, a new method developed for field measurements of free ammonia-N (Hach 2004), compared well with ISE results for free ammonia-N in split samples from one utility that participated in an evaluation of this method (Smith, 2005), but not from all of the utilities in a recent study. Higher concentrations of free ammonia-N or unquantified matrix interferences most likely accounted for the lack of agreement at some of the utilities. Nevertheless, the method was shown to be useful for field measurements of free ammonia-N.

The method produces results for both monochloramine and free ammonia-N. However, the "monochloramine" value appears to be subject to interference with organochloramines (pers. commun., T. Andrews, 2001). Since the presence of free ammonia indicates that dichloramine or trichloramine are not present, the method can be used to test for free ammonia with confidence. If free ammonia is present after adequate mixing of chlorine and ammonia in the treatment plant effluent water, the total chlorine measurement represents monochloramine.

For measurement of total ammonia-N, a colorimetric method with a range of 0.01 to 0.50 mg/L is also available from Hach and other vendors. In the Hach method, ammonia reacts with chlorine to form monochloramine, and the monochloramine reacts with salicylate to form 5-aminosalicylate. 5-aminosalicylate reacts with a sodium nitroprusside catalyst to form a blue color that is masked by excess reagent to form a green color. The concentration is determined by absorbance of the sample at 655 nm. Field measurements using this method have produced mixed results.

Ammonia results should be documented as "ammonia as nitrogen" (ammonia-N or NH_3-N) since all chlorine to ammonia ratios are based on ammonia-N. Ammonia can be expressed as nitrogen (ammonia-N) by multiplying the ammonia concentration by 0.824 (or 14/17—the atomic weight of nitrogen divided by the molecular weight of ammonia). When performing an analysis for ammonia, it is important to note whether the test equipment provides the result as ammonia or ammonia as nitrogen. The same is true for nitrite and nitrate (results should be reported as nitrite-N or nitrate-N).

Nitrite and Nitrate

Description. As described in previous chapters, the activity of AOB, such as *Nitrosomonas*, results in the production of nitrite (NO_2^-). Nitrite-oxidizing bacteria (NOB), such as *Nitrobacter*, oxidize nitrite to nitrate (NO_3^-). Complete nitrification occurs when nitrate is produced. Nitrite can be oxidized to nitrate through a chemical pathway as well. If the water does not have a background nitrite concentration, which is the case in most waters, the presence of nitrite indicates nitrification is occurring. Without the activity of the AOB, there would be no nitrite above the system's background levels.

When ammonia is consumed by AOB, the ammonia concentration decreases as the ammonia is converted to nitrite. Generally, the nitrite concentrations initially increase and then are expected to level off when ammonia is no longer available. However, as NOB consume nitrite and convert it to nitrate, the nitrite concentration will decrease and the nitrate concentration will increase. NOB grow very slowly in drinking water, which explains why many utilities observe nitrite but not nitrate during nitrification. Also, surface water supplies experience fluctuations in background nitrate and therefore may find it difficult to interpret whether an increase in nitrate is from nitrification or increased runoff into the source water (pers. commun., S. Barrett, 1998). Typically, the nitrate background concentration is much higher than nitrate formed from nitrification. Thus, an increase in nitrate concentration due

Table 7-8 Examples of usefulness and levels of nitrite

Location	Plant Effluent	Transmission System/Distribution System Entry Point	Distribution System Pipes	Storage Facilities
Usefulness	Limited Useful as background especially if biological filters are used	Very useful	Very useful	Very useful
Typical concentration*	<0.010	<0.010	0.010	0.01–0.15
Alert level*	>0.010	>0.010	0.010	0.010
Action level*	>0.010	>0.010	0.015	0.015

*Assumes surface water source.

Table 7-9 Examples of usefulness and levels of nitrate

Location	Plant Effluent	Transmission System/Distribution System Entry Point	Distribution System Pipes	Storage Facilities
Usefulness	Limited usefulness Useful as background especially in groundwaters	Useful as background especially in groundwaters	Useful	Useful
Typical concentration	Background	Background	Relative to background	Relative to background
Alert level	N/A*	N/A	Increase relative to background	Increase relative to background
Action level	N/A	N/A	Increase relative to background	Increase relative to background

*NA, not applicable.

to nitrification is often unnoticed. However, nitrate is very stable in drinking water and will persist in distribution systems (unless denitrification is occurring).

Nitrate can be a useful parameter to confirm nitrification. Smith and Smith (1996) showed increased levels of nitrate well above background in a utility that uses surface water. In addition to regular quarterly measurements, frequent monitoring during summer months at several key locations, such as entry points, reservoir outlets, and a few ends of the system, would be useful to maintain a database of baseline nitrate levels. Tables 7-8 and 7-9 characterize the usefulness of nitrite and nitrate as monitoring parameters for nitrification control within the utility.

Nitrite and nitrate regulatory issues. Current state and federal regulations require monitoring of nitrite and nitrate at the entry point to the distribution system, not within the distribution system. The maximum contaminant level (MCL) for nitrite-N is 1.0 mg/L and the regulatory limit for nitrite-N plus nitrate-N as nitrogen is 10 mg/L. These MCLs are based on public health concerns, primarily methemoglobulinemia, or "blue baby syndrome." Violation of these MCLs requires public notification. There are no known cases of a nitrite or nitrate MCL violation caused by nitrification alone (USEPA, 2002). However, it is stoichiometrically possible if background nitrogen

levels are near the MCL. Therefore, from a regulatory perspective, the concern is generally the decrease in the total chlorine residual concentration due to nitrification and resulting increase in microbial counts, including the possible presence of coliform bacteria, more than the increase in nitrite.

Nitrite and nitrate methods. Nitrite and nitrate can be monitored in the field with colorimetric methods. A common method for determining nitrite-N is the diazotization method, which has a range of 0.003 to 30 mg/L. This method is also described in *Standard Methods* (APHA et al., latest edition), which uses an absorbance of 543 nm. Field testing of nitrite along with the total chlorine is the most useful way to track nitrification in drinking water distribution systems. Since NOB are very slow growers in drinking water systems, nitrite will often persist. If the nitrite is oxidized either chemically or biologically, nitrate can be tested by a variety of methods, including a nitrate electrode or the cadmium reduction method (APHA et al., latest edition). The cadmium reduction method has been adapted for field use; however, some operators do not like this method because cadmium is a hazardous waste and reacted samples must be properly disposed. The colorimetric nitrite method is reliable and can reasonably measure differences between 0.005 and 0.010 mg/L N.

Exposure to sun may cause false positives so samples should be developed in the dark. A field method that uses two sample cells may yield a value slightly higher than the actual value if the cells are not perfectly matched. This can be tested by putting deionized water into both cells, zeroing one, and reading the value of the other as if it were a drinking water sample. The value imparted by the reagent can also be determined by adding reagent to deionized water in a matched sample cell and reading the value as if it were a drinking water sample. It may not be practical to perform these tests on a routine basis, but it is useful for the analyst to observe interferences, which may influence the interpretation of the nitrite results.

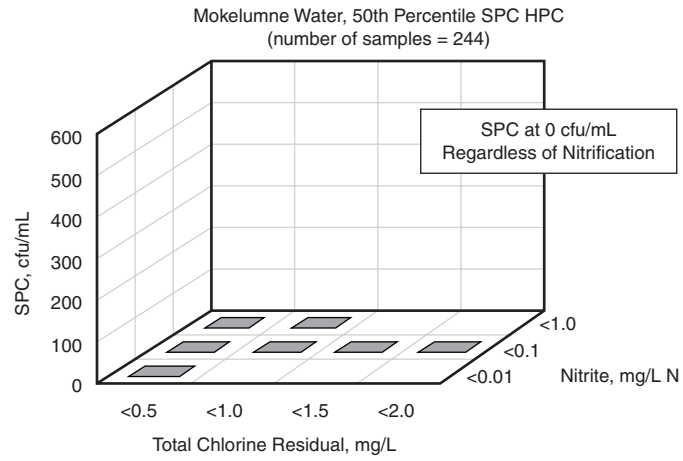
Heterotrophic Plate Count

Description. The most common method for measuring AOB, the culturing technique, is complex and time consuming. Therefore, heterotrophic bacteria are used as a surrogate for monitoring bacteria in the distribution system. Heterotrophic bacteria differ from autotrophs in that they use organic carbon for their carbon and energy sources. The organic material released by autotrophs can serve as a carbon source for heterotrophic bacteria. Further information on the interaction between heterotrophic and nitrifying bacteria is provided in chapter 5.

Heterotrophic plate count regulatory issues. For regulatory purposes (SWTR—40 CFR 141.74), if a system sample does not have a detectable chlorine residual, an HPC test result (using standard plate count agar) of less than 500 cfu/mL serves as a detectable chlorine residual. The pour plate method at 35°C and 48-hr incubation time is used for compliance. In this method, bacteria are subjected to heat shock, and those that survive are usually those that prefer higher temperature, and thus are not those that thrive in full-scale distribution systems, which have much lower water temperature. Therefore, low numbers are typically observed.

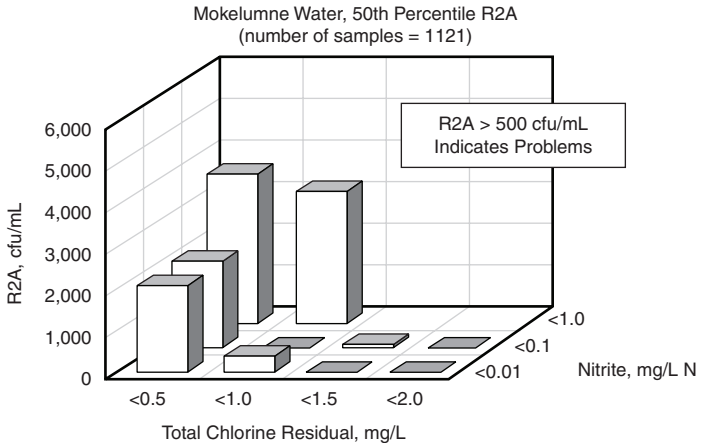
Heterotrophic plate count methods. Several tests are available for monitoring heterotrophic bacteria in drinking water. Variations exist for the media, the plating technique, and the incubation time and temperature. Results are also different depending on which method is used. After the agar is inoculated with a sample and incubated, colonies of bacteria are counted. Each colony represents thousands of individual bacterial cells that are counted as a single colony forming unit per volume of the sample.

However, a minimal nutrient agar such as R2A is more appropriate for a system using chloramine as a secondary disinfectant. Minimal nutrient agar and room temperature incubation for 7 days more accurately represents the condition of a drinking



Source: Wilczak, 2002, unpublished data.

Figure 7-3 HPC-plate count agar as an indicator of nitrification at various total chlorine and nitrite levels in a California distribution system



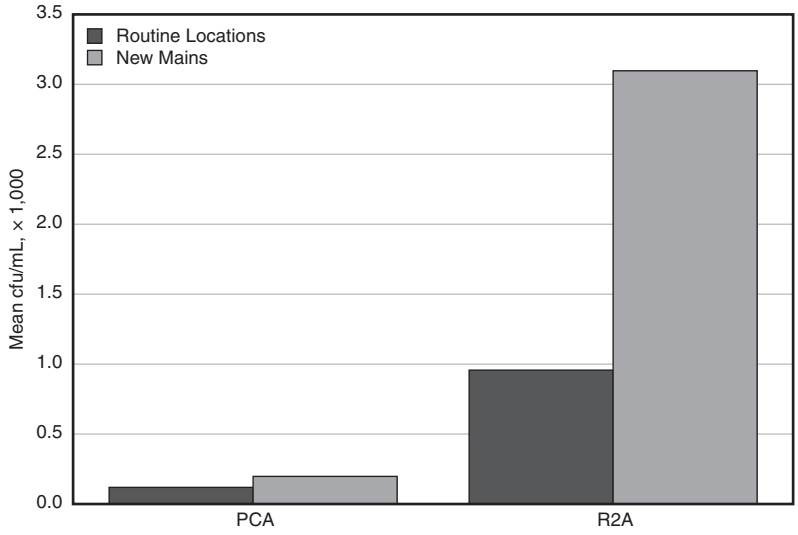
Source: Wilczak, 2002, unpublished data.

Figure 7-4 HPC-R2A as an indicator of nitrification at various total chlorine and nitrite levels in a California distribution system

water system, and analyses performed using R2A agar will predict nitrification more accurately than analyses using plate count agar (Wilczak, 2002, unpublished data).

Data in Figures 7-3 and 7-4 compare HPCs in split samples analyzed on standard plate count and R2A agar. These data clearly illustrate the increased sensitivity and usefulness of R2A agar.

As shown in Figure 7-5, Lisle (1989) observed an approximate 10-fold increase in mean bacterial counts when plotting R2A data versus standard plate count data in split samples taken from TCR sampling taps and new mains. HPC measurements using R2A agar are recommended as a routine monitoring parameter at tanks and reservoirs and at some low-flow areas since that is where nitrification most commonly occurs. Since the



Source: Lisle, 1989.

Figure 7-5 Relative counts: Plate count agar versus R2A agar in a Florida distribution system

HPC-R2A test requires up to a 7-day incubation period, the results are not available instantaneously. Therefore, HPC levels should be monitored for trends in the distribution system and evaluated in context with other nitrification monitoring parameters to better understand the system and evaluate the success of the nitrification control program over time. Because factors other than nitrification (such as increased water age) can cause HPC growth within the distribution system, HPC levels can be used to confirm nitrification but should not be the sole identifying factor.

Those systems that rely on tests with standard plate count agar for compliance with the SWTR may wish to use two tests: HPC-plate count agar for regulatory compliance and HPC–R2A for nitrification monitoring.

Ike and colleagues (1988) observed significant correlations ($\alpha = 0.05$) between the concentrations of AOB and temperature ($r = 0.81$), nitrite level ($r = 0.57$), and HPC ($r = 0.71$) in samples collected from a drinking water distribution system reservoir. However, Wolfe and colleagues (1990) did not obtain such good correlations when the number of sampling locations was increased within the same distribution system. Wolfe and colleagues (1990) still confirmed that, in general, an increase in AOB was detected by culturing technique when the water temperature was over 18°C; AOB were not detected below this temperature and the R2A HPC were between 350 and 500 cfu/mL. However, these effects are the result of nitrification and occur once nitrification is already well underway. They do not predict the onset of nitrification. This can be confirmed by the results of Ike and colleagues (1988) who observed that nitrite was usually not detected until the AOB concentration was approximately 1 MPN/mL. Also, these factors are system dependent and some of them may be observed during nitrification episodes in some systems, and not in others.

pH

Description. Adjustments to drinking water pH are made to optimize water treatment plant processes and for corrosion control. For example, coagulation is optimized at an acidic pH, whereas corrosion control is optimized under basic pH conditions.

Disinfection with free chlorine is more effective at low pH because hypochlorous acid (predominant at low pH) is 300 times stronger than the hypochlorite ion (predominant at high pH). However, following ammonia addition, higher pH is preferable to help maintain chloramine stability.

Work performed on the San Francisco (California) Public Utilities Commission's water confirmed that variation in pH was a significant factor affecting the chloramine decay rate (Palacios and Smith, 2002). The total chlorine residual decayed more slowly at pH values above 8.5 versus 8.0.

pH measurements are useful for understanding the effect of nitrification within the distribution system pipelines. Depending on its level, pH can promote or inhibit nitrification. Additionally, nitrifiers can decrease the pH of poorly buffered water, making low pH a possible indicator of nitrification. Using a target pH value above 8.5 will help maintain the total chlorine residual by minimizing the decay rate, although this may not be possible in very low alkalinity waters (Wilczak, 2003).

pH methods. pH is determined by an electrometric method (APHA et al., latest edition). The pH meter should be calibrated at the beginning of each series of tests. Either a two-point or three-point calibration may be used. The fact that calibration standards match the sample temperature when pH analyses are performed in the laboratory rather than in the field accounts in part for increased precision and accuracy in laboratory analyses. However, the level of accuracy of field pH measurements is generally sufficient for both process control and system monitoring. In low-alkalinity waters, additional quality assurance measures, such as use of low ionic strength pH probes, can improve the accuracy and precision of the measurements.

Temperature

Description. While this parameter alone will not identify cases of nitrification, temperature is a critical factor in the growth of ammonia and NOB (see chapter 6). Generally, there is little fluctuation in temperature throughout a distribution system on a daily basis. However, as described in chapters 9 and 10, storage facilities can experience enough temperature variation to create stratification within the water column (Grayman et al., 2000). Thermal stratification inhibits mixing within a reservoir, thereby encouraging the decay of chlorine and increasing the potential for nitrification. In addition, most utilities experience nitrification during summer months.

Temperature methods. Some pH instruments with temperature compensation display the temperature of the water when pH is measured. If such instruments are used, temperature can easily be included if pH is measured in the field. In addition to the use of thermistors (probes), a mercury-filled thermometer with 0.1-degree intervals is typically used for temperature measurement (APHA et al., latest edition). Temperature measurements should be calibrated periodically according to *Standard Methods* (APHA et al., latest edition).

Additional Parameters

Additional parameters indirectly related to nitrification include alkalinity and hardness and some regulatory compliance parameters (i.e., total coliform bacteria and disinfection by-products [DBPs]). The relationship of some of these parameters to chloramine disinfection and/or nitrification is discussed in the following paragraphs.

Alkalinity. Fluctuations in pH in the distribution system are governed by the buffering capacity of the water. For example, in poorly buffered waters, pH often increases as water moves through the distribution system. A drop in pH during nitrification will be more apparent in water with very low alkalinity. The alkalinity data is helpful in interpreting the pH data.

Hardness. Hardness in drinking water is often referred to as carbonate hardness or calcium hardness. In the first case, it is a measure of carbonate ion in the water and in the second case it is a measure of calcium and magnesium ion concentrations in the water. Hardness values above 30 mg/L have been observed to cause precipitation of calcium and magnesium in the pipes and equipment of the ammonia feed system (pers. commun., J.F. Smith and I. Nelson, 2001). If the hardness of the chase water used for the ammonia feed system is above 35 mg/L as $CaCO_3$, a softener or neat feed system should be used to prevent scaling of the feed system (Kirmeyer et al., 2004).

Specific conductivity. This parameter does not influence nitrification and is not an indicator of nitrification but can be a useful parameter in cases where multiple sources exist and the operator wishes to know which source is related to the sample or the percent blend. Different waters may exhibit different susceptibility to nitrification due to chloramine stability and bacterial growth potential.

Coliform bacteria. In severe nitrification occurrences, when the disinfectant has dissipated, excessive bacterial counts including the presence of coliforms have been observed (pers. commun., C. Kinner, 2003). Coliform bacteria act as an indicator for the occurrence of pathogenic bacteria in the water. The TCR requires an absence of coliform bacteria in 95% of the samples collected each month by a utility (if more than 40 samples are taken) or no more than 1 sample if less than 40 samples are taken. Nitrifying bacteria are not observed in this test.

Generally, coliform bacteria are nonpathogenic; however, some species can indicate fecal contamination such as *Escherichia coli* or avian contamination (*Salmonella* or *Campylobacter*). Other species such as *Klebsiella* may be present in a fecal coliform test since these bacteria can grow and reproduce at the temperature in which the fecal coliform test is performed, but they have no public health significance.

Presently the TCR only requires testing of *E. coli* or fecal coliform bacteria if a total coliform bacteria sample is positive. This provision may change in the next revision of the TCR. An assessment of indicator organisms, such as coliform bacteria, in the distribution system may be useful for assessing the success of the disinfection regime, distribution system operating procedures, and possible contamination of the distribution system from cross-connections and intrusions.

Disinfection by-products. Utilities typically convert to chloramine to limit the formation of halogenated DBPs. An evaluation of data from utilities that participated in the Information Collection Rule and use surface water as the source of supply indicates about a 300% increase in trihalomethane (THM4) levels (on average) as treated water travels from the treatment plant through chlorinated distribution systems. For systems with a chloraminated distribution system, there was an approximate 50% increase in THM4 (pers. commun., A. Obolensky, 2001). This means that in a system where the plant effluent THM4 concentration is 30 µg/L, in general, the highest THM4 concentration within the distribution system would be about 120 µg/L if the utility used free chlorine. If chloramine was used as a secondary disinfectant, the highest THM4 concentration in the distribution system would be approximately 45 µg/L. Haloacetic acid levels will also increase but not in the same percentage as THMs. Two DBPs related to chloramines—n-dimethylnitrosamine (NDMA) and cyanogen chloride—are not currently regulated.

Dissolved oxygen. This parameter is generally not routinely monitored, but a decline in dissolved oxygen (DO) concentration can support other data that indicate nitrification. DO should be considered as a parameter for special studies of nitrification but not for routine sampling.

Disinfectant Decay Rate

Chloramine demand and decay have been reviewed in chapter 4 and by Wilczak et al. (2003). An understanding of the factors that influence the decay of chloramine is

valuable for controlling the stability of chloramine in the distribution system. This review includes a discussion of water quality constituents, such as organic carbon and bromide, that should also be included in the monitoring program.

Monitoring locations. Designated monitoring locations for collection of bacteriological or chemical samples are an important component of a monitoring program. An adequate number of monitoring locations must be provided to fully represent all portions of the distribution system. While system-wide averaging is required for regulatory compliance, an assessment of water quality at *individual locations* in the distribution system is essential for proper interpretation of data developed under a nitrification prevention and control program. For example, entry point, storage facilities, high-flow areas, low-flow areas, and stagnant areas should be trended independently. Monitoring sites should represent variations in pipe materials, water age, and various system pressures. Mixed zones (areas influenced by more than one source of water, or areas that blend different final disinfectant, free chlorine with chloramine) should be included as well. Designated sample taps are critical to the integrity of the monitoring program and database. If sample taps are maintained to establish a historic database, data can be used to assess changes in treatment or operations. A compromise must be made between establishing new locations for adequate coverage of the system and maintenance of the historic database.

Sample taps should be protected from outside sources of contamination. Ideally, a drinking water sample tap is only used for monitoring drinking water. Both sample collectors and laboratory personnel should use standardized labels and forms. A chain-of-custody form should accompany each sample, which should be properly filed. Sample taps should allow for adjustment of flow rate in order to flush the sample line before the sample is drawn. Narasimhan et al. (2004) found that flushing was as effective as flaming or disinfecting (with chlorine or alcohol) the sample tap before sampling for coliform bacteria. Flaming is discouraged if the sample valve components can be degraded by excessive heat. Materials of taps and sample lines should be consistent with parameters to be analyzed (i.e., polyvinyl chloride [PVC] lines are inappropriate if samples will be analyzed for total organic carbon or volatile chemicals, which can leach from PVC).

Sampling within storage facilities requires specialized equipment. Portable, battery-operated pumps (e.g., Masterflex®, Cole-Palmer Instrument Company, Vernon Hills, Ill.) are useful since the exact depth can be determined and the sample tube can be disinfected before use. The ability to sample at various locations within a reservoir is important to capture possible stratification. Dip samples may not represent the depth of water for which a sample is desired if water from above the desired depth contaminates the sample. The location of samples within a reservoir is based on size, the symmetry of the reservoir shape, expected mixing conditions (internal flow pattern), and other factors. Generally, three 8-inch roof ports are adequate for round tanks that are symmetric in reference to the inlet and outlet. For more complex configurations and large facilities, more roof ports are required.

After the sample is collected, the holding time and storage conditions that are described in *Standard Methods* (APHA et al., latest edition) should be closely adhered to in order to maintain the integrity of the sample. Standard operating practices (SOPs) related to monitoring should be documented and accessible to utility staff. Periodic training or review of SOPs is advisable.

The monitoring program should be reviewed annually and adjustments made based on historical data trends, changes in water use patterns, operational procedures, or other changes that can affect water quality or water age. Utility staff should periodically examine the sample taps for leaks or other potential sources of contamination.

MONITORING FREQUENCY

The frequency of analysis for parameters described in this chapter is governed primarily by three factors: regulatory compliance, the importance or priority ranking of the parameter for making operational decisions, and the variability in the parameter. Monitoring frequency should vary depending on the location and the purpose of the data. For example, in the distribution system, the highest priority is the monitoring of total chlorine and nitrite. At the treatment plant, effluent pH, TOC, total chlorine residual, and free ammonia are the highest priorities (assuming there is no background nitrite). The data from these tests are used to control the process as well as predict water quality in the distribution system. Some systems, such as the City of Philadelphia, monitor nitrite when triggered by total chlorine residual and temperature values instead of as a routine parameter. When total chlorine is less than 0.5 mg/L and temperature is greater than 15°C, nitrite is tested (pers. commun., G. Burlingame, 2005).

Chlorine Residual

For total chlorine residual, continuous or daily measurements are required at the treatment plant and advisable at critical points in the distribution system. Guistino (pers. commun., J. Guistino, 2003) has described the value of continuous monitoring of storage facilities as part of the Contra Costa (California) Water District's nitrification control strategy. Reliable on-line chlorine residual and pH monitors are appropriate for continuous monitoring at water treatment plants and at critical points in the distribution system.

Free Chlorine

If a system switches to free chlorine as part of the nitrification prevention or control plan, free chlorine is measured in the distribution system for regulatory compliance purposes instead of total chlorine. Also, free chlorine should be measured if a storage facility is breakpoint chlorinated as an operational response.

Free Ammonia-N

Continuous monitors are also available for free ammonia. At a minimum, the free ammonia-N should be tested once during each water treatment plant operator's shift if on-line monitors are not available. Minimizing free ammonia exiting the plant is perhaps the most important aspect of nitrification control.

Nitrite-N

In general, a system practicing chloramination should monitor nitrite on a weekly basis in the distribution system. The entry-point nitrite level can be used for comparison and determination of background level. The entry-point nitrite level is more useful in treatment plants that use granular activated carbon filters, especially if biological filtration is practiced and chloraminated water is used for backwashing since AOB can populate these filters. Nitrite should be monitored weekly at storage facilities and in low-flow areas so that increasing trends can be observed.

Nitrate-N

In many surface water systems, the variability of nitrate in the water makes interpretation of nitrate values very difficult. However, if background nitrate concentrations

are consistent, nitrate can also serve as a useful parameter to characterize nitrification in a system. The utility should select a monitoring frequency that is practical and provides necessary information. That is, they may choose to monitor at the same frequency as nitrite-N so the data can be analyzed at a later date or they may choose to monitor nitrate when triggered by conditions in the system indicating the occurrence of nitrification in the system such as loss of chlorine residual at a specific site. Since nitrate is usually performed as a laboratory test rather than a field test, an additional expense and time delay may discourage some utilities (especially smaller systems) from incorporating this parameter into their routine monitoring program.

Heterotrophic Plate Count

HPC using R2A agar should be monitored at least monthly under most conditions but more frequently if there is a history of nitrification in a tank/reservoir or portion of the distribution system. In that case more frequent monitoring may be warranted to observe how operational changes such as increased reservoir turnover or flushing decrease the HPC values and for how long.

Temperature or pH

Temperature data (especially at the entry point and in water drawn from storage facilities) are useful for interpreting the loss of the total chlorine residual in the system and should be monitored at the same frequency as total chlorine residual or pH. Temperature can be measured simultaneously with pH.

Dissolved Oxygen

DO data can confirm nitrification and are sometimes useful during an investigation of nitrification. Similarly, disinfectant decay rate is not part of a routine monitoring program, but the data can be used to assist in the evaluation of treatment or operational changes.

Alkalinity

Alkalinity and hardness data from the distribution system are useful for feedback to operational personnel and should be monitored daily at water treatment plants and at least weekly at key points in the distribution system.

Parameters that show little variation may be monitored less frequently or in response to changes in other high-priority water quality parameters. In other words, changes in the trend of high-priority parameters can be used to trigger more frequent monitoring and/or the addition of parameters that aid in the interpretation of data. Utilities may also want to consider seasonal modification of monitoring frequencies to account for the increased occurrence of nitrification during the warmer months. The resources of the utility should also be considered when establishing the monitoring frequency. Water quality regulations describe monitoring frequency requirements and should be used to establish the minimum number of samples and schedule. Additions to the schedule should be based on trends in water quality and nature of the system. For example, a system using chloramine and operating 10 or fewer storage facilities should be able to monitor all of them on a weekly basis for parameters related to nitrification.

CONCLUSIONS

A monitoring program should be developed to track trends in parameters related to nitrification. The program should be evaluated periodically for its suitability and ability

to reveal trends in the data on a timely basis. If trends cannot be observed, the utility will be forced to take responsive actions that require more resources and are more disruptive to the system than proactive measures. Changes in drinking water process or operational changes provide an opportunity to re-assess the parameters, locations, and frequency of analysis that comprise the program. Data should be archived and accessible for analysis and interpretation. Software programs that allow for the trending of data over time are especially beneficial to a utility that wishes to prevent nitrification rather than respond to its effects.

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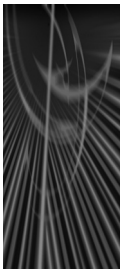


Chapter 8

Operational and Treatment Practices to Prevent Nitrification

Janice Skadsen
Y. Koby Cohen

INTRODUCTION

Good operational practices are essential for preventing nitrification and providing high-quality drinking water to customers. This chapter discusses treatment and operational protocols, both advantages and disadvantages, and makes recommendations that can help water utilities develop long-term best operational practices. The practices discussed are designed to help prevent nitrification from occurring in treatment plants, water distribution systems, and storage facilities. The recommendations are made based on real situations encountered by water utilities throughout the world. Some of the recommended approaches may or may not work at each utility due to differences in water quality, pipe materials, system demand, system configuration, and other utility-specific factors. Note that some of the approaches discussed in this chapter coincide with general water quality management practices that most utilities are familiar with and use, such as distribution system flushing, storage facility turnover and cleaning, and chemical feed control. Implementing the operational practices recommended in this chapter will be a good starting point for maintaining water quality in the distribution system at any utility, regardless of the type of disinfectant used.

The practices for prevention of nitrification include proper ammonia control, maintaining a minimum target chloramine residual, proper storage facility operations to minimize water age, good distribution system operations, and continual assessment of the effectiveness of these approaches. Table 8-1 summarizes these categories and the associated recommendations. At most utilities, the following practices are recommended:

Table 8-1 Key points from chapter 8

Ammonia Control	• Limit excess free ammonia leaving the treatment plant to as low as possible, at least below 0.10 mg/L N, preferably <0.05 mg/L. This is a prerequisite for nitrification prevention. However, even tight control of excess free ammonia has not always been effective and must be combined with other practices to consistently help prevent nitrification.
	• Maintain chlorine to ammonia-N weight ratio leaving the treatment plant between 4.5:1 and 5:1 in order to limit free ammonia.
	• Use anhydrous or aqua ammonia rather than dry ammonium sulfate. Dry ammonium sulfate clumps, thereby increasing manual labor and leading to potential underfeed or overfeed of ammonia. Anhydrous and aqua ammonia are relatively easy to use but require significant safety measures.
	• Monitor the source water for ammonia concentrations and adjust the ammonia feed accordingly.
	• Ammonia injection ports should be designed for several factors: redundancy, promotion of rapid mixing to form chloramine, and prevention or removal of scaling.
	• Provide good mixing of both chlorine and ammonia into the carrier water stream and subsequent reaction to properly control chloramine formation.
	• Perform on-line monitoring for both chlorine and ammonia residuals. The use of control loops to adjust feed rates may be beneficial.
Chloramine Residual	• Maintain a minimum concentration of chloramine leaving the treatment plant: recommend >2.0 mg/L.
	• Keep the chloramine concentration at all monitoring points in the distribution system at 0.5 mg/L or higher depending on system and site requirements. Based on experience, several utilities have established internal goals of 1.5 mg/L chloramine or higher for all distribution system sites.
Storage Facility Operation	• Maximize mixing in storage reservoirs and eliminate short-circuiting. By providing adequate mixing and eliminating stratification, it may be possible to reduce both water age and temperature, thus reducing the incidence of nitrification. Increasing the fill time of a storage tank and maintaining sufficient inlet velocity may be looked at as long-term responses to prevent nitrification by increasing turnover and decreasing water age.
	• Minimize water age in storage facilities. Turnover is accomplished when a percentage of the tank volume is being drawn and filled every day.
	• When repeated nitrification events are occurring within a storage facility that is not being used daily, a thorough analysis of necessary versus available storage should be conducted. Decommissioning excess storage can provide a long-term solution to nitrification problems.
	• Routinely inspect and clean storage tanks and reservoirs. Routine sediment removal and cleaning is a good operational practice that may decrease the frequency of nitrification.

Table continued next page

Table 8-1 Key points from chapter 8 (continued)

Distribution System Operation	• Decrease water age in the distribution system. • Practice systematic flushing. Unidirectional flushing is better than conventional flushing as it improves removal of biofilms, removes a greater amount of sediment, and is less expensive per mile of flushed pipeline. However, once nitrification occurs, flushing alone may be limited in effectiveness. • Routinely flush dead-end and other low flow areas. Routine flushing is an established practice for maintaining distribution system water quality. In a utility survey, hydrant flushing was rated as one of the most important perceived methods for prevention of nitrification. • Consider blending of waters. Blending can be either beneficial or detrimental regarding nitrification and water quality. • Evaluate booster chloramination or booster chlorination (if sufficient ammonia present). • Provide good corrosion control. • Evaluate periodic switch to free chlorine. Free chlorination is an effective strategy for controlling and even stopping nitrification episodes once they have begun but has met with mixed success for nitrification prevention. It is required by some states. • Evaluate increasing pH to >9 on a case-by-case basis. The use of pH control to prevent nitrification has met with mixed success. • Evaluate use of chlorine dioxide/chlorite. It appears that chlorite is effective for nitrification prevention. The issue of adding a regulated substance to the drinking water for prevention of nitrification needs to first be resolved by regulatory agencies, the utility, and its customers.

Always

- Minimize free ammonia and control the chlorine to ammonia-N ratio between 4.5 and 5:1
- Maintain a sufficient chloramine residual
- Routinely clean storage facilities and distribution system piping
- Practice systematic distribution system flushing
- Provide good corrosion control

Optimization of practices

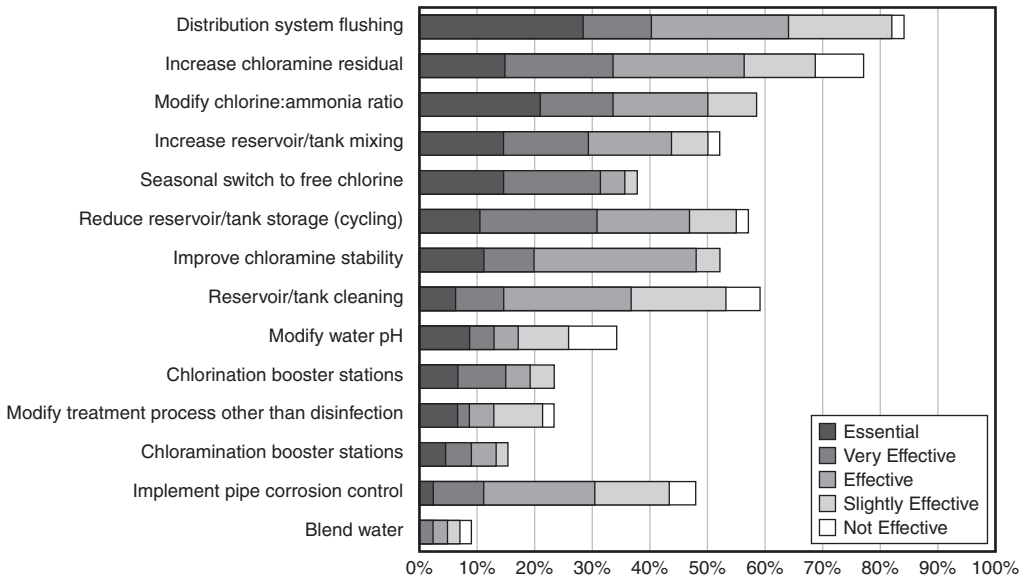
- Minimize distribution system water age
- Maximize storage facility turnover and cycling
- Maximize hydraulic mixing
- Optimize storage volume

Potential tools

- Blend waters to improve quality
- Evaluate booster chloramination
- Raise pH
- Evaluate use of chlorite ion

Last resort

- Switch to free chlorination (Note: Some states require an annual switch for various reasons.)



Source: Kirmeyer et al, 2004.

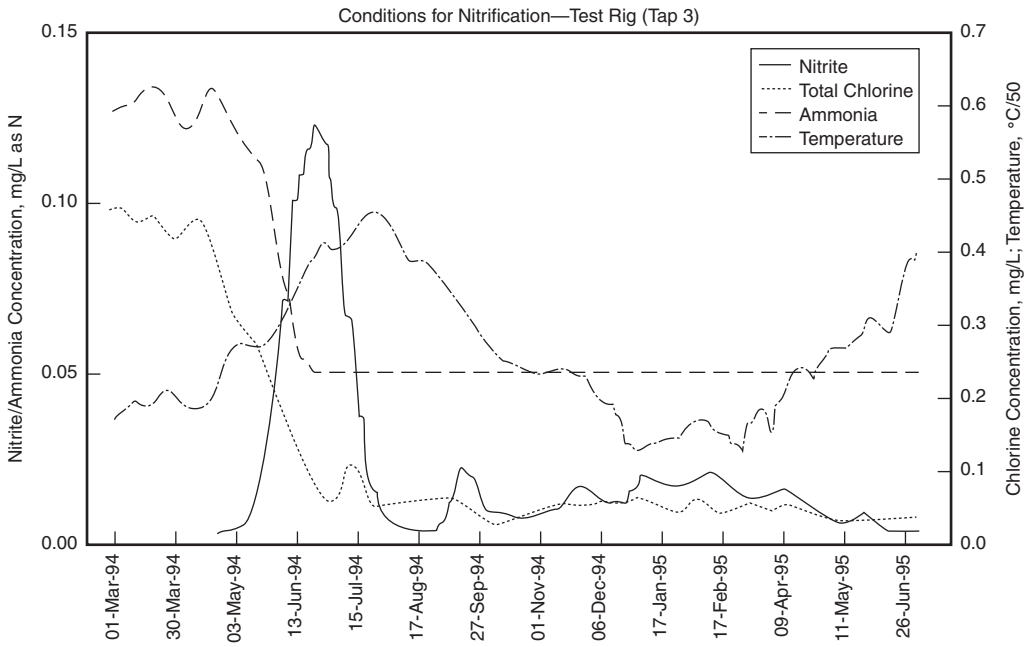
Figure 8-1 Utility practices and perceptions regarding prevention of nitrification. Number of responding utilities = 50.

In a nationwide survey of over 50 utilities, Kirmeyer et al. (2004) examined the most commonly used methods for prevention of nitrification and how the surveyed utilities rated the effectiveness. Actions such as distribution system flushing, increasing the chloramine residual, and modifying the chlorine to ammonia-N ratio were found to be the most commonly used preventative methods and were perceived to be the most essential (Figure 8-1). However, the actual effectiveness of these approaches has been demonstrated to vary with the utility. Not all surveyed utilities had tried all of these approaches.

AMMONIA CONTROL

Concentration and Ratio

Proper control of ammonia and chlorine dosages is essential for the prevention of nitrification. Since ammonia-oxidizing bacteria (AOB) thrive on ammonia, limiting the residual free ammonia available for these bacteria can be one of the major control strategies for preventing nitrification. It is recommended that excess free ammonia should be kept at less than 0.10 mg/L, preferably less than 0.05 mg/L if possible. There have been numerous examples of ammonia overfeed contributing to nitrification (Kirmeyer et al., 1995; Skadsen, 1993; Davis, 1990). In one study, reducing the free ammonia level from 0.11 mg/L to 0.05 mg/L correlated with a reduction in nitrite concentration, which was used as an indicator of nitrification (Holt et al., 1995). Holt et al. (1995) further examined the relationship between free ammonia and nitrification (as indicated by nitrite concentration, total chlorine concentration, and temperature) in a series of experiments in a test rig. Holt and colleagues observed simultaneously a decrease in the total chlorine residual, an increase in temperature, a decrease in ammonia concentration to below the method detection limit, and a spike



Source: Holt et al., 1995.

Figure 8-2 Correlations between free ammonia, temperature, total chlorine residual, and nitrite concentration

in nitrite concentration. Results from one of the test rigs depicting these water quality changes are shown in Figure 8-2.

In order to limit excess free ammonia, the proper ratio of chlorine to ammonia-N must be fed at the treatment plant when forming chloramines. A weight ratio of 4.5:1 to 5:1 as chlorine to ammonia-N is generally recommended. Utility-specific chlorine demand and other water quality parameters must be considered when selecting the target ratio. A lower ratio around 3:1 has been implicated in some occurrences of nitrification (Davis, 1990; Negrin et al., 1990; Wolfe et al., 1988). At the Metropolitan Water District of Southern California (MWDSC), maintaining a ratio of 5:1 has reduced the incidence of nitrification (Kirmeyer et al., 2004). The selected ratio may be dependent on the pH of the finished water. In Sydney, Australia, the finished water pH is in the 7.8 to 8.5 range. At the lower end of this range, an increase in chloramine decay rate has been observed when operating at a 5:1 chlorine to ammonia-N ratio. This effect is not apparent at the higher end of the pH range (pers. commun., Sydney Water, 2005). Note that even tight control of excess free ammonia and maintenance of proper chlorine to ammonia-N ratio have not always been effective at preventing nitrification (Kirmeyer et al., 2004; Skadsen, 1993; Negrin et al., 1990). This is due to the fact that chloramines will break down in the distribution system and release free ammonia. Therefore, while maintaining a proper ratio and limiting excess ammonia at the treatment plant is a necessary operational practice, it must be combined with other practices that minimize the extent and rate of chloramine decay to consistently help prevent nitrification.

Types of Ammonia

Different types of ammonia chemicals (dry versus liquid stock) have different benefits and drawbacks that may impact the formation of chloramines and thereby the potential

for nitrification. In a survey of over 50 chloraminating utilities, only 4% used ammonium sulfate, 2% added no ammonia as sufficient concentrations were present in the source water, 44% used aqua ammonia, and 50% used anhydrous ammonia (Kirmeyer et al., 2004).

The experiences of several utilities have shown that dry feed of ammonium sulfate is harder to control and requires more maintenance than liquid feed of aqueous or anhydrous ammonia. In Ann Arbor, Michigan, the first attempt at forming chloramines used dry ammonium sulfate (pers. commun., L. Sanford, 2005). The dry feeders routinely plugged and fed inaccurate amounts of dry product. This is due to the fact that ammonium sulfate is hydroscopic and therefore tends to form clumps, resulting in poor dosage control. Due to the unreliability of the dry ammonia feed system, the plant switched within a few months to anhydrous ammonia (pers. commun., L. Sanford, 2005). The East Bay Municipal Utility District (EBMUD) had similar experiences with ammonium sulfate (pers. commun., J. Smith, 2005). The chemical clumped in the hopper, requiring the operators to chop it up in order for it to pass through. Also, there are limited manufacturers of ammonium sulfate and most of them are located in the eastern United States. If a utility is located far from the manufacturing facility, transportation costs and clumping during transportation should be taken into account. Ammonium sulfate may also be obtained in 100-lb bags; however, these bags still have clumping problems as well as intensive lifting requirements for the operational staff. Due to all of these issues, it is not recommended that water utilities use ammonium sulfate to form chloramines at their treatment facilities.

Anhydrous and aqua ammonia are relatively easy to use but they do have potentially significant safety considerations. In general, aqua ammonia is safer than anhydrous since it consists of a lower 15 to 30% ammonia concentration by weight. A 20% concentration is typical in most systems (Harms and Owen, 2004). An example of an aqua ammonia feed system is shown in Figure 8-3. The system in this figure includes a double-walled steel tank for ammonium hydroxide storage (note the vapor release valve on top), stainless steel fill pipes with quick connects for the delivery truck, and a chemical injection pump.

Anhydrous ammonia is a hazardous substance that requires special handling and extra equipment such as explosion-proof electrical switches and sensors to monitor ambient air ammonia level (Kirmeyer et al., 2004). Depending upon the quantity stored, concentration, and local regulatory requirements, process safety management may be required. An example of an anhydrous ammonia feed system is shown in Figure 8-4. In the depicted system, a 1,000-gal nurse tank (bulk storage) with an ammonia vapor transfer pump (not shown) feeds two day tanks. The 500-gal day tanks are located on a platform scale for monitoring ammonia usage. Ammonia vapor is withdrawn through a vacuum regulator and applied to the water through ammonia injectors. Rotameters are used for flow control.

Both high and low temperatures can create problems for control of ammonia feed. High ambient temperature may cause ammonia to off-gas and alter the ammonia concentration. Therefore, both temperature control and proper exhaust ventilation will be important for ammonia storage. The ammonia supply lines will need to be insulated when the ammonia tank is located outside the facility to prevent them from overheating. In one utility using 19.4% aqua ammonia, vapor lock was observed in pumps and air gaps occurred in feed lines when the temperature was 85°F due to vaporization at high temperature (Harms and Owen, 2004). Both ambient temperature and sunlight exposure will be important factors to consider. Low temperatures can cause pressure drops and restrict feed rates (Harms and Owen, 2004). Therefore, where low temperatures are experienced, indoor storage and temperature control will be important in order to maintain the proper ammonia feed rate. Alternatively, the tank and effluent line must be heated if stored outdoors in areas where the temperature may drop below the ammonia freezing point. It is recommended that the utility always check with the

Source: Southern California Water Company.

Figure 8-3 Example of an aqua ammonia (ammonium hydroxide) 500-gal storage tank and metering pump

Source: City of Ann Arbor Water Treatment Plant.

Figure 8-4 Example of an anhydrous ammonia feed system

local fire department on safety requirements before starting to handle ammonia in any form.

Ammonia Feed Systems: Operation and Maintenance

There are several approaches used for forming chloramines, and some of these practices may or may not help to prevent nitrification. These approaches include introducing either chlorine or ammonia first or adding both simultaneously. In a survey of chloraminating utilities with 54 responses, it was found that 4% add ammonia first, 11% add chlorine and ammonia simultaneously, and 81% add chlorine first. In the same survey, it was also found that 4% of the utilities use multiple scenarios depending on water temperature (Kirmeyer et al., 2004).

In the case of simultaneous addition of chlorine and ammonia, disinfection efficacy will be solely dependent on chloramine contact time and dosage, which is a less effective disinfectant than free chlorine. Therefore, many utilities that operate surface water treatment plants find this approach more challenging due to the need for additional contact time to meet US Environmental Protection Agency (USEPA) CT (disinfectant concentration multiplied by disinfectant contact time) requirements. In some cases, water utilities use strong disinfectants such as ozone or chlorine dioxide to meet the CT requirements and then add chloramines at the treatment plant effluent. Kirmeyer et al. (2004) recommend that even when adding chlorine and ammonia together, at least 5 ft of separation distance should be kept between the feed points in order to prevent the formation of nitrogen trichloride.

It is generally not recommended to feed ammonia before chlorine as the free ammonia may encourage nitrification within the treatment plant processes (coagulation and sedimentation basins, filtration). For example, in Ann Arbor, Michigan, ammonia was fed pre-filtration and chlorine post-filtration (due to the availability of feed points). This approach was effective when using sand media filtration beds, but after the filtration media was changed to granular activated carbon (GAC), nitrification in the filters occurred within 2 weeks. This nitrification resulted in the complete removal of the available free ammonia and stopped the chloramine formation process (Skadsen, 1993). After 9 years of successful chloramination, nitrification in the distribution system was observed for the first time in Ann Arbor following this filtration media change from sand to GAC. It was theorized that the AOB, which colonized the GAC filters, entered the distribution system and led to distribution system nitrification as well (Skadsen, 1993). In the Ann Arbor case, all ammonia was consumed, but in other instances, the impact of treatment processes on ammonia concentration can be variable. Under these circumstances, it is possible to have inconsistent and variable concentrations of ammonia prior to chlorine application. This situation will greatly complicate process control and thereby make a utility more vulnerable to water quality problems and nitrification.

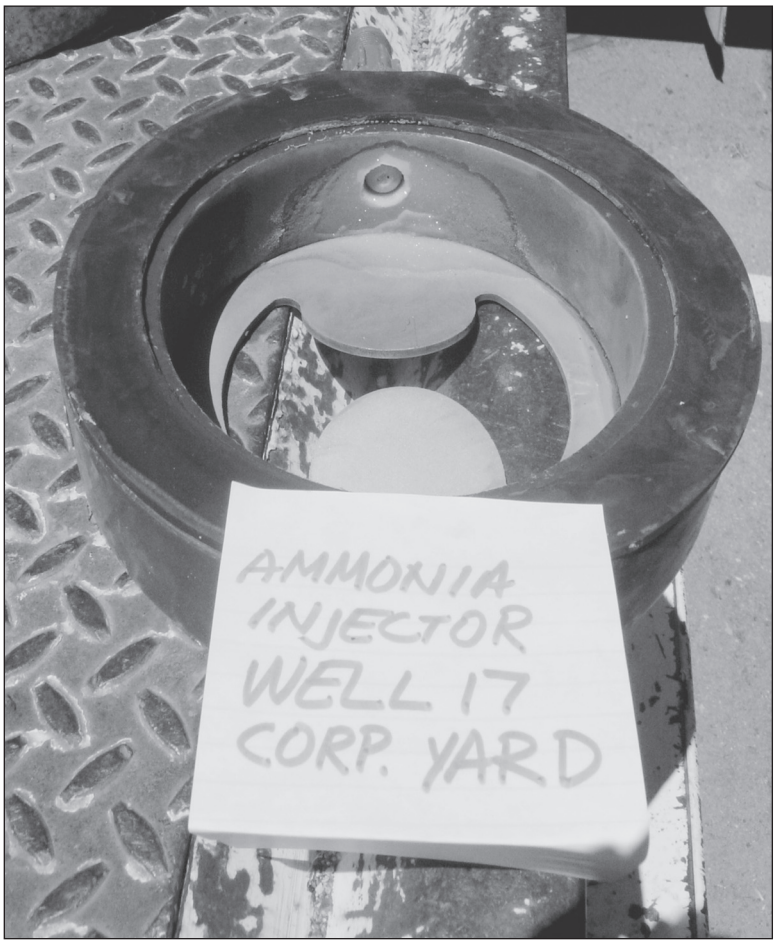
Application of free chlorine before ammonia addition is the most frequently used approach for chloramine formation. The use of a short free chlorine contact time will provide CT credit to meet disinfection requirements of the Surface Water Treatment Rule (SWTR). This is a common choice of surface water utilities, provided that disinfection by-products (DBPs) can still be controlled, particularly for compliance with the USEPA Disinfectant/Disinfection By-product (D/DBP) Stage 1 and recently published (Jan. 4, 2006) Stage 2 rules. Depending on the treatment process, some utilities have found that a short free chlorine contact time (from a few minutes to a few hours) before ammonia application results in a more stable final chloramine residual (Wilczak, 2003b). This contact time is important in order to help satisfy chlorine demand. This operational procedure has been recommended for plants using ozone followed by GAC filtration before chloramination. Further discussion of regulatory implications is provided in chapter 9. Figure 8-5 shows a chloramination system

Source: City of San Bruno.

Figure 8-5 Sodium hypochlorite and liquid ammonia feed system at a wellhead where chlorine is added first

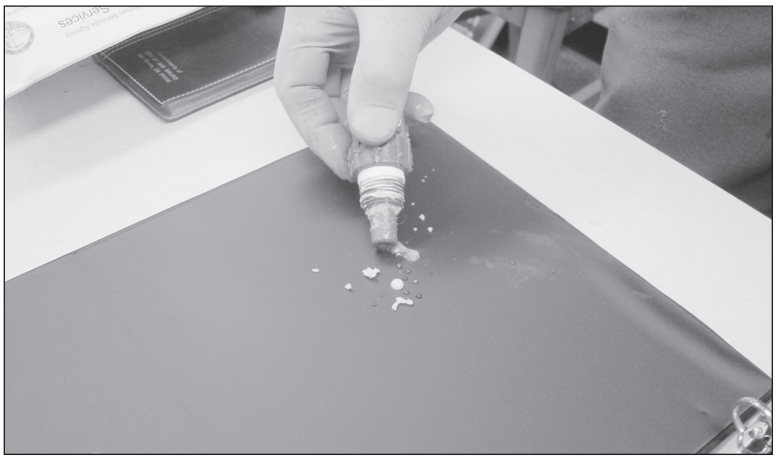
where chlorine is added first to a groundwater well effluent line. The system includes liquid chlorine and ammonia tanks, chemical injection pumps, an on-line chlorine analyzer, and an ammonia vapor sensor connected to an alarm.

Scale buildup can be a continuous occurrence when using ammonia feeders. When the ammonia is injected into the water stream, the resulting pH increase can initiate a calcium carbonate precipitation reaction (Kirmeyer et al., 2004). This results in solid calcium carbonate forming on the injection equipment and in chemical feed lines. This typically occurs when the water contains 30 mg/L or more of hardness (as $CaCO_3$) (Kirmeyer et al., 2004). The rate of scale buildup is proportional to the hardness of the water and must be considered when developing plant-specific maintenance guidelines (Kirmeyer et al., 2004). Examples of calcium carbonate buildup and removal are shown in Figures 8-6 and 8-7. These figures show mineral buildup next to the ammonia injection point on a static mixer and mineral buildup at the injection line fittings. In some cases, even weekly cleaning may be necessary for proper operation. The continuous buildup on the injectors will decrease the ammonia feed rate, potentially leading to breakpoint chlorination and a decrease in total residual chlorine (see chapter 9 for discussion of breakpoint chlorination and an example of the chlorine breakpoint curve). Therefore, ammonia injectors should be routinely removed and



Source: City of San Bruno.

Figure 8-6 Calcium carbonate precipitation at injector and in-line mixing device



Source: City of San Bruno.

Figure 8-7 Calcium carbonate precipitation removed from an ammonia injector

rinsed with acid, such as hydrochloric, until the deposits are dissolved. The use of flexible feed lines can be beneficial for breaking up scale formation. Likewise, multiple injection points at the same location may be useful. The redundancy of multiple injection points allows for flexibility if feed problems are encountered. It may be beneficial to have spare injectors available so that when one is removed for cleaning, it is immediately replaced without interrupting the disinfection process.

Alternatively, it may be more beneficial to soften the water supply that is used as ammonia chase water. The use of carrier/dilution water, which is softened, will minimize the pH effects. Softened water can be supplied by a point-of-use softening device or small household reverse osmosis unit. In this case, scaling may be prevented. Any time that the operator is observing decreased ammonia feed, decreased formation of chloramine, or the presence of free chlorine, one of the first actions should be to check the ammonia injectors and mixers. Mixers and feed lines exhibit the same problems and symptoms due to hard water. Mechanical propeller mixers suffer from similar issues. They can be quickly covered with precipitation leading to equipment malfunction. Therefore, they are not a typical approach for feeding ammonia.

Utilities that use direct ammonia gas feed systems can avoid the calcium carbonate precipitation problems by using special diffusers that are designed to prevent deposit buildup. If a utility has severe calcium buildup problems, converting to a direct gas feed system may be a viable option. There are few direct feed systems in use in the United States and there is only one vendor who supplies these units, so experience and availably are limited (Harms and Owen, 2004).

At EBMUD, 19% aqua ammonia is fed neat until the injection point, upon which it is chased through a T-connection with unsoftened water. Chase water provides for better ammonia mixing, which is important if a limited run of pipe is available prior to the plant effluent or sampling station. A vertical straight injection line should be opened periodically (e.g., every 6 months at EBMUD) to break up brittle precipitates with a steel rod. A spare injection port should be provided to allow for redundancy. This type of ammonia injection is used at EBMUD to provide for water treatment plant effluent ammonia addition and promote rapid chloramine formation (Figure 8-8).

Ammonia Control Systems

In order to control chlorine and ammonia feed rates, control loops may be used to adjust the chemical pumps. Two common approaches are control based on the total chlorine residual level or pacing of chemical pumps based on water flow. These approaches have different advantages and disadvantages and must be evaluated before implementation.

Controlling the chemical injection pumps based on total chlorine residual level will be applicable when the utility's goal is to maintain a target residual concentration. This allows for adjustments based on total chlorine disinfectant demand but will not respond to changes in the level of free ammonia in both raw water and finished water. If a varying level of ammonia in the water is an issue, a compound control loop system that utilizes both total chlorine residual and free ammonia levels may be an option.

Flow pacing will provide a means to adjust chemical pump feed rates as water treatment flow rates change. This type of control is based on a simple relationship whereby the chemical feed rate increases directly with the flow rate. If water quality chlorine demands are constant, this approach can provide a stable formation of chloramine and adequately limit excess ammonia. Flow pacing will not be a good option when the influent ammonia concentration varies or the chlorine demand is not constant. This approach is not recommended where such variations exist as the control system will not respond to varying water quality, only varying flow. To properly

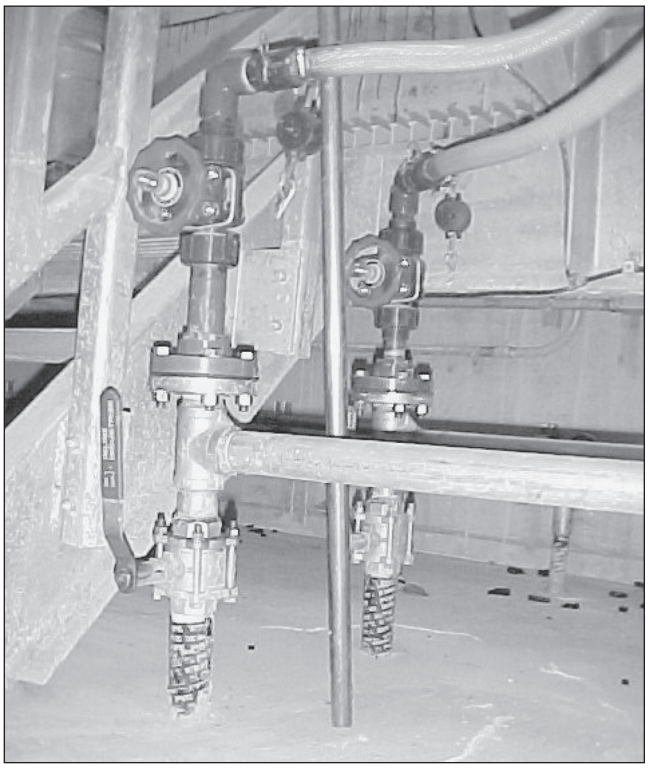


Photo courtesy of Andrzej Wilczak

NOTE: The redundant ammonia feeds with chase water (not softened) fed through the metal tee. Ammonia is fed through the flexible line. Periodically (every 6 months or so), when the deposits form in the open-ended injection pipe, the flange is opened and deposits are broken up with the 7-ft steel rod also shown in the photo.

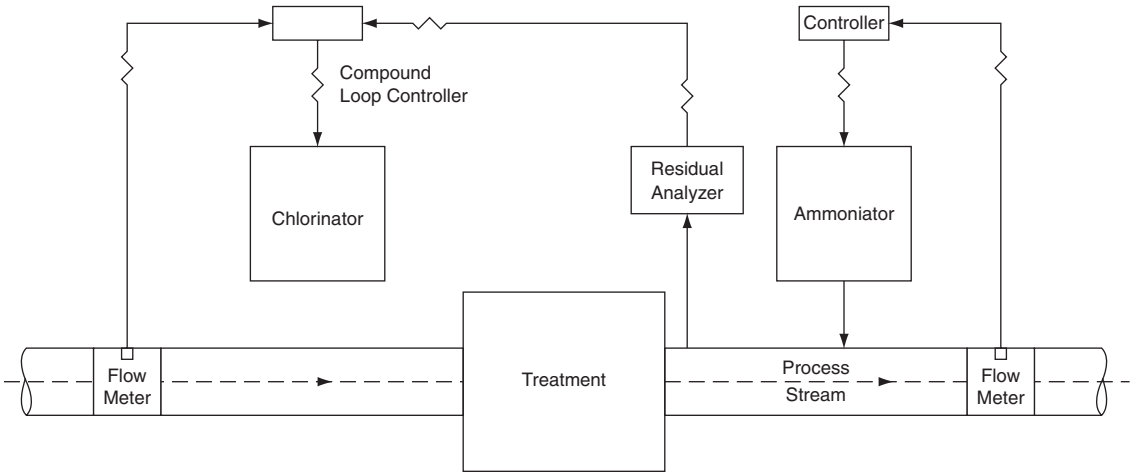
Figure 8-8 Direct ammonia feed system

control both ammonia feed and chloramine formation, good mixing of both chlorine and ammonia into the carrier water stream and subsequent reaction are all essential.

If the utility is facing changes in chlorine demand, free ammonia levels, and water flow rates, a compound control system may be needed. A compound control loop will take into account all three parameters and make the necessary adjustment(s) to the chemical feed rates. All of this information must be available in real time, necessitating the use of on-line analyzers. This type of control system may be difficult to operate due to lag time between sampling, analysis, and actual chemical pump adjustments; therefore, it must be designed and operated properly. An example of such a control system is shown in Figure 8-9. Additional information about control systems for chloramination can be found in Kirmeyer et al. (2004).

Source Water Impacts

Surface water sources can contain varying concentrations of ammonia based on activities within the watershed. Surface water ammonia levels may vary based on storm events, sewage discharges/upsets, fertilizer applications (residential and/or agricultural), and domestic activities. During these events and activities, the ammonia concentration in the source water can vary suddenly and dramatically. Therefore, it is important to know the land use activities within the watershed and monitor for events that will affect influent ammonia levels. As the ammonia level fluctuates in the



Source: Kirmeyer et al., 2004.

Figure 8-9 Example of control schematic for chloramine formation

source water, it will be necessary to adjust the ammonia feed rate in order to prevent either over- or underfeeding. If the ammonia feed rate is not adjusted to compensate for increasing source water ammonia, the plant may overfeed free ammonia and make the distribution system more vulnerable to nitrification. Conversely, unexpected low source water ammonia can lead to underfeed and inadvertent free chlorination.

Some groundwater sources may also contain naturally occurring ammonia or ammonia that has entered the groundwater due to agriculture and farm activities. In this case, ammonia addition may or may not be needed. For example, in southern California, wells have naturally occurring ammonia levels between 0.2 and 0.5 ppm; therefore, there is no need or little need for ammonia addition. Rittman and Snoeyink (1984) observed 1.3 mg/L of ammonia-N influent to sand filtration in one utility. In Germany, a river was found to have varying concentrations of ammonia between 0.05 and 4.2 mg/L (Uhl and Gimbel, 2000). These high and variable ammonia levels will impact chloramine formation. If the ammonia concentration is sufficient, the utility may just add the appropriate ratio of chlorine and obtain the desired chloramine residual. Since groundwater quality is typically more stable than surface water quality, it is usually easier to control chlorine and ammonia dosages.

If ammonia concentrations in source water are above the level needed to form chloramines, it may be necessary to breakpoint chlorinate the water before chloramine formation. Very high concentrations of ammonia would require high doses of chlorine for the breakpoint operation. In this scenario, ammonia removal becomes an issue before final chloramine disinfection can be properly developed. In Lansing, Michigan, this situation occurred when the groundwater became contaminated with high and variable concentrations of ammonia. The company responsible for the contamination was originally required to reduce the ammonia concentration only to 34 mg/L as ammonia. Therefore, the water utility would have been receiving 34 mg/L ammonia in their source water. The cost to breakpoint this groundwater was prohibitive. Later negotiations between the utility, regulators, and the responsible party resulted in an agreement to lower the ammonia concentration to 1.2 mg/L—the maximum amount desired by the utility to properly form chloramines. Between the cleanup of the groundwater and removal of contaminated wells from service, the utility has been able to continue to successfully chloraminate and meet water demands (Maier, 2003).

Monitoring

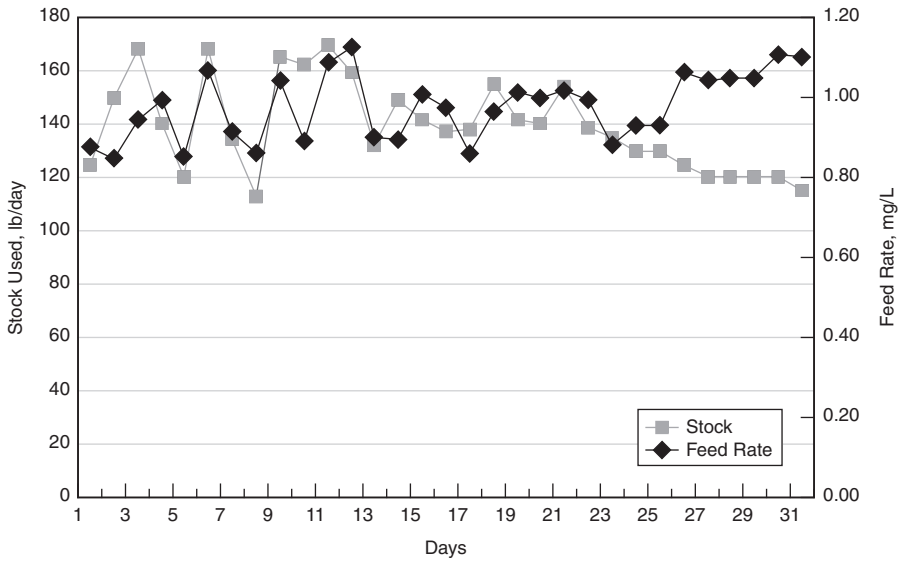
It is important to monitor water quality parameters to ensure that proper levels of ammonia and chlorine are injected and the correct chlorine to ammonia-N ratio is achieved. By obtaining the level of total chlorine, free ammonia, and total ammonia in the effluent water, the ratio can be calculated.* Achieving the proper ratio is important because if the chlorine to ammonia-nitrogen ratio increases beyond 5:1, formation of dichloramine can occur, which can lead to customer complaints due to taste and odor. If the ratio is below 4:1, excess free ammonia will enter the system and may lead to nitrification.

Monitoring can also directly detect overfeed of free ammonia in the effluent water. Grab sample or on-line free ammonia residual monitoring can be used for determination of both source water and finished water free ammonia. Based on the free ammonia level, the operator can adjust the feed rate accordingly. As recommended in chapter 7, grab sample monitoring should be done daily at the plant effluent and at least weekly at the source water (if there is ammonia in the water). There are several methods available for bench analysis of lab samples (see chapter 7).

Reliable, continuous ammonia on-line analyzers are relatively new technology. Manufacturers are developing new and better equipment every year. Currently, on-line monitors are based on either colorimetric or ion selective electrode (ISE) methodologies. Experience at Tampa Bay (Florida) Water has found that the use of on-line ammonia monitoring has improved water quality and consistency by optimizing finished water ammonia concentrations (Kirmeyer et al., 2004). At MWDSC, both colorimetric and ISE monitors have been tested. In comparisons with grab samples using lab ISE technology, it was observed that the on-line colorimetric monitor compared favorably. However, results from an on-line ISE monitor were approximately double the lab grab sample ISE results (Kirmeyer et al., 2004). Spectrophotometric on-line ammonia analyzers have improved over the last 10 years but still pose a maintenance challenge, especially if applied on water with elevated hardness and manganese. On-line ammonia analysis should still be considered a difficult measurement because small differences of under 0.1 mg/L ammonia-N concentration are significant in drinking water. At this point, on-line ammonia analyzers may be considered for process verification rather than control and as an alarm measure to avoid either loss of ammonia feed or gross overfeeding.

Another method to determine chemical dosages and ensure that overdosing of free ammonia is not occurring is by monitoring chemical storage tank level or weight. Daily checks of ammonia inventory will allow an independent verification of feed rates. By comparing the dosage and the changes in quantity of stock, the operator can verify that the two measurements are comparable. Discrepancies between feed rate and inventory will indicate a potential problem with ammonia usage that should be investigated and corrected. An example of feed rate versus stock usage is depicted in Figure 8-10. A hypothetical divergence in the data is shown beginning at day 25, which might indicate a feed problem. Monitoring of chemical inventory should be used in addition to methods such as residual analysis, calculation of chlorine to ammonia ratios, and feed control loops.

*An Internet search for on-line interactive spreadsheets that can be used to determine this ratio based on water quality parameters yielded one source (at the time of the search). It is available at: http://www.charlottesmith.us/documents.html#ExcelSpreadsheets. You will need to request a username and password. This can be done by sending an e-mail to smith.csa@earthlink.net.



Source: Data modified from City of Ann Arbor records.

Figure 8-10 Comparison of ammonia feed rates (as pumped) versus stock used (as weight). A problem is indicated by the diverging hypothetical data late in the month.

CHLORAMINE RESIDUAL

Residual at Point of Application

The concentration of chloramine entering the distribution system will be important for the prevention of nitrification. In an Awwa Research Foundation (AwwaRF) survey, an adequate chloramine residual was found to be a significant factor in preventing nitrification (Kirmeyer et al., 2004). The exact concentration of chloramine needed in the treatment plant effluent will vary with the extent of the distribution system and water quality characteristics. In general, it is recommended to maintain between 2.0 and 3.0 mg/L of chloramine residual at the entrance to the distribution system (Kirmeyer et al., 1995; Davis, 1990). However, once the nitrifier population is established, these doses may not be inhibitory. Nitrifying bacteria have been found at chloramine residuals >5.0 mg/L (Cunliffe, 1991) and increases in nitrite and nitrate concentrations observed at chloramine residuals of 3 to 6 mg/L entering the system (Wilczak et al., 1996). Increasing the chloramine dose will increase the ammonia available to AOB (Harrington et al., 2002). Whenever the AOB growth rate exceeds the AOB inactivation rate, the utility will be vulnerable to nitrification (Harrington et al., 2003). See chapter 4 for more discussion on chloramine residual and decay in the distribution system.

Distribution System Residual

The chloramine residual leaving the treatment plant must also take into consideration the chloramine decay rate and losses in the distribution system. The rate of decrease will depend on multiple factors, including water quality characteristics, distribution system demands, and residence times. Systems with extensive service areas and/or long residence times will experience greater decreases in chloramine residuals and

therefore are more vulnerable to nitrification. Such systems may want to consider a relatively higher initial residual in order to maintain an adequate residual throughout the distribution system. However, USEPA regulations (Stage 1 D/DBP Rule) also now limit the use of chloramine to ≤4 mg/L average residual in the distribution system.

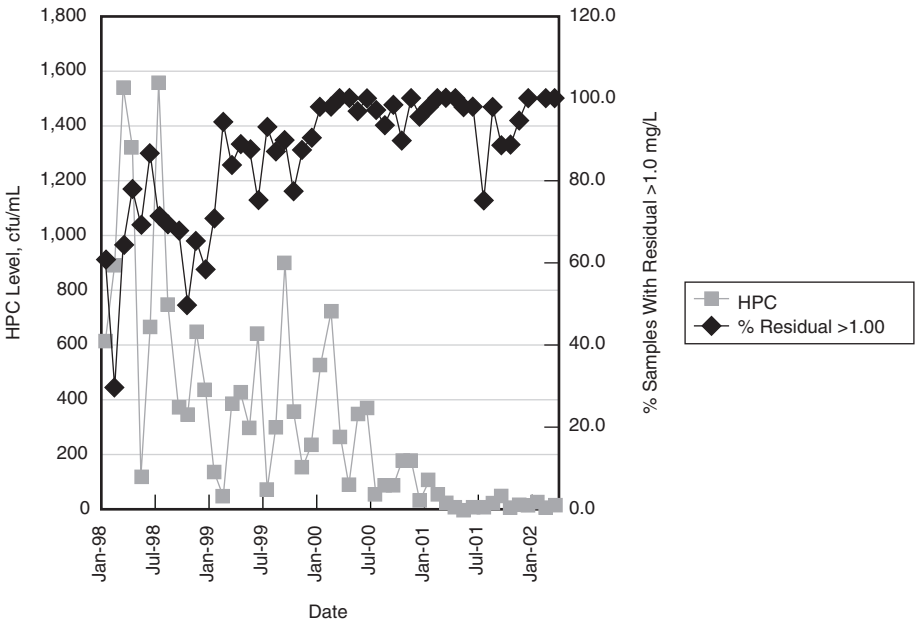
The SWTR federal regulation requires an entry point total chlorine residual of 0.2 mg/L and detectable total chlorine in 95% of the distribution system sample sites (sampled monthly). However, many utilities using chloramine set higher voluntary minimum distribution system residuals and nitrification trigger or target values. Some states target even more stringent regulations. A chloramine residual in distribution system storage tanks of >2.0 mg/L has been found to prevent nitrification (Harrington et al., 2002; Odell et al., 1996; Kirmeyer et al., 1995). Palacios and Smith (2003) examined over 120 samples from a chloraminated distribution system and found that nitrification was more likely to occur when the total chlorine residual was less than 1.5 mg/L. In Ann Arbor, the target chloramine residual leaving the treatment plant is 3.0 mg/L, with a distribution goal of all sample sites over 1.5 mg/L (Skadsen, 2002). Ann Arbor recommends that all locations in the distribution system maintain a chloramine residual preferably above 2.0 mg/L in high flow/low retention time areas and 0.5 mg/L in low flow/high retention areas in the summertime.

Since temperature is an important factor, seasonal adjustments of chloramine residual may be appropriate. Some utilities may increase the chloramine residual entering the distribution system when the temperature is higher, though this practice is not currently common. Some researchers have recommended that a residual of 1.5 mg/L in the winter and 2.0 mg/L in the summer at the entry point to the distribution system may be appropriate (Palacios and Smith, 2003). In Newport News, Virginia, the utility's chloramine residual goal is 3.5 mg/L in the winter and 4.0 mg/L in the summer at the entry point to the distribution system. The distribution goal is to have at least 90% of the sample sites used for Total Coliform Rule compliance with a chloramine residual of at least 2.0 mg/L (pers. commun., M. Hotaling, 2005). The elevation of the residual in the summer should help maintain distribution system residuals when decay rates are likely to be higher and thereby help prevent nitrification. This action must consider the impact on customers, in particular dialysis units and aquarium owners, as these groups may be adversely impacted.

Booster Chloramination

Booster chloramination is a potential method for raising the distribution system residual. However, it is much less commonly practiced than booster chlorination. The principle remains the same whether using free chlorine or chloramines. There are two basic approaches to booster chloramination: both ammonia and chlorine may be added in the distribution system or chlorine alone may be added. As when forming chloramines at the treatment plant, it is still critical to maintain the proper chlorine to ammonia ratio and minimize excess free ammonia.

When boosting both chlorine and ammonia, close attention must be given to the total chlorine residual, total ammonia, and free ammonia levels. The concentration of these parameters may vary daily at the influent to the booster station due to varying chloramine decay rates in the system. Therefore, daily water quality measurements and adjustments of chemical pumps are strongly recommended. If not properly controlled, this approach to booster chloramination could even enhance nitrification by overfeeding ammonia. If the utility is able to assess and manage the ammonia and chlorine concentrations, the elevated chloramine residual achieved may help prevent the occurrence of nitrification. Booster chloramination at reservoir sites, as practiced by Golden State Water Company, can be particularly beneficial when attempting to reduce heterotrophic plate count (HPC) levels and maintain a minimum residual in remote ends of the distribution system (Figure 8-11) (Cohen, 1998). Boosting of



Source: Cohen, 1998.

Figure 8-11 Relationships between total chlorine residual and HPC levels

chloramine residual as a practice requiring engineering improvements and capital expenditures is discussed in detail in chapter 10.

Some utilities have successfully added only chlorine to boost the chloramine residual, but this requires that sufficient ammonia is already present. Maintaining this excess ammonia would increase the vulnerability of the utility to nitrification before booster chlorine application. If sufficient ammonia is not present for the proper formation of more chloramine, application of chlorine alone will shift disinfection past breakpoint, resulting in a decrease in total chlorine residual, potential free chlorine formation, and potential dichloramine formation. It is important when using chlorine only for booster operations that careful monitoring and process control are performed in order to avoid breakpoint reactions while achieving the goal of tying up free ammonia.

Another approach is to closely monitor the available ammonia at the influent to the chlorine booster station. Since the decay of chloramine releases ammonia in the distribution system, chlorine can be added to react with the amount of free ammonia available. The City of Glendale, California, practices "trimming," where they increase the distribution system chloramine residual by boosting it with chlorine only to react with the free ammonia released from chloramine decay (Sykes, 2003). The chlorine dose is measured based on the free ammonia concentration and the target chlorine ratio. The amount of ammonia available for the reaction is monitored and controlled in order to achieve a ratio of 4.75:1 chlorine to ammonia-N at the chlorine boosting station. This strategy may be useful for reservoirs with long detention times or reservoirs in series and where chlorine boosting facilities already exist (Palacios and Smith, 2003). In bench scale tests, this strategy demonstrated an initial increase in total chloramine residual, but the "recombined" residual appeared to decay at a slightly faster rate than the nonboosted sample. This observation was not verified in field data as the system nitrified and the free ammonia from chloramine decay was consumed (Palacios and Smith, 2003). Additional studies and data would be beneficial to assess the condition(s) under which chloramine boosting is effective.

Influence of Treatment Processes

Some treatment processes affect the formation and stability of chloramines. At EBMUD, after ozonation followed by biologically active GAC filtration was implemented, the chloramine demand substantially increased despite lower concentrations of total organic carbon (TOC) (Wilczak et al., 2003a), presumably due to the demands of a less biologically stable water. In the City of Arlington, Texas, similar results were observed with decreased chloramine residuals in the distribution system following installation of ozone and GAC filtration (pers. commun., T. Andrews, 2001). At minimum, 1 hour of free chlorine contact time was necessary in order to see good chloramine stability following an ozone/biological activated carbon treatment process (Wilczak et al., 2003a). In general, total chlorine demand that was satisfied at the treatment plant was not exerted in the distribution system. At this utility, increases in the concentration of hydrogen peroxide resulted in a decrease in chloramine stability followed by nitrification in the distribution system (Wilczak et al., 2003a). Therefore, it is important to assess the impact of treatment changes on chloramine demand and stability as well as nitrification potential.

Other treatment processes may also impact the potential for nitrification. In one pilot evaluation, it was found that enhanced coagulation delayed the onset of nitrification (Harrington et al., 2002). An extensive discussion of treatment practices and their impact on chloramine stability is given in chapter 4.

STORAGE FACILITY OPERATION

There are numerous factors that may contribute to nitrification in storage facilities. The major factor is high water age due to poor mixing, inadequate turnover, and stratification combined with oversized capacity. The accumulation of sediments and development of biofilm are also contributors.

Water Age

High water age has been implicated as a major factor in the occurrence of nitrification (Kirmeyer, 1995; Skadsen, 1993; Davis, 1990; Negrin et al., 1990; Barrios and Stone, 1989; Wolfe, 1988). For example, at the MWDSC, nitrification was observed after the residence time in Orange County reservoirs increased from 3.3 to 4.5 days (Wolfe et al., 1988). Therefore, it is important to implement operational controls to reduce water age. This can be done by increasing turnover, improving mixing, reducing storage capacity, or even taking tank(s) off line if possible. Elimination of dead zones in any storage facility will be critical. Such dead zones can contribute to high water age.

Turnover, Drawdown, and Recirculation

Turnover of water in storage facilities is crucial to reducing water age. Turnover is the exchange of an existing volume of water with a new one, so that water age is minimized. Storage tanks with inadequate turnover can result in depletion of chloramine residual, increase in microbial activity, and nitrification. Changes in facility operation, such as increased turnover, can help avoid or minimize future nitrification events in storage facilities. For example, the Philadelphia (Pennsylvania) Water Department lowered their tank levels for a number of years in order to improve turnover and prevent nitrification (Odell et al., 1996).

Turnover is accomplished when a percentage of the tank volume is being drawn and filled every day. There are no established standards for water turnover in tanks; it is based on several factors such as tank volume, inlet/outlet configuration, mixing, demand, and water quality. Some states have made recommendations for optimal

turnover that range from 20% of the volume per day (Ohio) to 50% daily turnover (Georgia).

It should be noted that even with frequent turnover, stagnation can still occur. Water storage that floats on the system can stratify and allow water in the unused portion of the tank to reach significant age and higher than normal temperatures. For example, a 10-mil gal storage tank with a common inlet/outlet pipe at the bottom and 20% turnover can still stratify and develop nitrification. Nitrification in the unused portion of the tank can potentially go undetected for a period of time until that water is used or tested. An example of this practice would be the use of the lower portion of an elevated tank, where the water in the upper portion of the tank is not turned over or used. This is common practice where an elevated tank or a standpipe tank is used primarily for pressure control (Grayman et al., 2000).

A utility may find it beneficial to artificially reduce water age by deliberately drawing down storage facilities in order to increase circulation and decrease water age. Drawdown of tanks in order to remove "old" water can help improve water quality. Exercising tanks to minimize detention time can control and eliminate nitrification (Harms and Owen, 2004).

Recirculating water in standpipes and elevated storage can create a uniform water age and thereby reduce the occurrence of nitrification (Kirmeyer et al., 1995). In Fort Worth, Texas, the use of recirculation pumps in tanks resulted in an improved chloramine residual and provided promising results for preventing nitrification (Kirmeyer et al., 1995). Cascaded pumping operations and/or scheduled concurrent pumping operations can be beneficial for reducing water age in remote storage facilities. In addition, changes in operational control set points to increase turnover and decrease water age may be feasible. In all cases, operators should strive to use fill-and-draw operating strategies to maximize tank turnover.

Hydraulic Mixing and Filling

Improving mixing in storage tanks will generally improve water quality by equalizing water age, reducing stratification, and creating a uniform water quality. By providing adequate mixing and eliminating stratification, it may be possible to reduce both water age (in the unused portion of the storage tank) and temperature, thus reducing the incidence of nitrification. It is recommended that analysis of tank mixing characteristics and water age be done to determine if such stratification is occurring.

There are two ways in which water may be hypothetically considered to flow through storage tanks: completely mixed flow or plug flow (Grayman et al., 2000). Most facilities operate somewhere in between these two modes. A tracer study can be used to illustrate how close a tank is to either extreme. A tracer study can also illustrate how much "dead volume" is in a tank. Therefore, one of the most important aspects from a water quality standpoint is deciding whether a storage facility will minimize dead zones via operational conditions that approximate completely mixed flow or operational conditions that approximate plug flow. (Note that plug flow also has no dead zones, due to complete mixing in the direction perpendicular to the flow.) Due to the fact that the rate of disinfectant decay is concentration dependent, the tank operating under plug-flow conditions will generally lose more disinfectant than one operated under mixed-flow conditions (Grayman et al., 2000). Conversely, the plug-flow mode will be capable of killing more suspended organisms than the completely mixed-flow mode, so there is some trade-off if there are ammonia oxidizers suspended in the tank. Simply put, a plug-flow tank with no dead zones produces a greater extent of reaction per unit volume than a completely mixed-flow tank with no dead zones. This is why an attempt is made to achieve plug flow in tanks intended to achieve CT targets. A completely mixed-flow tank is better equipped to handle variations in input quality and flow rate than a plug-flow tank. Therefore, the water storage facility should be

designed to encourage good mixed-flow behavior rather than plug-flow behavior (Grayman et al., 2000). Completely mixed flow results in a lower average water age.

It is easier to achieve good mixed flow than plug flow. For fill-and-draw operation, particularly for elevated circular tanks, it is not clear how true plug-flow conditions can be maintained. On the other hand, some storage tanks have no problem achieving close to complete mix conditions without the use of special structural additions or mixing devices. The main deterrents to achieving well-mixed conditions in tanks appear to be improper placement, orientation, and size of inlet/outlet pipes and the possibility of temperature differences between the inflow and tank contents. Both of these factors can be dealt with through minor structural or operational changes (Grayman et al., 2000).

Mixing time primarily depends on the facility's diameter or width, water height, and inlet momentum (Grayman et al., 2000). For a tank operating in a fill-and-draw mode, mixing occurs primarily during the fill cycle and, as a result, if the tank is relatively well mixed at the end of the fill cycle, mixing problems are unlikely. Fill time must exceed theoretical mixing time. This can be calculated using the following equation:

$$\Delta V/V > 9.03\, d/V^{1/3} \tag{8-1}$$

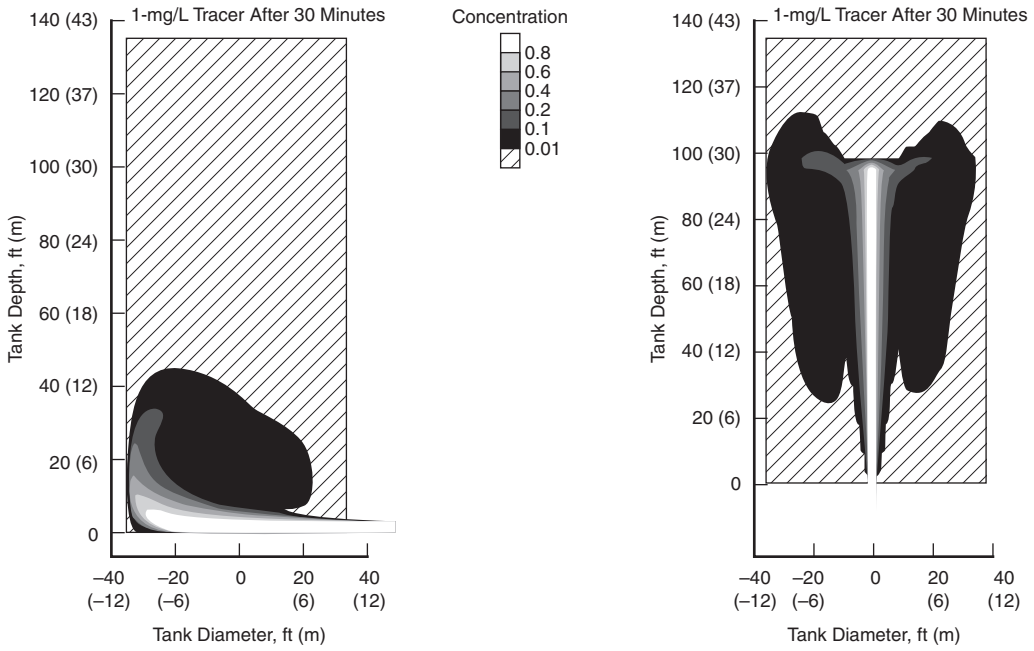
Where ΔV is the change in water volume during the fill period, V is the volume of water at the start of the fill period, and d is the inlet diameter (Grayman et al., 2004).

Another consideration is the location and orientation of inlets (Grayman et al., 2000). In Ann Arbor, Michigan, a simple addition of a bend at the entrance of the inlet tube to a 5-mil gal storage tank improved tank circulation and reduced water age. This storage tank had nitrified in the past, but no definite conclusions on the impact on nitrification by improved mixing could be determined due to the low frequency of nitrification observed following other treatment changes coincident with this modification.

In another study on steel and concrete tanks, the related technique of cycling (operating the reservoir to reduce water age) did not completely prevent nitrification from occurring (Baribeau et al., 2001). In Wichita Falls, Texas, isolated pockets of nitrification were controlled by water cycling in storage tanks (Harms and Owen, 2004). Tank samples taken at different depths found AOB in all liquid and biofilm samples. However, it is well known that poor mixing in storage facilities creates dead zones, which lead to impaired water quality including reduced chloramine residual and increased bacterial growth. Therefore, improvements in mixing should reduce bacterial activity including AOB (Grayman et al., 2000).

Mahmood et al. (2005) used computational fluid dyamics (CFD) modeling to predict mixing characteristics of different facilities under different conditions. They examined the impact of inlet structure, both size and orientation, on mixing in a 4-mil gal standpipe. When the inlet pipe discharges horizontally, the water jet will hit the far wall and mixing will not reach the top of the standpipe. When the inlet is placed vertically, the flow path is in the direction of the maximum water height and better mixing is achieved (Figure 8-12). An example of a design change converting a horizontal inlet to a vertical inlet, at Virginia Beach, Virginia, is shown in Figure 8-13.

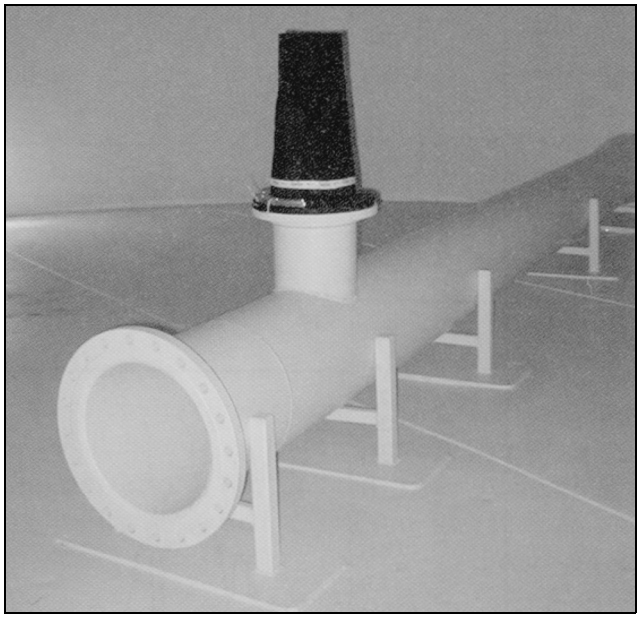
Increasing the fill time of a storage tank may be looked at as a long-term response to prevent nitrification. It is important to maintain sufficient inlet velocity during fill cycles to provide mixing. Therefore, simply reducing the fill rate to prolong the fill time will not improve mixing; a combination of increasing the fill time by reducing the flow and increasing the velocity by reducing the inlet pipe diameter may be needed. The increase in momentum is key for improving mixing in water tanks. Mahmood et al. (2005) demonstrated the effect of changing inlet momentum using CFD modeling for a 1-mil gal elevated tank. Velocity was altered by changing the inlet diameter. As the



Inflow rate = 2,000 gpm (126 (L/s); 36-in. (900-mm) vertical inlet; inlet velocity = 0.6 fps (11 m/min); isothermal condition = 68°F (20°C).

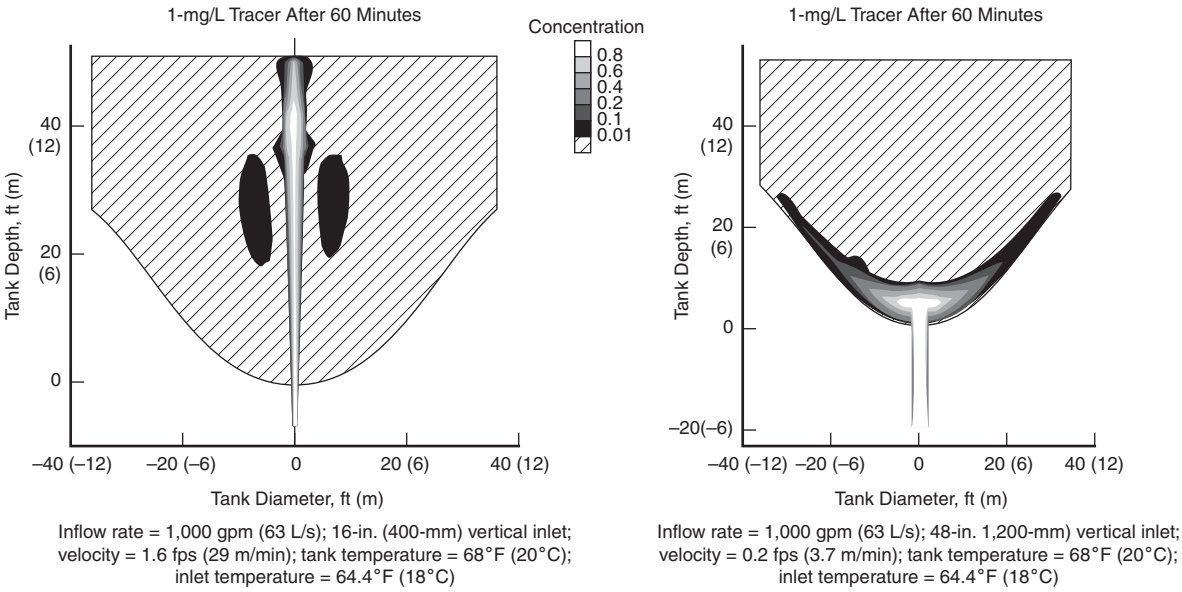
Source: Mahmood et al., 2005.

Figure 8-12 Effect of pipe inlet orientation, horizontal versus vertical, in a 4-mil gal standpipe using a 36-in. inlet, fill time of 30 minutes at 2000 gpm



Source: Mahmood et al., 2005.

Figure 8-13 Recommended design change on storage tank inlet pipe to direct water flow vertically instead of horizontally for improved mixing



Source: Mahmood et al., 2005.

Figure 8-14 The effect of inlet momentum on mixing characterisitcs of a 1-mil gal elevated storage tank using CFD modeling

inlet diameter was decreased, the velocity and momentum increased, resulting in a mixing zone that extended nearly to the surface of the elevated tank. Lower momentum (lower velocity and greater inlet diameter) showed a mixing pattern where the mixing zone only existed in the area surrounding the inlet (Figure 8-14).

If a storage facility has many short fill cycles in a day, changing tank operations to have fewer or one longer fill cycle(s) can also improve mixing. If a tank already has only one fill cycle per day, it may be possible to extend the duration of the fill cycle by draining the tank to a lower level before beginning the fill cycle.

Mixing may be further complicated by temperature. Temperature differences between the tank influent and the bulk water in the tank lead to stratification and poor mixing (Mahmood et al., 2005). For example, in the summer, water temperature in a tank will usually be higher than the temperature of the water entering the tank. The cooler influent, being denser, will remain at the bottom of the tank (Mahmood et al., 2005). Similar effects can occur in cold weather as well as where sunlight can increase the temperature of the stored water.

The ability of a system to implement these changes will largely depend on system demand, hydraulics, and fire flow requirements. General factors that should be evaluated to improve mixing include:

- Increase inlet momentum
- Increase flow rate
- Decrease inlet diameter (increase velocity)
- Evaluate orientation and location of inlets
- Monitor for temperature differentials and potential stratification

For more details on storage tank filling and design/modification considerations, see chapters 9 and 10.

Storage Capacity and Removal From Service

Distribution storage facilities have historically been sized with little consideration for water quality. Storage capacity has primarily been determined based on hydraulic issues, such as current and future system demand, pressures and flows, as well as fire flow requirements (Theiss and Antoun, 2000). Systems have generally sized storage facilities to provide uninterrupted service and fire flows.

A storage tank that is located below the system hydraulic grade line will become stagnant and will not contribute to the day-to-day operation and demand requirements. Water stagnation will lead to disinfectant residual degradation, increased microbiological activity, and nitrification.

As recommended by the *Recommended Standards for Waterworks*, also known as the "Ten States Standards" (GLUMRB, 1997), the "…minimum storage capacity for systems not providing fire protection shall be equal to the average daily consumption. This requirement may be reduced when the source and treatment facilities have sufficient capacity with standby power to supplement peak demands on the system." The recommendations also state, "Excessive storage capacity should be avoided where water quality deterioration may occur." Storage requirements may differ with different regulators. When a storage tank is oversized to address future system needs, it will cause inadequate volume turnover in the tank and excessive water age, which can potentially lead to nitrification.

Therefore, another means to decrease distribution system water age is to remove storage facilities from service, either temporarily or permanently. In particular, a combination of removal from service with regular cleaning and removal of deposits in affected facilities may reduce the occurrence of nitrification. It may be beneficial to remove facilities from service only seasonally when a utility has demonstrated seasonal vulnerability to nitrification (Ike et al., 1988). Permanent removal may be appropriate if the system has excess storage capacity. When repeated nitrification events are occurring within a storage facility that is not being used daily, an analysis of necessary versus available storage may determine a storage tank is not needed. Decommissioning excess storage can provide a long-term solution to nitrification problems. However, decommissioning of any storage facility should only be considered after a thorough analysis of distribution system demand and capacity to make sure that the facility is not needed for equalization storage, fire flow, or emergency conditions such as main breaks or treatment plant shutdowns. Reservoir decommissioning was performed by EBMUD after its distribution system was converted to chloramines in 1998. Since then, several water storage facilities were taken out of service for water quality reasons (Table 8-2). The EBMUD's Pressure Zone Planning Program (PZPP) project list includes tanks to be decommissioned and flow-control valves/regulators for water quality management. Projects will be identified in the PZPP process to replace any large excess storage reservoirs when these facilities require major rehabilitation (pers. commun., J.S. Hurlburt, 2003). Based on the required capacity projected in 2030 for large EBMUD reservoirs and smaller tanks in the same pressure zones, the capacity in these storage facilities could be reduced, on average, by approximately 50% from the existing volumes (from around 520 mil gal to 260 mil gal).

A creative solution to simultaneously decreasing storage while maintaining fire protection is practiced by the Newport News, Virginia, utility. This utility has a 5-mil gal tank that is kept full but isolated from the distribution system and only used for fires or emergencies. A rechlorination facility maintains the tank residual above 2.0 mg/L. The tank is periodically dumped and refilled with fresh water to minimize water quality degradation (pers. commun., M. Hotaling, 2005).

Proper master planning and hydraulic modeling of the distribution system are recommended in order to understand system dynamics and to properly size storage. If a storage facility is removed from service, it will need to be properly disinfected and

Table 8-2 Reservoirs taken out of service for water quality at EBMUD after chloramine conversion in 1998

Years	Reservoir Volume Range (mil gal)	No. Reservoirs Taken Out of Service	Total Volume (mil gal)
1998–2003	<1	4	1.2
	1–5	1	1.0
	>5	2	33.3
Future	<1	5	1.0
	1–5	8	18.2
	>5	2	26.4
Total		22	81.1

Source: Heaney, 2003, pers. commun.
NOTE: Total number of distribution system water storage facilities at EBMUD is approximately 170 with an approximate combined overflow volume of 1,000 mil gal.

tested before it is returned to service. A utility may wish to notify customers of these actions. For more discussion on return-to-service practices and customer notification procedures and issues, see chapter 10.

Sediments and Biofilm in Reservoirs

Microorganisms are routinely associated with sediments and biofilms in storage facilities and in the distribution system. Researchers investigating the occurrence of nitrifying bacteria in sediments and biofilms found that they occur in both environments (Lipponen et al., 2002; Kirmeyer et al., 1995). In addition, it was found that both sediment and biofilm contribute to nitrifying bacteria survival by shielding them from disinfectant residuals (Wolfe et al., 1990). Higher numbers of AOB have been observed in sediment than in biofilm (Ike et al., 1988; Wolfe et al., 1990). EBMUD found that deposits on the bottom of a reservoir were contributing to nitrification (pers. commun., A. Wilczak, 2004). In one utility, sand leaking through malfunctioning underdrains was transported into a finished water reservoir, which was nitrifying. When the sand was removed, the utility was able to maintain a chloramine residual in that reservoir and nitrification stopped (pers. commun., L. Vestal and A. Wilczak, 2005). A study of covered reservoirs in southern California detected AOB in both liquid and biofilm samples (Baribeau et al., 2001), and AOB have been isolated from sludge and wall surfaces in a coated steel tank (Stewart and Lieu, 1997).

Routine inspection of reservoirs will detect both floor and wall deposits. Routine sediment removal and cleaning is a good operational practice, which may decrease the frequency of nitrification. The frequency of this inspection and cleaning has not been universally determined, although general guidelines have been recommended by EES et al. (1999). While likely to be site-specific based on water quality characteristics and past experience, a general recommendation would include annual inspection with cleaning every 1 to 5 years. At one utility, a combination of raising the chloramine residual to 3.0 mg/L at the entry to the distribution system and cleaning the storage tanks to remove sediment accumulation was effective at controlling nitrification (Harms and Owen, 2004). At another utility, cleaning of storage reservoirs improved the general hygiene but did not resolve nitrification (Song et al., 1999). When cleaning

is performed, it is always important to provide adequate disinfection prior to returning the unit to service.

DISTRIBUTION SYSTEM OPERATION

Hydraulics

Hydraulic models can be used to predict distribution system water age and identify high water age areas to be addressed. Low-flow and high-age areas, such as dead-ends, are the most likely nitrification locations. Therefore, it is important to understand distribution system hydraulics and identify areas of high age. There are numerous computer models for assessing age and water quality.

Tracer studies conducted using conservative substances or monitoring approaches are another method for determining water age and water quality. Tracer studies are often performed using fluoride or another similar substance whose feed rate can be modified (increased or decreased) and then monitored throughout the distribution system (Vasconcelos et al., 1996). By tracking the change in concentration of a substance, the residence time at different points can be estimated. A number of different tracer substances or chemical parameters have been successfully used, such as UV 254, conductivity, and calcium chloride (Grayman et al., 2000). It is important to use a tracer substance, like fluoride, that can be closely controlled, has no adverse health effects, and has no taste or odor impact. In the absence of a tracer study, historic chlorine residual values may aid in the determination of areas with relatively higher residence times. The selection of monitoring points will be crucial in order to properly determine where the older water exists.

The expertise of the distribution system operators will be very important both for selecting points for tracer studies but also for verifying the results of any hydraulic modeling. Operations staff typically have extensive knowledge of distribution system operations and will be able to identify areas of excess water age based on their experience. Both modeling and system knowledge should be used to identify and pursue actions to reduce water age.

Systematic Distribution System Flushing

Routine flushing is an established practice for maintaining distribution system water quality. Dead-ends and other areas with long detention times are particularly noted for nitrification incidents (Smith et al., 1996; Kirmeyer, 1995; Skadsen, 1993; Davis, 1990; Negrin et al., 1990; Barrios and Stone, 1989; Wolfe et al., 1988). By reducing distribution system water age and removing sediments and biofilm, it may be possible to reduce the frequency of nitrification. There is limited literature documenting the effectiveness of this approach (Kirmeyer et al., 1995). In an AwwaRF survey of utilities, hydrant flushing was rated as one of the most important perceived methods for prevention of nitrification (Kirmeyer et al., 2004). It should be noted that once nitrification occurs, flushing is only sometimes effective at eliminating spot nitrification.

Types of flushing. There are basically two types of system-wide flushing: conventional and unidirectional flushing. The differences in each approach are discussed in the following sections. A third alternative, spot flushing, is discussed in chapter 9 as a response to nitrification.

Conventional flushing. Conventional flushing is conducted by opening one or more fire hydrants or flush-outs and is primarily utilized to react quickly to water quality problems. Conventional flushing may also be used as a preventative action to maintain distribution water quality. This type of flushing does not include directing the flow with valves.

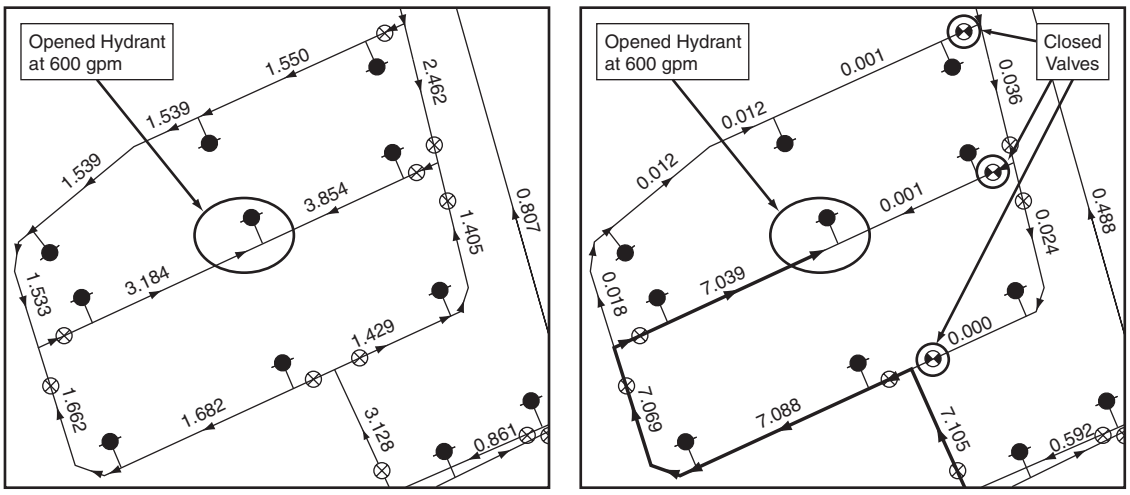
With conventional flushing it is difficult to control the quality of water entering the main being flushed, and it is possible that the quality of this water may not be superior to that leaving the system. Conventional flushing of distribution system pipes can sometimes even result in more water quality problems because of changes in flow directions and velocities, which can detach biofilms and stir up sediments. In addition, conventional flushing may be less than optimal in controlling other factors that can contribute to nitrification, since, in most pipes, the velocity of 5 to 6 fps required to scour pipe walls is not achieved.

Conventional flushing requires minimum planning and training by the water utility. A one-person crew with no special equipment can perform conventional flushing. Therefore, this is a simple and inexpensive approach, but the long-term benefits for nitrification prevention are questionable.

Unidirectional flushing. Unidirectional flushing is generally a more effective approach to maintaining water quality and preventing nitrification because of its planned approach. It is conducted in a systematic manner directing the flow to enhance the flushing of the desired main by isolating particular sections of pipes. A properly designed and implemented unidirectional flushing program can achieve water velocities greater than 5 fps and can scour the pipe.

For a successful unidirectional flushing program, the order in which pipes are flushed, the hydrants that must be opened, and the valves that must be closed or opened must be carefully planned. Unidirectional flushing should be configured to maximize water velocity when a hydrant is opened while minimizing the chance of dirty water reaching customers. Water that enters the main being flushed flows from other sections that have already been cleaned. Usually, this requires that flushing start at a source of supply and worked outward in the distribution system. Accurate maps of the distribution system, hydraulic models, and a complete database of valves and hydrants facilitate planning and execution of unidirectional flushing programs.

Comparisons of the differences between conventional and unidirectional flushing are shown in Figure 8-15. These models demonstrate the differences in flow patterns, velocities, and affected areas achieved by the two different approaches in a distribution system.



Courtesy of InfraMetrix, LLC (www.inframetrix.com).

Figure 8-15 Difference in flow pattern and pipe velocity with conventional and unidirectional flushing. The numbers on the charts are water velocities in ft/sec.

Before starting a flushing program, the benefits of flushing will need to be weighed against the drawbacks in order to maximize the effectiveness of the program. Water from flushing should be dechloraminated before disposal to the environment, thus necessitating treatment (see chapter 9). In addition, depending on the extent of flushing, there can be a significant loss of water and an associated increase in cost to the utility. The trade-off between artificial water demand and conservation needs should be considered. The frequency of flushing will depend on the effectiveness and duration of the water quality improvement. In Ann Arbor, Michigan, weekly conventional flushing of areas with high water age is done. Flushing is continued until the target total chlorine residual is restored (>2.0 mg/L; when the finished water leaves the treatment plant at 3.0 mg/L). These flushing programs vary with location and season (temperature). Flushing can be an effective system-wide nitrification-prevention strategy for small systems; however, large systems typically focus flushing on selected subset areas of the entire system. For more discussion on flushing, see chapter 9.

It is also possible to create artificial water demand, thereby reducing water age in storage facilities and the distribution system. The resulting reduction in water age may prevent nitrification. This can be done by continuous hydrant flushing, continuous blow-off, or programmable blow-off. These practices provide continuous water flow in dead-end pipes or other low-flow areas where water age is high. In Fort Eustis, Virginia, and the City of San Bruno, California, auto-flushing has been implemented on a routine or adjustable basis (Harms and Owen, 2004). An example of a programmable blow-off used by the City of San Bruno is shown in Figure 8-16. The resulting reduction in water age will have the potential to decrease corrosion, decrease biofilm, and decrease nitrification. Additional information regarding flushing in response to nitrification is provided in chapter 9.

Corrosion and Distribution System Piping Materials

Distribution system cleaning, pipe replacement, and corrosion control will all help reduce bacterial populations, including nitrifying bacteria in the sediment and biofilms. Nitrifying bacteria have been observed in all types of distribution system pipe materials. In one distribution system, AOB have been observed as high as 100,000/cm^2, although the levels of AOB found in cast iron pipes were inconsistent (Camper et al., 1996). In another study, the numbers of AOB were found to be inconsistent in unlined iron pipe but were the lowest in concrete pipe (Stewart and Lieu, 1997). In a survey of Finnish drinking water systems, high concentrations of AOB were observed in pipe sediments (Lipponen et al., 2002). In Ann Arbor, Michigan, extensive nitrification was observed in areas of low flow and unlined cast iron pipes, which were experiencing extreme iron corrosion problems, as shown in Figure 8-17 (pers. commun., J. Skadsen, 2004).

Blending of Distribution Waters

One distribution system operation that may impact nitrification is blending. Blending of different distribution waters will alter the chemistry and microbiology of those waters, thus affecting the potential for nitrification. Such blending must be carefully evaluated, as the blending can be either beneficial or detrimental regarding nitrification and water quality in general.

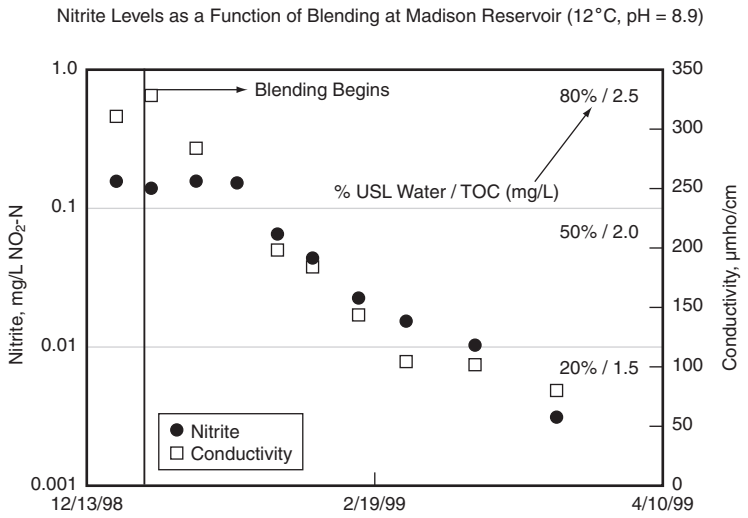
An example of the detrimental effect of blending on disinfectant residual was reported by Sykes (2003). When combining chlorinated with chloraminated water, the free chlorine residual destroyed the chloramines, which resulted in a lower total chlorine residual. This occurred in the City of Glendale (California) when their wholesale supplier switched disinfection from free chlorine to chloramines. The City of Glendale continued using free chlorine, and the blending resulted in a lowered chlorine residual

Source: City of San Bruno.

Figure 8-16 Programmable blow-off next to a hydrant used to flush dead-end to increase residual

Figure 8-17 Section of distribution pipe where extensive iron corrosion and nitrification were occurring

due to breakpoint effects. The utility is currently more successful at controlling the breakpoint effect but maintains some areas of its distribution system with a chloramine residual and some with a free chlorine residual. The formation of dichloramine and odor sometimes occurs in the interface area. Nitrification in the chloraminated sections remains a challenge (Sykes, 2003). Therefore, utilities must practice caution when blending water with different disinfectants due to the possibility of a decrease or loss of the total chlorine residual, potentially leading to nitrification and other water quality problems.



Source: Kirmeyer et al., 2004.

Figure 8-18 Reduction in nitrite levels following water blending

Some utilities have reportedly managed to successfully deal with the issue of blending a chloramine with a free chlorine water (Harms and Owen, 2004). In Portland, Oregon, this is commonly practiced at the outlets of major distribution system storage facilities (Ireland and Knudson, 1998). In some cases, the mixing zone is minimized such that only a local area of the distribution system is in the blending zone.

The positive benefits of blending have been demonstrated at EBMUD. The blending of two different waters (Mokelumne River water with other East Bay area water reservoirs with differing TOC concentrations) increased the pH and lowered the TOC of the blended product and thereby improved the chloramine stability in the distribution system (Song et al., 1999). An example of nitrite reduction following blending at the distribution storage Madison reservoir is shown in Figure 8-18. In this case, Upper San Leadro (USL) water was blended with Mokelumne River water, resulting in lower total TOC. As the percent of USL water decreased and the percent of Mokelumne River water increased, the resulting blend of water resulted in changes in the distribution storage Madison reservoir including a reduction in nitrite and conductivity. High nitrite concentrations dropped significantly.

A very thorough understanding of distribution system behavior is necessary when blending different waters. It is best if the chlorine to ammonia-N ratio is maintained during blending. The issues with blending distribution waters are similar to the issues with booster chloramination.

Periodic Switch to Free Chlorine

Periodic switching to free chlorine is practiced by some water utilities as a nitrification prevention and control strategy. In some states, this practice is required annually. Free chlorination will inactivate the AOB and remove the free ammonia from the water, thus preventing new growth. In an AwwaRF survey, 35% of respondents from chloraminated utilities indicated that they periodically switch to free chlorine; most switch once per year (67%), some switch seasonally (11%), and others as needed (22%) (Kirmeyer et al., 2004). Routine free chlorination of the distribution

system is more common in warmer climates, such as Florida and Texas (Harms and Owen, 2004). When switching, most respondents indicated that they free chlorinate for 1 month (Kirmeyer et al., 2004). The regulatory and public perceptions of free chlorination on DBPs need to be assessed by any utility. As the regulatory DBP limits have decreased and the public awareness has increased, many utilities are opting to not routinely free chlorinate their system (for more discussion, see chapter 9). The frequency of free chlorination needed to prevent nitrification has not been established and it is utility dependent based on water quality, temperature, pipe material, demand, and other utility-specific factors. In some states, regulatory agencies have required an annual period of free chlorination for a variety of reasons, including prevention of nitrification.

In some cases, free chlorination of only one area of the distribution system where nitrification typically occurs is conducted as a preventative measure. In this situation, the utility breakpoint chlorinates only a storage reservoir or a low-flow area of the distribution system. The practice of switching to free chlorine in an isolated area of the distribution system minimizes the disruption of the entire system and the impact on customers and focuses on the affected area. However, this practice will require remote chlorination operations, flushing of the affected area, and targeted public notification. Contra Costa Water District (California) routinely practices free chlorination of distribution system storage tanks in lieu of booster chloramination (Guistino, 2004). At EBMUD, free chlorination of remote reservoirs has been used but has not been effective at long-term prevention of nitrification (Song et al., 1999). Guistino (2004) has described several methods for breakpoint chlorinating treated water storage facilities. The most important factor is that the sodium hypochlorite be mixed within the tank. Since sodium hypochlorite is denser than water, slug dosages can settle on the floor of the storage facility. Therefore, a mixer may be needed inside the reservoir to lift the slug of hypochlorite from the floor and disperse it throughout the reservoir.

Free chlorination has some undesirable effects that should be addressed before implementing a routine program for prevention of nitrification. When switching disinfectant types, the need for public notification including dialysis units and other critical facilities is important. Formation of trihalomethanes (THMs) and haloacetic acids (HAAs), plus chlorinous taste and odor, are some of the important concerns. Since most utilities practicing chloramination have done so to limit formation of THMs and HAAs, it is likely that high levels of these chlorine DBPs will form, which may threaten regulatory compliance and raise public concerns. Therefore, it is often desirable to keep the frequency and duration of free chlorination to a minimum. The use of free chlorination for control of nitrification episodes is discussed in more detail in chapter 9.*

Temperature

The effect of water temperature may be a mechanism for the prevention of nitrification. In climates where seasonal temperature fluctuations occur, the decrease in water temperature in winter months may act to reduce nitrification. In one system, AOB were isolated during the summer but not the winter (Wolfe et al., 1990). In some cases, nitrification subsided as water temperatures dropped (Skadsen, 1993). However, the literature suggests that this is not universally true but more likely utility specific. In warm climates such seasonal variations will not be effective, as temperatures remain high enough for year-round nitrification. Mixing of storage facilities can

*An Internet search for on-line interactive spreadsheets that can be used to determine this ratio based on water quality parameters yielded one source (at the time of the search). It is available at: http://www.charlottesmith.us/documents.html#ExcelSpreadsheets. You will need to request a username and password. This can be done by sending an e-mail to smith.csa@earthlink.net.

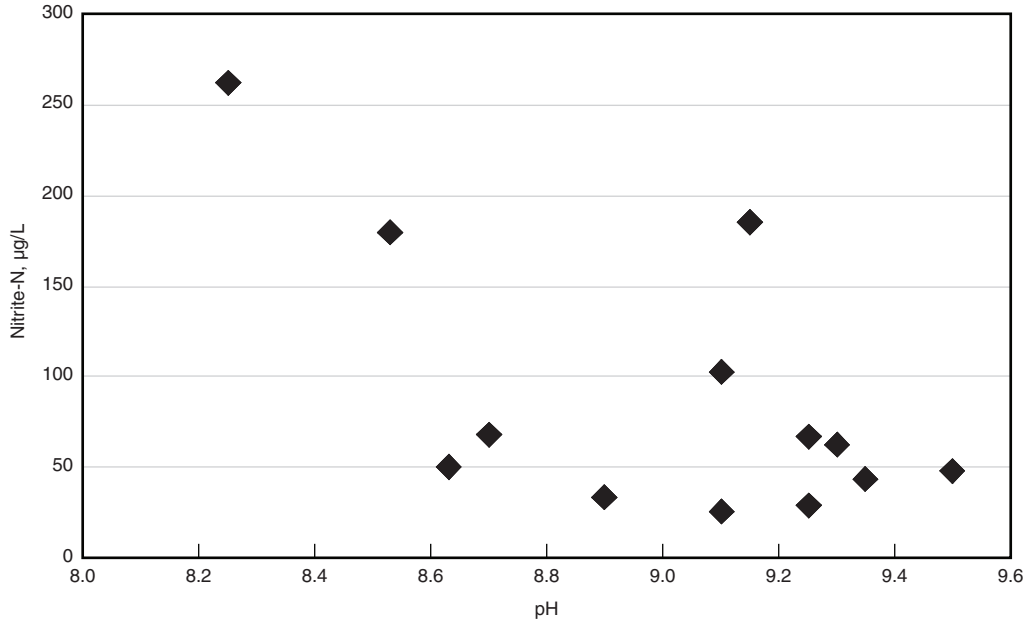
help to reduce thermal stratification. If colder waters are available, preferential use of those waters might reduce nitrification. However, the practicality of this approach will be limited due to availability of low-temperature water.

pH and Nitrification Prevention

The use of pH control to prevent nitrification has been explored by some utilities and has met with mixed success. The optimal pH for AOB growth is 6.5 to 8.5 (Kirmeyer et al., 1995; Odell et al., 1994; Jolley et al., 1984). Theoretically, either raising or lowering the pH outside the optimum growth range should reduce the growth of AOB and thereby limit nitrification.

AOB have been shown to be highly sensitive to pH. Growth of AOB stops at pH ≤6.5 (Keen and Prosser, 1987). However, since utilities are concerned with corrosion control, the option of reducing the pH is less attractive than raising the pH. Optimal AOB growth is at pH 8.0. Growth of AOB at pH 7 and 9 exhibits an 80% decrease in growth rate compared to pH 8 (see chapter 6 for more discussion on factors affecting the growth of AOB). Harrington et al. (2002) observed that the time to onset of nitrification was fastest around pH 8.5.

In one distribution system study, the use of a finished water of pH 9.3 versus pH 8.5 prevented nitrification (Skadsen, 1993). Long-term studies at this utility found the elevated pH 9.3 to be effective at eliminating the occurrence of nitrification for 7 out of 8 years (Skadsen, 2002). An inverse correlation between pH and nitrite concentrations in the distribution system was observed over the pH range studied and is depicted in Figure 8-19. In another utility, a study comparing pH 9.5 versus pH 8.5 found that the lower pH utility was more likely to nitrify (Schrempp et al., 1994). In the Florida Keys, lowering the pH from 9.5 to 7.8 coincided with nitrification in storage tanks (Cates and Lavinder, 1996). In a limited experiment, Song et al. (1999) found that raising the pH to 9 appeared to prevent nitrification in one distribution



Source: Skadsen, 2002.

Figure 8-19 Correlation of pH and nitrite at a distribution system sampling location

system but not in another when using system blending. Increasing the pH from 8.6 to 9.0 had mixed success on reduction of nitrification incidents. Wichita Falls, Texas, saw a 50% reduction in nitrite concentration in 24 hours during a nitrification episode when the pH was raised from 8.5 to 9.2 (Harms and Owen, 2004). Operation of a pilot system at pH >9 during the summer was unable to induce nitrification, even after dropping the total chlorine residual to 0.5 mg/L (pers. commun., P. Broad, 2005).

Not all experiences have supported this pH control hypothesis. Nitrification in distribution systems has been observed over a wide range of pH from 6.6 to 9.8 (Wilczak et al., 2003a; Odell et al.; 1996; Kirmeyer et al., 1995). Laboratory inactivation experiments have found that AOB were more easily inactivated with chloramines at pH 7 versus pH 9 (Noguera et al., 1999). Oldenburg et al. (2002) found that the rate of inactivation decreased as pH increased. However, this study noted that the inactivation rates were culture dependent, with the MPN rates being significantly higher. Harrington et al. (2002) found that a biocide to food ratio of ≥1.9 mg Cl_2/mg N was necessary to inhibit nitrification. The balance between growth and inactivation will need to be considered when using pH as a potential prevention mechanism.

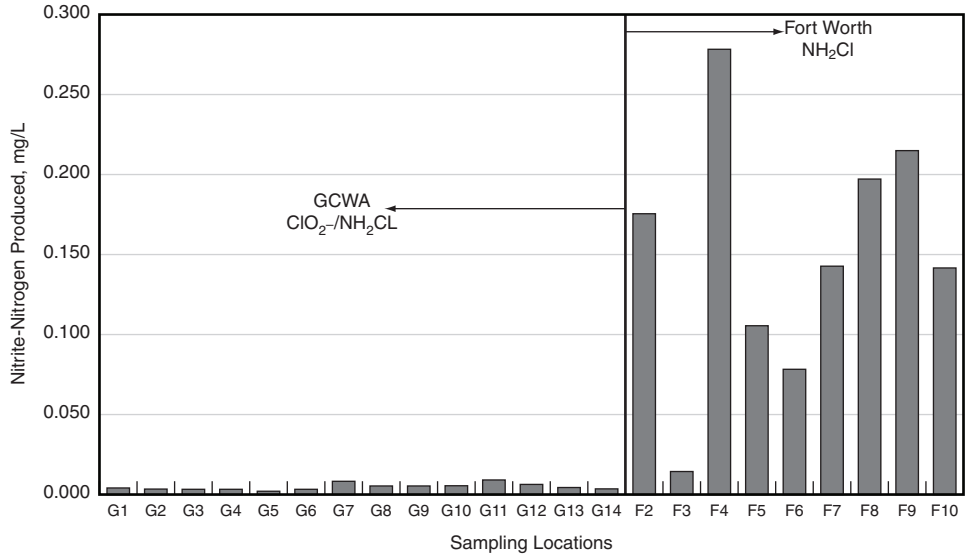
The elevation of pH will have other consequences on water quality that need to be evaluated if electing to use this approach for preventing nitrification. The elevated pH will favor the formation of monochloramine and eliminate the potential for dichloramine, thus preventing dichloramine taste and odor incidents. Most important is the fact that the decay rate of monochloramine decreases as pH is raised, creating a more stable chloramine residual in the distribution system. The higher pH may decrease lead and copper solubility. These benefits must be balanced with less desirable water quality changes. In particular, excessive scaling on pipes may affect water flow and customer satisfaction. Depending on the chemical used for pH adjustment, increases in both cost and sodium concentrations may occur.

Chlorite Ion Effects

The occurrence of chlorite ion has been proposed as a means to prevent nitrification. The Gulf Coast (Texas) Water Authority (GCWA) uses chloramines as a final disinfectant but has not observed nitrification in their distribution system. Given the warm temperatures and long detention times, this result was unexpected. This water system uses chlorine dioxide as a primary disinfectant, and significant concentrations of chlorite have been observed in their distribution system (0.25 to 0.35 mg/L). It was hypothesized that the chlorite reduced or eliminated the potential for nitrification (McGuire et al., 1999). A comparison of two utilities in Texas, one that practiced chloramination only and one that used chlorine dioxide for primary disinfection and chloramination for secondary disinfection, is shown in Figure 8-20. High concentrations of nitrite were observed at sample points throughout the distribution system of the chloraminating utility, but much lower nitrite levels were concurrently observed in the chlorine dioxide/chloramine utility.

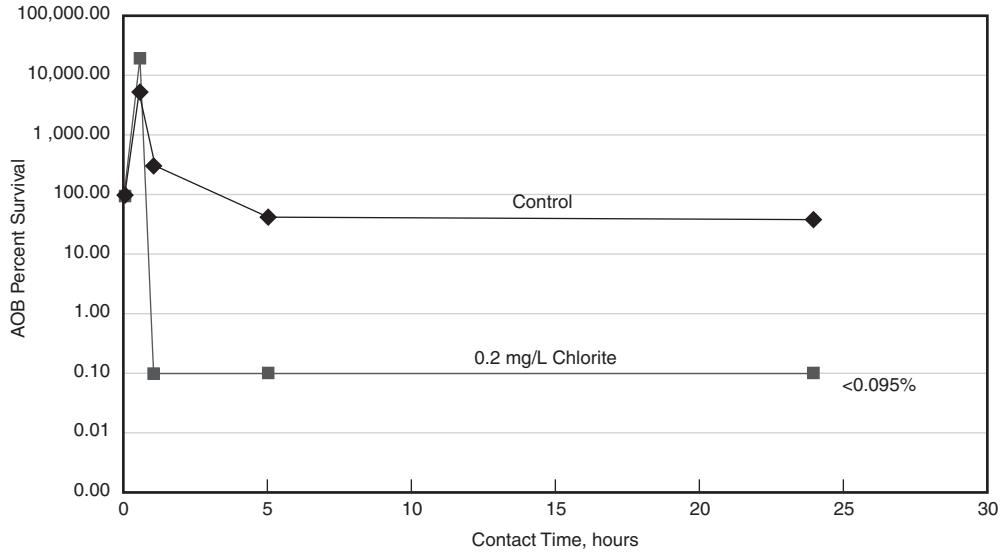
Laboratory tests were conducted using chlorite ion concentrations of 0, 0.2, 0.5, and 1 mg/L to assess the effects on AOB. All concentrations were found to reduce the survival of AOB. As shown in Figure 8-21, the percent survival of AOB cultures was significantly reduced in the presence of 0.2 mg/L chlorite (McGuire et al., 1999). Field studies also found that the presence of chlorite delayed the development of nitrification in distribution systems in warm climates at two of three utilities. One system noted nitrification still occurred. High concentrations of ammonia-N may have limited the effectiveness of the chlorite (McGuire et al., 1999).

Recent work using plug-flow reactors and Tucson, Arizona, water has found that continuous chlorite feed as low as 0.1 mg/L prevented nitrification from becoming established. In full-scale distribution systems, it appears that nitrification can be prevented by short-term applications of 0.2 mg/L chlorite ion (McGuire et al., 2004).



Source: McGuire et al, 1999.

Figure 8-20 Comparison of chloraminated distribution waters in two Texas communities, one with and one without chlorine dioxide primary disinfection



Source: McGuire, 2004.

Figure 8-21 Survival of AOB as affected by chlorite ion

Since chlorite ion is a by-product of chlorine dioxide, a nitrification preventative measure may be to feed chlorine dioxide. Alternatively, sodium chlorite could be added directly to a treatment plant effluent. The issue of oxidation of chlorine dioxide to chlorite over time has the potential to increase chlorite concentrations within the distribution system. Chlorite ion concentration has been shown to change within a distribution

system (Baribeau et al., 2002), so it will be important to monitor for chlorite in different distribution areas with different residence times in order to determine the exposure and effectiveness of chlorite at inhibiting nitrification.

It is important to consider that chlorite concentration is regulated under the USEPA Stage 1 D/DBP Rule, with a maximum contaminant level of 1.0 mg/L at the entry point to the distribution system and within the distribution system. The maximum contaminant level goal for chlorite is 0.8 mg/L. Therefore, any use of chlorite, either through addition of sodium chlorite or the use of chlorine dioxide, for the prevention of nitrification would need to be strictly controlled. Additional experimental work with this approach needs to be completed to verify the effectiveness of chlorite in field studies. However, even low concentrations of chlorite ion appear to be effective. The issue of adding a regulated substance to the drinking water for prevention of nitrification is a debatable issue that would need to be further evaluated by a utility, its regulators, and its customers. Customer acceptance of the practice needs to be included and carefully considered before implementation. The appropriate state agency should also be consulted before this approach is used.

The hazards associated with chlorine dioxide formation should be considered. As with all preventative measures, this approach should be combined with other good operational practices such as the limitation of excess ammonia and minimization of detention times.

ASSESSMENT OF PREVENTATIVE OPERATIONAL MEASURES

An important part of nitrification prevention will include continuous assessment of water quality and the effectiveness of the nitrification prevention measures. Indicators of nitrification in the distribution system include (Odell et al., 1996; Wilczak et al., 1996):

- Low total chlorine residual
- High nitrite concentration
- Low free ammonia concentration (indicating ammonia consumption)
- Increased nitrate concentration
- High HPC R2A counts
- Decrease in pH

These parameters should be routinely evaluated for changes that might indicate developing nitrification. Utilities should track background concentrations and assess changes and trends. An action plan and trigger levels should be developed. It is important to assess the normal background levels of these parameters and monitor for any change in relative concentration. A detailed discussion of assessment is given in chapters 7 and 9, including a flow chart for decision-making in Figure 9-1.

CONCLUSIONS

There are many approaches and operational practices that can be used to prevent nitrification in the distribution system. However, most have met with mixed success. Many of these approaches may be utility-specific due to differences in water quality and distribution operations. Others need more investigation to determine how universally applicable and effective they are over time. Many of these approaches coincide with good water quality management practices and therefore will be a good starting point for any utility using chloramines. A utility should select those approaches that are most appropriate to their situation. The frequency of nitrification episodes will help determine the type and extent of prevention measures selected.

The most common prevention measures include the proper control of ammonia application to form monochloramine without leaving excess ammonia in the water.

Utilities should maintain a chlorine to ammonia-N ratio between 4.5:1 and 5:1. Utilities should maintain a minimum concentration of chloramine leaving the treatment plant at >2.0 mg/L and keep the chloramine concentration at all monitoring points in the distribution system at >0.5 mg/L (preferably >1.5 mg/L). The source water should be monitored for ammonia concentrations and the ammonia feed adjusted accordingly. All actions to minimize water age in the distribution system should be considered, including maximizing mixing in storage facilities, eliminating stratification, eliminating and/or flushing dead-ends and low-flow areas, and minimizing residence time in storage tanks. Proper system maintenance, such as routinely inspecting and cleaning storage facilities and practicing corrosion control, are good practices. In some cases, periodic switching to free chlorination may be beneficial. More innovative approaches including blending of waters, booster chloramination, increasing pH to >9, and use of chlorine dioxide/chlorite may be evaluated.

Despite prevention measures, many utilities will experience nitrification. Therefore, all chloraminating utilities should have a response plan prepared including public notification for nitrification events.

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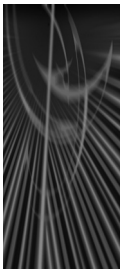


Chapter 9

Assessment and Operational Responses to Nitrification Episodes

Christopher P. Hill
Sabine Arweiler

INTRODUCTION

This chapter provides guidelines for conducting a nitrification assessment to determine when nitrification is occurring and discusses water quality indicators of nitrification in drinking water distribution systems. This chapter also discusses development of a nitrification response plan and operational responses to nitrification in the distribution system and finished water storage facilities.

When loss of disinfectant residual or any unusual change in water quality occurs in a system, one must determine if the cause is nitrification to be able to respond in an effective manner. It is important to learn and understand the impacts of system operation on nitrifications events and consequently to be able to prevent nitrification in the future. Table 9-1 presents a summary of the key points presented in this chapter.

NITRIFICATION ASSESSMENT

This section discusses the impacts of nitrification on finished water quality and how to use water quality data to determine when nitrification is occurring. It first identifies common water quality characteristics of nitrification. It then provides examples of how water quality data can be used to identify nitrification in the distribution system and storage facilities. Finally, it discusses the importance of identifying the cause of a nitrification episode to effectively respond and prevent future nitrification events.

Water Quality Indicators of Nitrification

Chapter 7 provides a discussion of alert levels and action levels. Indicators of nitrification in the distribution system include (Odell et al., 1996; Wilczak et al., 1996):

- Low total chlorine residual
- High nitrite concentration

Table 9-1 Key points from chapter 9

Nitrification Assessment	• A nitrification monitoring plan is needed to assess distribution system water quality and determine when nitrification is occurring.
	• Low total chlorine residual concentrations compared to baseline concentrations can be indicative of excessive chloramine degradation or nitrification.
	• Progressively higher nitrite concentrations indicate that nitrification is occurring. High nitrite and/or nitrate concentrations are among the best indicators of nitrification.
	• Higher than normal free ammonia concentrations may indicate there are sufficient nutrient levels present to promote AOB growth. Lower than normal free ammonia levels can indicate that nitrification is already occurring
	• Nitrification is often accompanied by increased HPC R2A counts.
	• Nitrification can also result in a depression in pH in low alkalinity waters. As such, localized reductions in pH, coupled with any of the other indicators, may also be an indicator of nitrification
	• After it has been determined that nitrification is occurring, it is important to respond in a timely and effective manner. To prevent recurring nitrification it is important to identify the cause of the nitrification.
	• Determining the cause of nitrification requires utilities to assess the impacts of distribution monitoring, finished water quality, treatment plant operation, distribution system and storage tank operation, and distribution piping on nitrification.
Responses to Distribution System Nitrification Episodes	• Breakpoint chlorination can be an effective short-term response to nitrification but is not a long-term solution. The goals of breakpoint chlorination relative to nitrification response are: (1) oxidize any free ammonia in the distribution system, depriving nitrifying bacteria of a nutrient source; (2) inactivate the nitrifying bacteria in the system; and (3) oxidize nitrite, which exerts an oxidant demand and increases chloramine degradation.
	• Flushing can be an effective emergency response to both nitrification and indicators of the potential for nitrification. Flushing can remove distribution system biofilms and sediments, reduce disinfectant demand, and bring fresher water into areas of the distribution system with low flow.
	• Increasing chloramine residual is primarily used to prevent nitrification and has never been demonstrated to be effective as a response measure even during early stages of nitrification.
Responses to Nitrification in Distribution System Storage Facilities	• Breakpoint chlorination of storage tanks can be an effective response to nitrification.
	• Deep cycling of storage facilities can be an effective means to prevent or respond to nitrification, but is only effective in well-mixed tanks. The ability to implement deep cycling is dependent on system pressure and emergency flow requirements.
	• Draining and disinfection may be practical and effective for small (<1 mil gal) storage facilities. Before taking the facility off-line, it is important to assure the ability to maintain system pressure and fire-flow requirements with the facility out-of-service.

NOTE: AOB, ammonia-oxidizing bacteria; HPC, heterotrophic plate count.

- High free ammonia concentration
- Low free ammonia concentration
- Increased nitrate concentration
- High HPC (heterotrophic plate count) R2A counts
- Low pH
- Increased temperature (not a direct indicator of bacterial activity, but some systems may use it as an indicator of nitrification potential and alter operations, e.g., summer versus winter operation)

Temperature should be monitored simultaneously with the above parameters. Ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) activity and growth increase with temperature, as discussed in chapters 2, 3, and 6. Therefore, utilities can expect some or all of the water quality trends listed above to coincide with rising water temperature and reverse with decreasing temperature.

Low total chlorine residual concentrations compared to baseline concentrations can be indicative of excessive chloramine degradation. Excessive chloramine degradation can release more free ammonia, which is a nutrient source for AOB, and can cause nitrification. Excessive chloramine degradation may also be the result of nitrification. Nitrite is a product of nitrification and can cause chloramine degradation, resulting in the further release of ammonia and AOB growth, which leads to a complete destruction of chloramine residual.

Nitrite and nitrate are products of nitrification, and as such high nitrite and/or nitrate concentrations are among the best indicators of nitrification. Similarly, progressively higher nitrite concentrations indicate that nitrification is occurring. Higher than normal free ammonia concentrations, particularly in areas of high water age and low disinfectant residual, indicate there are sufficient ammonia levels present to promote AOB growth. When ammonia levels are lower than normal, it can indicate that nitrification is already occurring and nutrient levels are being depleted. Nitrification is often accompanied by increased HPC R2A counts. The increase in HPC R2A bacterial densities can result from both the low monochloramine residual (insufficient disinfectant) and the presence of organic-rich products released by AOB, which provide a nutrient source for HPC bacteria. Nitrification may result in a depression in pH in low-alkalinity waters. As such, localized reductions in pH coupled with any of the other indicators may also be an indicator of nitrification.

Because several related phenomena can occur simultaneously or sequentially, for best diagnostics, all related water quality indicators should be reviewed jointly along with the assessment of system operations. Note that AOB are not considered at present to be useful indicators of nitrification because of time (up to 1 month) required to assay these organisms (see chapters 3 and 5). Similarly, correlations between nitrite and AOB and HPC R2A and AOB are tentative at best and system specific. Although it is more time consuming to monitor HPC R2A compared to nitrite, HPC R2A can be a good indicator of microbiological water quality. Increased HPC R2A counts can occur for a number of reasons, but consistently high and/or unstable HPC R2A counts in the absence of high nitrite can indicate that conditions are ideal for nitrification and an appropriate preventive response is warranted. On the other hand, increased AOB counts mean that AOB is already well established in system biofilms and nitrification is likely already occurring (Cunliffe, 1991; Stewart and Lieu, 1997). For these reasons, AOB monitoring is not part of nitrification response at this point. If and when less time-consuming AOB detection and enumeration methods are available for field use, AOB monitoring may become the primary water quality indicator. Until then, measurements that reflect AOB activity will continue to serve as the main tools primarily available to operations.

Table 9-2 Examples of water quality characteristics of various stages of nitrification

Parameter	Background (No Nitrification)	Beginning of Nitrification	Incomplete Nitrification (NOB not active)	Complete Nitrification (NOB active)
Total chlorine (mg/L Cl_2)	>1.5	0.5–1.5	<0.5	0
Nitrite (mg/L N)	0–0.010	0.010–0.050	>0.050	0
Free ammonia (mg/L N)	0–0.1	>0.1	0	0
HPCs R2A (cfu/mL)	<500	1,000	>1,000	>1,000
Temperature (°C)	<15	15–20	15–20	>20
pH (units)	Normal	Normal	Less than target	Less than target

NOTE: HPC, heterotrophic plate count; NOB, nitrite-oxidizing bacteria.

Table 9-2 presents an example of how these indicators might be used to determine if nitrification is occurring. It should be noted that the concentrations presented in Table 9-2 will be highly system specific and as such may not be applicable to all systems, e.g., background R2A levels will depend on the concentration of organic carbon in the water. Chapter 7 discusses development of a water quality monitoring plan to identify when nitrification is occurring.

Identifying Nitrification in Drinking Water Distribution Systems

A nitrification monitoring plan is required to assess distribution system water quality and determine if nitrification is occurring. Chapter 7 discusses development of a nitrification monitoring plan. If no nitrification monitoring plan exists, but nitrification is suspected, a utility should monitor the following minimum number of parameters in the area(s) of suspected nitrification: total chlorine residual, nitrite, and free ammonia. A nitrification monitoring plan should then be developed as soon as possible. Figure 9-1 presents a flowchart to determine if nitrification is occurring. It is based on the use of monitoring parameters recommended in chapter 7 and is prioritized based on their usefulness in assessing whether or not nitrification is occurring.

Low total chlorine residual is the primary screening parameter for identifying areas in which nitrification might be occurring. Although nitrification has been shown to occur in distribution systems in the presence of chloramine residuals 2 mg/L or greater, it generally requires the presence of sufficient free ammonia such that the rate of AOB growth exceeds the rate of AOB inactivation (Wolfe et al., 1988, 1990; Harrington et al., 2003).

Increased nitrite and/or nitrate concentrations, particularly in areas with low total chlorine residuals, are indicative of nitrification. In fact, unless high nitrite or nitrate levels are observed, it is not likely that nitrification is occurring. Low total chlorine residuals accompanied by high free ammonia concentrations indicate conditions are ideal for nitrification. Low total chlorine residuals, high nitrite or nitrate concentrations, and low free ammonia concentrations indicate that nitrification is occurring.

Figure 9-2 shows how monitoring results can be used to identify when nitrification is occurring in a distribution system storage facility and evaluate the effectiveness of the response action taken. In this example, water quality in a 3-mil gal steel distribution system reservoir located low in a pressure zone (i.e., not turning over very

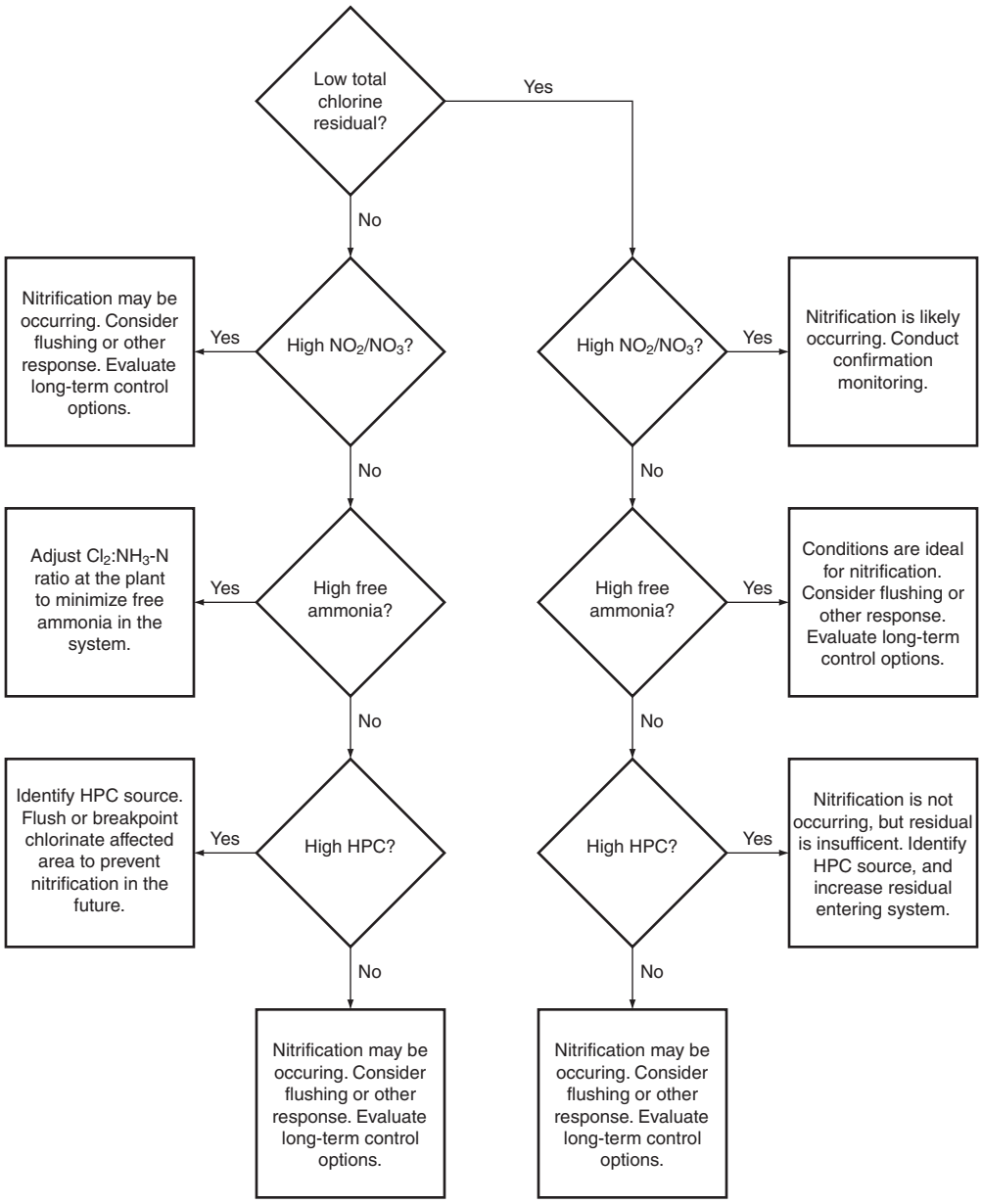
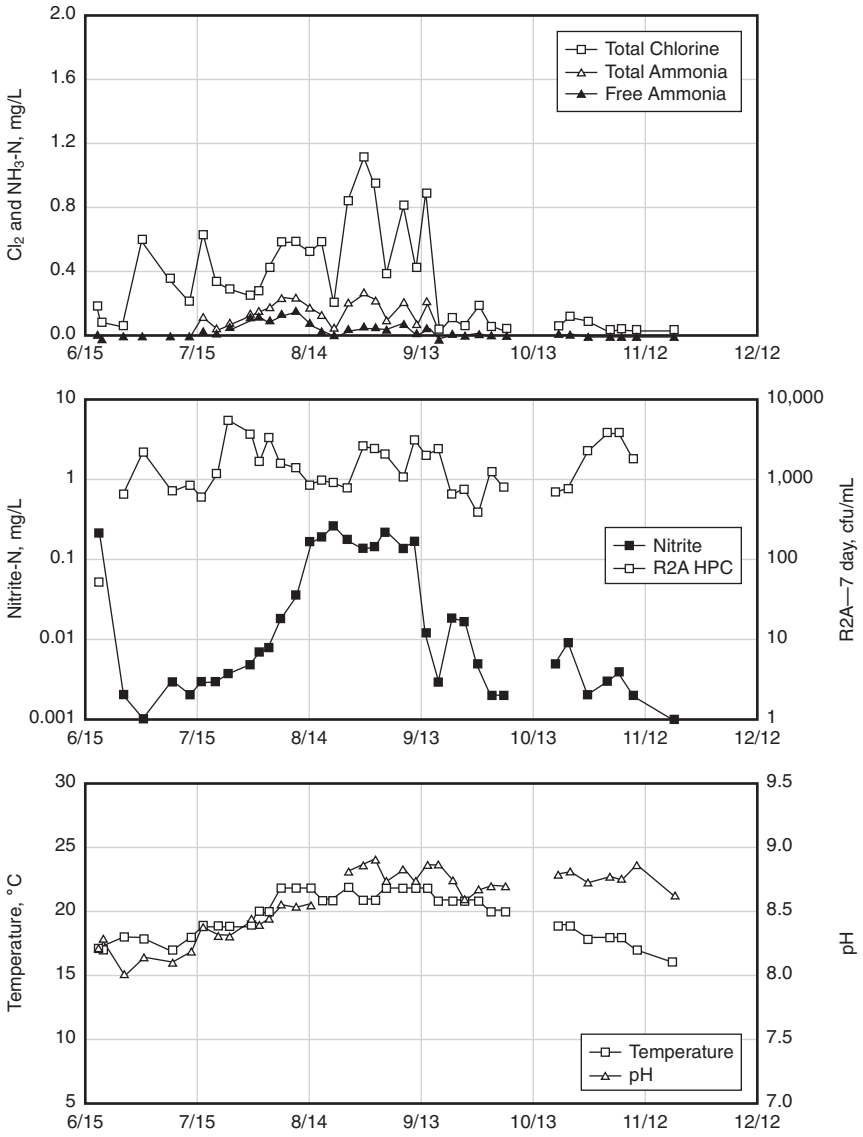


Figure 9-1 Nitrification assessment flowchart

well) was initially characterized by low total chlorine residual (≤0.1 mg/L Cl_2), high nitrite concentrations (0.2 mg/L N), nondetectable levels of free ammonia, pH of 8.3 (about 0.5 unit less than normal), and temperature of 17°C. Based on this data, it was determined that the tank was nitrifying.

A decision was made to breakpoint chlorinate the tank on June 22, 1999, in an attempt to eliminate nitrification and improve water quality. Following chlorination, the total chlorine residual increased to approximately 0.5 mg/L Cl_2 and nitrite was completely eliminated. Concurrent with the chlorination, attempts were made to improve tank turnover. Approximately 1 month after chlorination, nitrite levels began to increase. The total chlorine residual trend was characteristically "jagged," displaying a pattern of unstable water quality. Traces of free ammonia were detected in July, but by

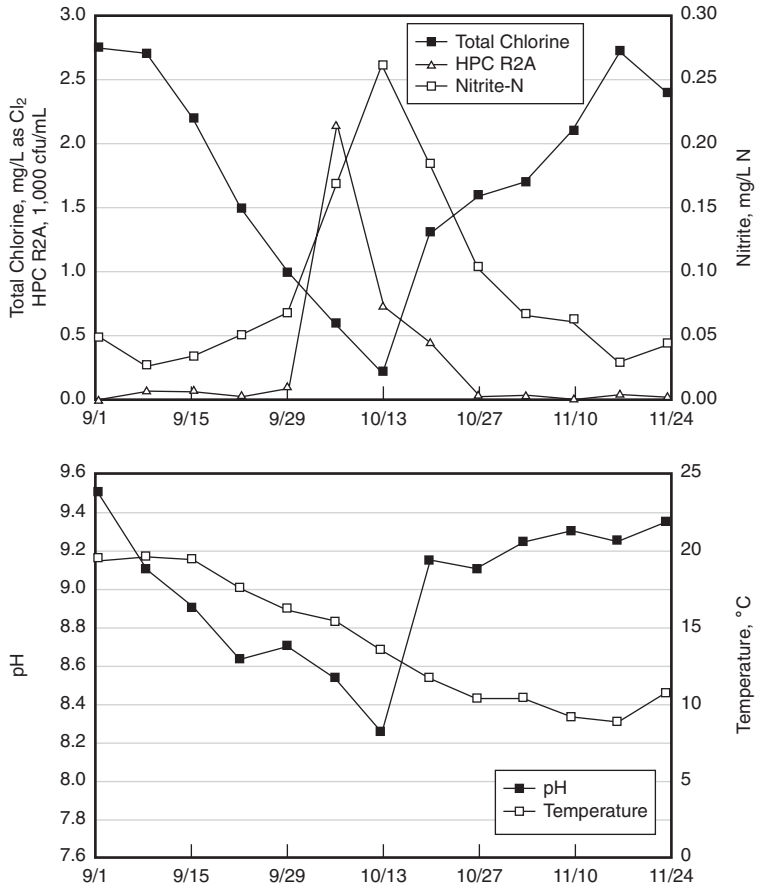


Source: Wilczak, 1999, unpublished data.

Figure 9-2 Example of nitrification assessment for a storage tank

mid-August all of the free ammonia was gone and prior nitrite levels were established. Over the entire study period, the R2A HPC bacterial counts were high (approximately 1,000 colony-forming units [cfu]/mL and greater), indicating bacterial regrowth was not arrested by the tank chlorination. This is an example of an insufficient response that did not resolve the root cause of the nitrification, most likely due to an insufficient free chlorine dose and inadequate tank cycling.

Figure 9-3 shows another example of how water quality changes during nitrification. In this example, total chlorine, nitrite, pH, temperature, and HPC R2A are presented for one distribution system monitoring location. This location was characterized by initial total chlorine concentrations of approximately 2.7 mg/L Cl_2, low nitrite (<0.05 mg/L N), and low HPC R2A (<100 cfu/mL). As nitrification began to occur in early September, total chlorine levels began to drop significantly at this monitoring location before reaching a low of 0.2 mg/L Cl_2 in mid-October. The drop in



Source: Skadsen, 2004, unpublished data.

Figure 9-3 Example of distribution system nitrification assessment

residual was accompanied by significant increases in nitrite (from less than 0.05 mg/L N to 0.26 mg/L N) and HPC (from less than 10 cfu/mL to greater than 2,000 cfu/mL). Nitrification also resulted in a drop in finished water pH from 9.5 to 8.2. In this case, as the system water temperatures decreased, the nitrification subsided and water quality parameters returned to their baseline concentrations.

Determining the Cause of Nitrification

After it has been determined that nitrification is occurring, it is important to respond in a timely and effective manner. However, to prevent, or at the very least minimize, recurring nitrification, it is also important to identify the cause of the nitrification. Chapter 4 presents an overview of the causes of nitrification in drinking water distribution systems.

Determining the cause of nitrification requires utilities to examine existing data and create new data, where necessary, to assess the impacts of the following on nitrification:

- Distribution system monitoring
- Finished water quality
- Treatment plant operation

Table 9-3 Example nitrification alert and action levels

Parameter	Target at Reservoir Inlets	Target at TCR Sampling Stations	Action Level 1 (Alert Level)	Action Level 2 (Operational Responses Required)	Action Level 3 (Regulatory Violation Possible)
Total chlorine (mg/L)	>1.7	>.1.5	1.0–1.5*	<1.0	<0.2
Nitrite-N (mg/L)	<0.01	<0.01	>0.02	>0.03	>0.05
HPC-R2A (cfu/mL)	<100	<100	>100	>200	>500
Free ammonia-N (mg/L)	<0.1	<0.15	>0.15	>0.2	NA†

Source: Charlotte D. Smith & Associates, 2003.

NOTE: cfu, colony-forming units; HPC, heterotrophic plate count; TCR, Total Coliform Rule.

* Use 1.0 for TCR sampling stations representative of low flow in the pipes.

† Not applicable. Assumes free ammonia-N has been converted to nitrite-N.

- Distribution system operation
- Storage tank and reservoir management
- Infrastructure (distribution piping)

Chapter 7 discusses development of a nitrification monitoring program and identifies appropriate monitoring parameters and methods necessary for prevention and detection of nitrification. Chapter 8 presents operational practices to prevent nitrification. Chapter 10 summarizes nitrification prevention measures that require capital improvements.

DEVELOPING A NITRIFICATION RESPONSE PLAN

When there is indication that nitrification is occurring or that conditions are right for nitrification to occur, it is important to respond in a timely manner. Delaying response can result in further deterioration of water quality. However, it is also important that a response be well planned and coordinated to prevent spreading the problem and exacerbating the effects of nitrification. It is equally important for the response to be effective. In instances when the first response is ineffective, it is critical to understand the causes of nitrification and the possible reason(s) the response may not have been effective. It is counterproductive to repeatedly apply measures that do not result in long-term solutions to nitrification (e.g., increasing chloramine in a nitrifying tank without improving turnover rates or to repeatedly breakpoint chlorinate an area of the system without taking steps to reduce water age in that area of the system). This section discusses development of a nitrification response plan to ensure an effective and appropriate level of response.

Prior to development of a nitrification response plan, it is critical to develop a nitrification monitoring program and establish system-specific baseline concentrations for nitrification monitoring parameters (e.g., total chlorine, nitrite, free ammonia, total ammonia, nitrate, and HPC), alert levels, and action levels. The nitrification monitoring plan will identify system-specific alert and action levels, which can be used to determine the appropriate level of nitrification response. Table 9-3 provides example baseline concentrations, alert levels, and action levels. It is intended to be used only as a guide, and it is recommended that utilities determine system-specific alert levels and action levels and develop their own nitrification response plans accordingly.

After the baseline concentrations are determined, alert levels and action levels can be set to develop a nitrification response plan. The level of response should be commensurate with the alert level or action level. That is, an alert-level response will be less

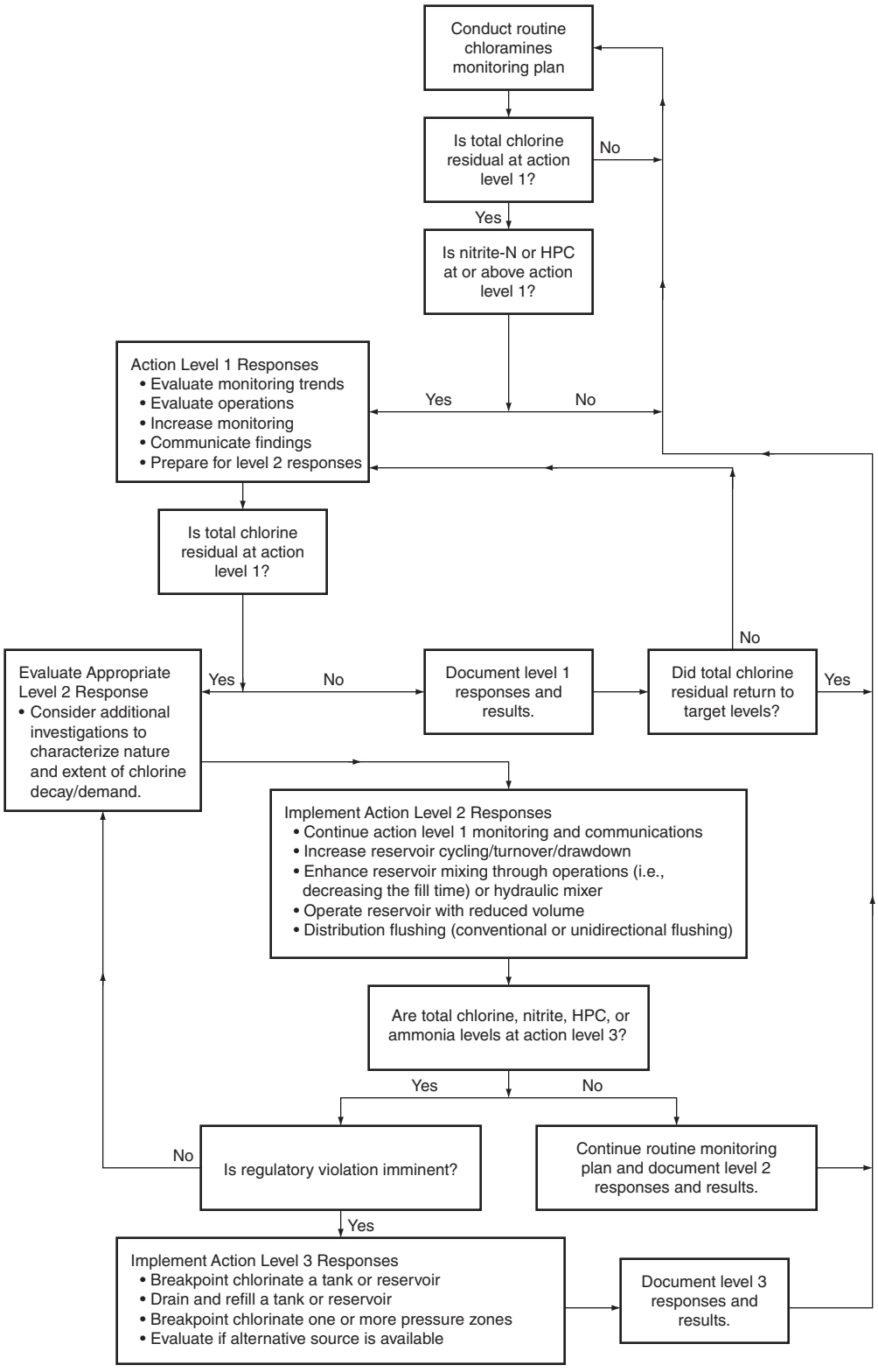
Table 9-4 Example of nitrification responses

Action Level	Programmatic Activities	Operational Activities
Action Level 1 (Alert)	• Increase water quality monitoring and operational vigilance • Initiate internal communications • Review historical monitoring trends • Review recent operating conditions • Prepare for situation escalation • Identify possible operational responses if action level 2 is attained. • Increase reservoir cycling/turnover to decrease water age.	• Increase monitoring (locations or frequency) • Increase reservoir cycling/turnover to decrease water age
Action Level 2 (Operational Responses)	• Evaluate which operational alternatives are appropriate for situation • Initiate action level 2 operational response(s): — Continue increased operational and water quality monitoring. — Initiate increased communication with utility staff, and if appropriate, public notification (i.e., for increased flushing and potential dirty water or loss of pressure or other complaints). — After action is initiated, document water quality changes for the evaluation of the success of response in mitigating nitrification. • Evaluate and document effectiveness of response • Evaluate and document any conditions that influenced the success of the response • Evaluate and implement any operating strategies for nitrification prevention that may help prevent recurrence of nitrification in this location	• Increase reservoir cycling/turnover to decrease water age • Enhance reservoir mixing through operations (i.e., decreasing the fill time) • Perform distribution system conventional flushing (to decrease water age) • Operate reservoirs with reduced volume or basin out of service • Enhance reservoir mixing with mechanical mixers • Perform unscheduled distribution system unidirectional flushing (to reduce chlorine demand from loose sediment or corrosion products on pipe walls). This means conducting a small-scale unidirectional flush of an area not scheduled in the routine unidirectional flushing program.
Action Level 3 (Regulatory Violation Possible)	• Determine whether regulatory violation is imminent • Determine whether emergency communications and actions are necessary • If regulatory violation occurs, follow appropriate customer notification requirements in accordance with state requirements	• Breakpoint chlorinate a tank or reservoir • Completely drain and refill a tank or reservoir • Breakpoint chlorinate one or more pressure zones • Switch water supplies

Source: Charlotte D. Smith & Associates, 2003.

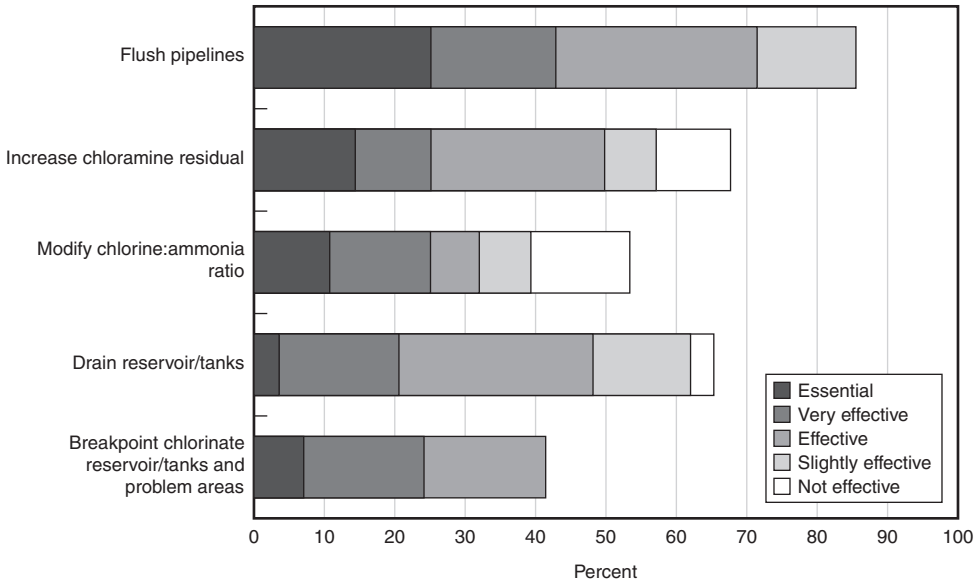
severe than an action-level response. For example, if the nitrite concentration in a storage tank increases above the alert level, the appropriate response may be increased monitoring. However, if the nitrite concentration continues to increase and exceeds action level 1, the response may be to initiate deep cycling (i.e., increase drawdown) to ensure maximum volume turnover. Finally, if the nitrite concentration exceeds action level 2, it may be necessary to initiate breakpoint chlorination of the storage tank. Table 9-4 presents an example of alert-level and action-level responses.

A decision tree can be a useful tool in developing a response plan, as discussed in the following section. Figure 9-4 presents an example nitrification response decision tree. The decision tree is based on system-specific alert and action levels and is



Source: Charlotte D. Smith and Associates, 2003.

Figure 9-4 Example of nitrification response decision tree



Source: Kirmeyer, et al., 2004.

Figure 9-5 Utility survey of effectiveness of various nitrification responses

provided only as an example. Utilities using this manual to develop a nitrification response plan should determine system-specific alert-level and action-level responses.

If nitrification is suspected in an area of the distribution system or in a storage tank, there are several options for remedying nitrification, and the level of response should be proportional to the extent of the nitrification event. These responses, in order of increasing operational effort, include:

- Increased monitoring (suspected or possible nitrification)
- Checking and optimizing ammonia feed rates and chloramine demand/decay
- Increasing volume turnover in storage tanks (lower operational levels)
- Flushing the affected area
- Free chlorine burnout of targeted areas within the distribution system
- Draining and disinfecting storage tanks
- Switching to a more stable water source (if available)
- Taking excess storage out of service (where possible, seasonally or long-term)
- Free chlorine burnout of the entire distribution system
- Increasing chloramine residual entering the distribution system (providing other operations have already been optimized) (This should be considered a "last resort" operational measure.)
- Engineering improvements to be considered where necessary (see chapter 10)

Many of these responses are discussed in greater detail in the following sections.

Figure 9-5 presents the results of a utility survey regarding the effectiveness of various nitrification responses (Kirmeyer et al., 2004). The figure is based on the responses of 29 utilities and reflects the judgment of the effectiveness of various responses based on the number of utilities that use that response. For example, slightly more than 40% of the utilities surveyed practice "breakpoint chlorination of reservoirs/tanks and problem areas." Of those utilities, approximately 20% determined

breakpoint chlorination was essential to control nitrification. Approximately 40% rated it very effective and the remaining 40% rated it effective.

Following any response activity (e.g., targeted free chlorine burnout of the affected area followed by flushing), total chlorine residual and other key indicators of nitrification should be resampled after the activity. The length of time following a response before remonitoring is system specific and activity specific; however, a maximum of 2 days is recommended. If it does not appear that the nitrification problem has been solved, additional remedial activities may be required. For example, following breakpoint chlorination of a storage tank, Irvine Ranch Water District of California resamples within 12 to 30 hours. If water quality parameters still exceed the action level, the tank is rechlorinated (Irvine Ranch Water District, 2003).

RESPONSES TO DISTRIBUTION SYSTEM NITRIFICATION EPISODES

Once nitrification has begun to occur, it is critical to respond in a timely and effective manner. This section describes responses to nitrification in the distribution system, including breakpoint chlorination and flushing. It is a guide intended to present responses to nitrification that can be implemented in a timely manner to eliminate nitrification and minimize water quality degradation. Operational strategies and engineering improvements to prevent nitrification are discussed in chapters 8 and 10, respectively.

Breakpoint Chlorination

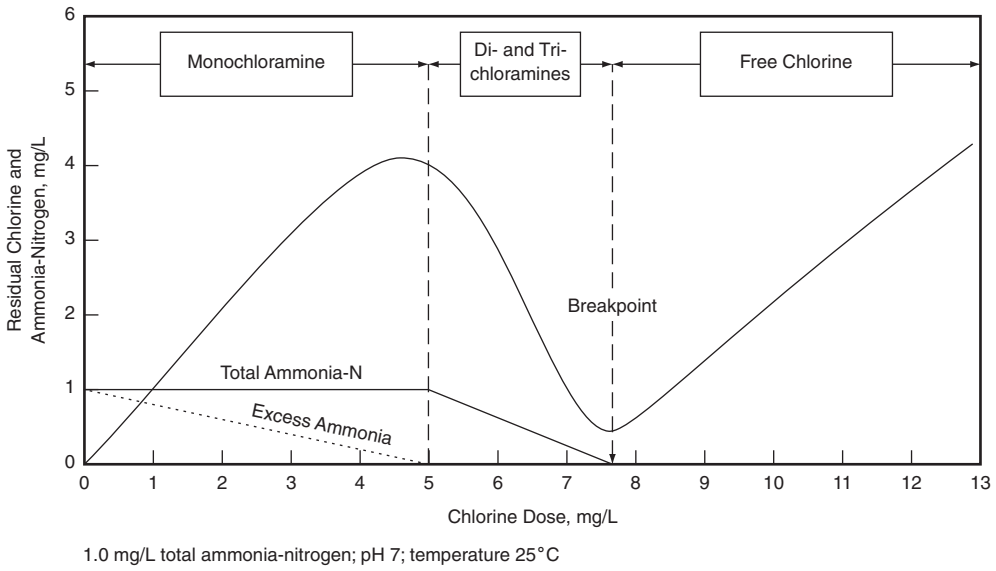
Breakpoint chlorination is probably the most effective short-term nitrification response but may not prevent nitrification from reoccurring (Odell et al., 1996). Breakpoint chlorination refers to the addition of chlorine to water at a concentration whereby all of the ammonia has been oxidized to nitrogen, resulting in a free chlorine residual. Figure 9-6 presents an ideal breakpoint curve in laboratory or ultra-pure water without chlorine-consuming substances such as natural organic matter (NOM) or nitrite. In field applications, nitrite, which is typically present in nitrifying waters, will also need to be oxidized. Nitrite exerts a free chlorine demand of 5:1 (i.e., 0.2 mg/L nitrite as N will exert 1.0 mg/L free chlorine demand as Cl_2).

As Figure 9-6 demonstrates, at weight ratios of less than about 5:1 (chlorine dose on the x-axis in Figure 9-6 is equivalent to the chlorine-to-ammonia-N [Cl_2:NH_3-N] weight ratio as the initial concentration of total ammonia in this example is 1 mg/L), there is an excess of free ammonia (a critical component in the onset of nitrification) and monochloramine is the predominant combined chlorine species formed. As discussed in chapter 8, it is preferred that the Cl_2:NH_3-N ratio be maintained between approximately 4.5:1 and 5:1, although this can vary depending on the system. This keeps the amount of free ammonia entering the system to a minimum and prevents formation of dichloramine and trichloramine, which are formed at ratios greater than about 5:1. Dichloramine and trichloramine can cause taste and odor issues in the system.

During breakpoint chlorination, the ammonia molecule becomes progressively more chlorinated, i.e., $NH_3 \rightarrow NH_2Cl \rightarrow NHCl_2 \rightarrow NCl_3$, as the Cl_2:NH_3-N weight ratio increases and the amount and type of chlorine present changes according to Figure 9-6 (Kirmeyer et al., 2004). The following equation presents the overall breakpoint reaction (Woolschlager et al., 2001):

$$NHCl_2 + HOCl \rightarrow N_2 + 3HCl^- + H_2O \qquad (9\text{-}1)$$

When chlorine is present at ratios in excess of 5:1, monochloramine is formed and the breakpoint reactions proceed by two main groups of reactions: (1) the disproportionation of monochloramine to form dichloramine and (2) the decomposition of



Adapted from Wolfe et al., 1984.

Figure 9-6 Ideal breakpoint curve

dichloramine. Both reactions require an excess of free chlorine (Kirmeyer et al., 2004; White, 1999). Disproportionation of monochloramine to form dichloramine occurs according to the following reaction:

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad (9\text{-}2)$$

Dichloramine will undergo a series of complex decomposition and oxidation reactions in the presence of excess free chlorine to form nitrogen-containing products, including nitrogen gas (N_2), nitrate (NO_3^-), nitrous oxide (N_2O), nitric oxide (NO), and others (Kirmeyer et al., 2004). Dichloramine may also react with excess free chlorine to form trichloramine, as follows (White, 1999):

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad (9\text{-}3)$$

At a Cl_2:NH_3-N ratio of 7.6:1 (i.e., the dip in the breakpoint curve), all of the available ammonia is oxidized to N_2 and other oxidized nitrogen products and chlorine residuals are greatly reduced or eliminated. At this point, any remaining chlorine residual occurs as dichloramine with some trace amounts of monochloramine and free chlorine (Kirmeyer et al., 2004). This is known as the "breakpoint" because, above this weight ratio, free chlorine is the predominant chlorine residual present and nitrogen species have been oxidized to form nitrogen gas. Beyond that point, any additional chlorine added results in an equal and proportional increase in the free chlorine residual (Wolfe et al., 1984).

To achieve breakpoint chlorination in ultra-pure waters, Cl_2:NH_3-N ratios of greater than about 7.6:1 are needed. However, in drinking water distribution systems, the breakpoint Cl_2:NH_3-N ratio may be much higher than 7.6:1 depending on pH, temperature, and the presence of other substances, such as nitrite and organic nitrogen, that can react with free chlorine. In nitrifying distribution systems, nitrite may exhibit a significant chlorine demand and significantly impact the required breakpoint chlorination dose. Nitrite is oxidized by free chlorine according to the following reaction (White, 1999):

$$NO_2^- + HOCl \rightarrow NO_3^- + H^+ + Cl^- \quad (9\text{-}4)$$

Kirmeyer et al. (2004) reported breakpoint Cl_2:NH_3-N ratios ranging from 7:1 to 16:1 in an Awwa Research Foundation (AwwaRF) survey of chloraminated systems. A 10:1 ratio is often used for convenience of calculations and generally matches actual chlorine requirements quite well. Additional chlorine may also be added at a ratio of 5:1 (Cl_2:NO_2-N) to account for the chlorine demand exerted by nitrite. Site-specific breakpoint ratios should first be determined experimentally for each water supply; once determined, they can be used for all breakpoint operations in the system. It is also important to note that breakpoint reactions do not occur instantaneously, since their kinetics are highly pH dependent. At a relatively high pH of 8.5 or above, typically recommended for corrosion control and chloramines stability, it takes several hours for the breakpoint equilibrium demonstrated in Figure 9-6 to develop. Therefore, monitoring of resulting free chlorine levels should be done several hours or overnight after dosing of chlorine has been completed allowing time for mixing and all reactions to completely occur.

The goal of breakpoint chlorination relative to nitrification response is three-fold (Dennis et al., 1991):

- First, breakpoint chlorination oxidizes any free ammonia in the distribution system, depriving nitrifying bacteria of a nutrient source.
- Second, upon oxidation of the free ammonia and conversion of dichloramine and trichloramine to free chlorine and nitrogen, the free chlorine acts as a disinfectant and inactivates the nitrifying bacteria in the system.
- Third, nitrite is oxidized to satisfy any nitrite demand for either free chlorine or chloramine. The length of time and free chlorine residual at which breakpoint chlorination should be maintained depends on water quality and system needs and goals.

If factors such as poor tank mixing, excessive water age, or inadequate control of the Cl_2:NH_3-N ratio are the root cause of the nitrification event, breakpoint chlorination is not likely to be an effective long-term solution. In these cases, utilities should consider more permanent control strategies, such as changes in operation or engineering improvements (see chapters 8 and 10).

Breakpoint chlorination of the entire system. Breakpoint chlorination of the entire distribution system, often referred to as "free chlorine burnout," involves discontinuation of ammonia addition and adjusting the chlorine dose at the treatment plant to achieve a free chlorine residual at the ends of the distribution system. Free chlorine burnout is appropriate as both a nitrification prevention measure (see chapter 8) and as a response to a nitrification episode in the distribution system. Target free chlorine concentrations entering the distribution system and at the end of the distribution system will vary from system to system. Orange Water and Sewer Authority of North Carolina feeds free chlorine at 1.5 to 2.0 mg/L in an attempt to maintain a free chlorine residual of at least 0.2 to 0.3 mg/L at the ends of the system (pers. commun., Orange Water and Sewer Authority, North Carolina, 2004). However, a 2- to 3-mg/L free chlorine residual entering the system and residual of greater than 0.5 mg/L at the ends of the system are typical goals. Ann Arbor, Michigan, feeds free chlorine at 2 mg/L at the entry to the distribution system in an attempt to maintain at least a detectable chlorine residual at the most distant ends of the distribution system (pers. commun., J. Skadsen, City of Ann Arbor, Mich., 2004).

The extent to which systems are able to achieve these targets is dependent on a number of system factors. The US Environmental Protection Agency (USEPA) has established a maximum residual disinfectant level of 4 mg/L for chlorine, which may limit the free chlorine concentration entering the system and make it difficult to achieve a free chlorine residual of 0.5 mg/L at the ends of the system. In these instances, a longer burnout period (maybe 1 month as opposed to 1 or 2 weeks) or use of booster chlorination may be necessary. The length of time over which utilities practice system-wide

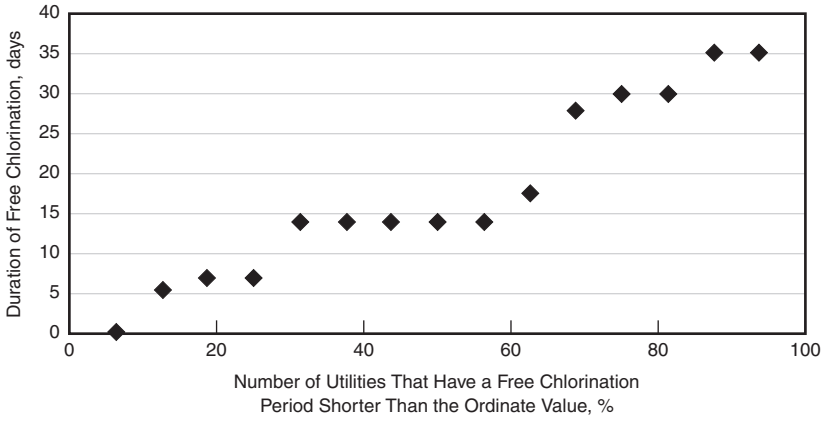
free chlorine burnout depends on a number of system-specific factors, including system size, water temperature, pH, and extent of the nitrification problem.

A number of utilities throughout the United States practice routine, annual, or semi-annual free chlorine burnout as a preventative measure (Kirmeyer et al., 2004). In fact, the North Carolina Department of Environment and Natural Resources requires chloraminated systems to practice free chlorine burnout at least annually (North Carolina Administrative Code 15A 18C.1500) and the Florida Department of Environmental Protection recommends periodic breakpoint chlorination for chloraminated systems (Mulford, 2003).

The duration of the free chlorine burnout period can vary from system to system. From a recent AwwaRF survey, Kirmeyer et al. (2004) reported most utilities switch for a period of approximately 30 days. The Metropolitan Water District of Southern California (MWDSC) used to practice free chlorine burnout for a 4- to 5-week period annually before the process was recently discontinued due to short-term increases in disinfection by-product (DBP) concentrations. Ann Arbor typically practices free chlorine burnout for approximately 2 weeks: 1 week to allow time for the free chlorine to reach the extremities of the distribution system and 1 week of free chlorine contact time in the distribution system (pers. commun., J. Skadsen, City of Ann Arbor, Mich., 2004). Some utilities may prefer to avoid this annual burnout period due to increased DBPs, as stated above, and customer complaints. In such a case, utilities may consider targeted free chlorine burnout of the affected area or storage facility (this is discussed later in this chapter) or increasing chloramine residual entering the distribution system. Increasing the chloramine residual entering the system may be a viable method of prevention for nitrification but may also result in increases in both free chlorine and chloramine DBPs, more ammonia available to nitrifiers, greater chemical cost for chlorine and ammonia, and potential increases in the number of customer complaints regarding chlorinous taste and odors, as well as perceived excessive amounts of chemicals added to the water.

In a survey of chloraminated utilities, 35% of the 68 survey respondents indicated that they periodically switch from chloramines to free chlorine for secondary disinfection (Kirmeyer et al., 2004). Of the utilities that periodically switched to free chlorine, 67% did so on an annual basis, 22% switched as needed, and 11% changed disinfectants seasonally. The burnout period is less than 1 month for 82% of the respondents (15 participants provided information about the duration of the disinfectant change period). Figure 9-7 shows the duration of the free chlorine period for those utilities responding.

The procedure by which a utility breakpoint chlorinates the entire distribution system will be largely system specific. Figure 9-8 presents an example system-wide breakpoint chlorination protocol. When using this example to develop a system-specific procedure, it is important to realize that shutting off the ammonia feed system will result in Cl_2:NH_3-N ratios in excess of 5:1 at the chlorinated/chloraminated water interface. To minimize the potential for water quality degradation, including taste and odor, it is recommended that this be accompanied by flushing to more quickly displace chloraminated water in the distribution system and particularly in the nitrifying areas of the system. Another strategy is to conduct free chlorine burnout in the spring to take advantage of increasing water demand and to inactivate nitrifying bacteria before warm summer temperatures. In dry regions, conducting burnout in the spring may also minimize fire-flow concerns related to lower reservoir operating levels. It is also recommended that storage facilities be taken off line and breakpoint chlorinated separately (using one or more of the methods discussed later in this chapter) to further minimize the potential for water quality degradation at the chlorinated/chloraminated water interface. Where it is not possible to take the storage facility off line, the tank level should be lowered to the minimum level possible to maintain fire flow and emergency storage requirements. It is important to note that some systems have experienced an



Source: Kirmeyer et al., 2004.

Figure 9-7 Free chlorine burnout period duration survey results

Step 1.
Conduct background monitoring (chlorine, nitrite, HPC R2A).

Step 2.
Determine chlorine dose required to achieve the target free chlorine residual in the problem areas of the distribution system.

Step 3.
Conduct any necessary customer or state agency notifications.

Step 4.
Reduce tanks levels to lowest level possible or remove tanks from service.

Step 5.
Have flushing crews ready.

Step 6.
Discontinue the ammonia feed at the water treatment plant and any booster disinfection stations and adjust chlorine to the dose determined by step 2.

Step 7.
Breakpoint storage tanks.

Step 8.
Measure free chlorine and HPC in the known nitrifying areas of the distribution system.

Step 9.
Continue to operate under free chlorine conditions until desired free chlorine residual and baseline HPC levels are achieved in the nitrifying areas of the distribution system.

Step 10.
Resume ammonia feed.

Figure 9-8 Example of system-wide breakpoint chlorination protocol

increase in HPC in nonnitrifying areas during periods of free chlorine burnout (Skadsen, 1993). After resuming ammonia feed, the same strategies that were used to accelerate the movement of chlorinated water can be used to increase movement of chloraminated water throughout the distribution system and particularly in those areas with high water age.

In the early 1990s, Ann Arbor, Michigan, experienced isolated nitrification events within the distribution system (Skadsen, 1993). The events were characterized by decreases in chloramine residual (from an average of 3.2 mg/L to an average of 1.4 mg/L) and increases in HPC (from an average of 68 cfu/mL to an average of 2,000 cfu/mL) and nitrite concentrations (from an average of 16.6 µg/L to an average of 86.6 µg/L). The city attempted several solutions to remedy the nitrification, including adjusting the Cl_2:NH_3-N ratio, increasing the chloramine residual (to 8.0 mg/L), low-velocity flushing of affected areas, and free chlorine burnout of the entire system. Free chlorine burnout was shown to be the only effective strategy for controlling nitrification. The burnout period extended approximately 10 weeks. Almost immediately, the city saw a reduction in HPC and nitrite concentrations in the nitrifying areas and was able to maintain a free chlorine residual throughout the distribution system. It is interesting to note, however, that the city experienced increases in HPC counts in nonnitrifying areas of the distribution system during the chlorine burnout period. It was theorized that this increase was the result of granular activated carbon (GAC) carryover in the finished water. Fine particles, such as GAC, are capable of harboring bacteria. Monochloramine is a superior disinfectant for such bacteria (LeChevallier et al., 1984, 1987, 1988; Stewart et al., 1990).

Breakpoint chlorination of the affected area of the distribution system. Where nitrification is localized in an isolated part of the distribution system, a targeted free chlorine burnout can be as effective as a system-wide free chlorine burnout period and can minimize disruptions to treatment plant operations and negative impacts on distribution system water quality. When conducting a targeted free chlorine burnout, it is important to isolate the affected area, to the extent possible, to minimize the mixing of chlorinated and chloraminated water. The primary reason for this is that the Cl_2:NH_3-N ratio at the chlorinated water and chloraminated water interface will often exceed 5:1 and can result in di- and trichloramine formation with destruction of any chlorine residual, free or combined (Barrett et al., 1985; Muylwyk et al., 1999; Mahmood et al., 1999).

Breakpoint chlorination of an isolated area of the distribution system requires that there is a location available at which to inject the chlorine, such as an injection vault or booster chlorination station. It also requires that the affected area be small enough that it can be reasonably contained by manipulation of distribution system valves. This response method typically involves addition of chlorine at a dose sufficient to achieve a 1- to 2-mg/L free chlorine residual. The MWDSC (pers. commun., 2004) applies a dose sufficient to achieve a free chlorine residual of approximately 0.5 mg/L and holds that concentration for 1 day. EBMUD (pers. commun, 2003) holds a 1-mg/L free chlorine residual for 1 day.*

The significant chlorine dose required to achieve breakpoint will likely result in taste and odor issues, as well as high DBP concentrations, and may result in increases in bacterial and/or coliform counts. If at all feasible, it is recommended that the water in the nitrified area be flushed from the system. This serves three purposes. First, it will prevent customers from receiving drinking water of poor quality. Second, flushing will help to remove the water of poor quality and may remove excess system sediments

*An Internet search for on-line interactive spreadsheets that can be used to determine this ratio based on water quality parameters yielded one source (at the time of the search). It is available at: http://www.charlottesmith.us/documents.html#ExcelSpreadsheets. You will need to request a username and password. This can be done by sending an e-mail to smith.csa@earthlink.net.

and biofilms. Finally, flushing will aid in drawing the chlorinated water into the affected areas of the system.

Superchlorination. Superchlorination involves dosing chlorine at concentrations sufficient to achieve a free chlorine residual of 50 mg/L or more for up to 24 hours; the typical hold time is approximately 2 hours. Even more so than other targeted burnout activities, it is critical that the response area be relatively small and easily isolated from the remainder of the distribution system. This is one approach to respond to nitrification in isolated areas of the distribution system. This approach is sometimes used as a last resort response to nitrification episodes that cannot be remedied by other methods discussed in this chapter, such as old areas of the distribution system with severe tuberculation. Even in these cases, superchlorination may only temporarily relieve nitrification.

When superchlorination is practiced, customers in the affected area should be notified of the burnout activities and advised that water service will not be available until such activities are complete. Utilities should notify customers 3 to 4 days in advance that they will be without water for 8 to 9 hours. Prior to addition of chlorine, utility personnel shut the valves at the meter box into each home in the affected area. The line is purged during chlorine addition to improve the effectiveness of the response. After the targeted hold time has been achieved, the distribution main is flushed and dechlorinated (for more on dechlorination, see the Flushing section of this chapter). Before valves are opened to restore service to individual customers, hose bibs at each customer residence or business are opened to flush any remaining superchlorinated water from the service line.

Impact on water quality and D/DBP Rule compliance. Introduction of free chlorine into a chloraminated distribution system may result in an increase in DBP concentrations, specifically trihalomethanes (THMs) and haloacetic acids (HAAs). Because of concerns over short-term exposure to DBPs, some utilities have ceased to practice scheduled breakpoint chlorination of the distribution system (Mann et al., 1998; pers. commun., Sweetwater Authority, 2004).

At the chlorine–chloramine water interface, the Cl_2:NH_3-N ratio is likely to be in excess of 5:1; as a result, systems may experience short-term taste and odor problems. Introduction of free chlorine into the distribution system may also result in sloughing of biofilms, causing short-term increases in HPC or coliform concentrations (Odell et al., 1996). Skadsen (1993) also noted an increase in HPC concentrations in nonnitrifying areas during free chlorine burnout resulting from the decreased effectiveness of free chlorine for some bacteria. To minimize these impacts, some systems flush free chlorinated water from the distribution system (see the Flushing discussion presented in this chapter).

If a system routinely, e.g., every August, switches from chloramines to free chlorine for a scheduled burnout period and is required to collect Stage 1 or Stage 2 Disinfectant/Disinfection By-products (D/DBP) Rule compliance samples during that period, those analytical results are to be included in the compliance determination (63 FR 69390). However, if an immediate response is needed to a nitrification event, samples collected during that period may not be required to be included in the compliance determination. In these cases, depending on the DBP concentrations in the chloraminated system and the resulting increase in DBP concentrations, a system could be in jeopardy of violating the Stage 1 or Stage 2 D/DBP Rule maximum contaminant levels.

The Stage 1 and Stage 2 D/DBP rules require monitoring to be conducted "…during normal operating conditions." Thus, a system that routinely switches to free chlorine for a burnout period is under normal operating conditions. On the other hand, assume a system is experiencing nitrification in the selected areas of the distribution system and opts to convert to free chlorine for 2 weeks to correct the problem as part of a response activity rather than typical operating conditions. Under this scenario, if the utility is required to collect samples during that period, the state may allow the

sampling to be postponed until normal operating conditions return or may decide that those samples would not be used for determining compliance (USEPA, 2001).

As previously mentioned, breakpoint chlorination is more appropriate as an emergency response to nitrification, rather than a long-term solution. As such, it is recommended that utilities explore operational (see chapter 8) and engineering (see chapter 10) strategies for long-term nitrification control. However, it is recommended that utilities planning to use breakpoint chlorination as a mitigation response consult with their state agency to determine whether monitoring conducted during a free chlorine burnout period will be used for compliance determination.

Monitoring. Utilities should monitor free chlorine, as well as total chlorine, and continue to monitor for key nitrification parameters (e.g., nitrite and HPC R2A) during breakpoint chlorination periods. In addition, utilities may wish to increase monitoring frequency in known problem areas in the distribution system, as well as storage facilities. Following breakpoint activities, increased monitoring in known nitrifying areas should continue until it is evident the response was effective. Chapter 7 identifies key nitrification monitoring parameters and discusses the relevance of each during breakpoint chlorination periods.

Necessary approvals and customer notification. Prior to conducting breakpoint chlorination of the entire distribution system, whether scheduled or as an emergency response to a nitrification episode, the state should be notified and approval requested. Targeted free chlorine burnout and breakpoint chlorination of a storage tank or reservoir may be considered maintenance activities and not require notification in some states. Contact the state regulatory agency to determine when it is necessary to seek approval for breakpoint chlorination activities.

Customers should be notified when a change in disinfectant, either from chloramines to free chlorine or vice versa, is planned. Customers should be informed that they may notice changes in taste and odor or color (as a result of biofilm sloughing). When superchlorination is practiced, customers should be advised several days in advance that they will not have water service during the superchlorination period.

Flushing

As discussed in chapter 8, flushing can be an effective practice for preventing nitrification. However, flushing can also be an effective emergency response to both nitrification and indicators of nitrification, such as declining chloramine residuals, increases in free ammonia, nitrite, and HPC concentrations. Flushing can remove distribution system biofilms (including AOB and NOB) and sediments, reduce disinfectant demand, and bring fresher water into areas of the distribution system with low flow, which results in an increase of residuals.

Flushing is usually performed based on water quality parameters such as total chlorine residual, nitrite, HPC, odor, etc., and is also based on customer water quality complaints. A well-planned routine flushing program that is implemented on a regular basis can help decrease the possibility of water quality deterioration and consequently prevent nitrification.

There are basically two types of system-wide flushing: conventional and unidirectional flushing. These two types and the differences in each approach are discussed in chapter 8. A third alternative is spot flushing. Spot flushing, as opposed to system-wide flushing, may be a more appropriate response to nitrification. Spot flushing can be either conventional or unidirectional flushing.

Spot flushing. Spot flushing (or emergency flushing) is often performed in response to customer complaints for color, taste, or odor problems and in response to other water quality problems, such as insufficient disinfectant residual, evidence of nitrification, or positive coliform results. Spot flushing is mainly used to respond to acute or chronic water quality problems. This type of flushing is not necessarily used

for pipe cleaning, but rather for replacing a large volume of water from low-demand areas (e.g., dead-ends) and areas that show signs of nitrification or other water quality problems.

Flushing the affected area. Where nitrification has occurred in the distribution system, flushing can be an appropriate response to remedy the situation. Care must be taken to ensure the affected area is flushed completely and the conditions that led to the nitrification incident are mitigated. Although both conventional and unidirectional flushing can achieve these objectives, unidirectional flushing offers the best chance of mitigation and preventing (or at least minimizing) the potential for future nitrification incidents. Unidirectional flushing, as previously discussed, results in higher pipe scouring velocities and will likely remove more of the system biofilms, sediments, and corrosion by-products that may have caused the nitrification episode. A well-planned unidirectional flushing response plan can also help to prevent movement of water that has begun to undergo nitrification to other, previously unaffected areas of the system.

Where excessive water age is the likely cause of nitrification, flushing offers a short-term solution. However, unless a maintenance flushing program is initiated (as discussed in chapter 8), flushing will not offer a long-term solution. In these cases, more permanent engineering solutions (see chapter 10) may be most effective for preventing future nitrification episodes.

Flushing after breakpoint chlorination. As discussed earlier in this chapter, breakpoint chlorination can also be an appropriate response to nitrification. Following breakpoint chlorination, excess free chlorine will remain in the distribution system. When operations return to chloramination, the free chlorine–chloramine boundaries in the distribution system will have Cl_2:NH_3-N ratios in excess of the recommended 4.5:1 to 5:1. In these regions of the distribution system and wherever chlorinated and chloraminated water mix, the potential exists to form the less-effective and more problematic (from a taste and odor perspective) dichloramine and trichloramine. One way in which utilities can minimize this impact is to utilize flushing to move the chlorine–chloramine interface before and after breakpoint chlorination. This can be effective for distribution system piping; however, other strategies such as preconversion may be better alternatives for storage tanks and reservoirs.

When the entire system is breakpoint chlorinated, a combination of flushing and operational changes may be the most effective approach. This can help to reduce water losses to flushing and still ensure that the switch to chloramines is done with as little impact as possible on distribution system water quality. When only the affected area (area in which nitrification has occurred or potential for nitrification has been identified) is breakpoint chlorinated, it may be beneficial to flush as much of the chlorinated water from the system as is possible. It is also important to flush the customer service lines after breakpoint chlorination of the distribution system.

Impacts on water quality, regulatory compliance, and customer satisfaction. Generally, flushing can improve distribution system water quality, help to achieve regulatory compliance, and result in increased customer satisfaction. Flushing can remedy water quality problems such as nitrification, color, taste, and odor. A routine, system-wide flushing program can result in sustainable improvements in distribution system water quality.

A poorly implemented flushing program, on the other hand, can contribute to a deterioration in distribution system water quality. Improperly sequenced flushing activities can move degraded water within the distribution system, actually resulting in a spread of the problem, rather than a solution. For this reason, flushing activities should be carefully planned and sequenced to avoid potential exacerbation of water quality problems.

Flushing can aid utilities in achieving regulatory compliance. Routine flushing or flushing as a response to nitrification or the indicators of potential nitrification can

prevent loss of disinfectant residual. Flushing can help to reduce water age in system dead-ends or areas with low water demand, resulting in lower DBP concentrations. (Spot flushing in the vicinity of a sampling location solely for the purpose of improving sampling results is not recommended—routine flushing or flushing of areas to prevent water quality degradation is recommended.) Flushing can improve microbiological water quality by periodically removing system biofilms, sediments, and corrosion by-products that can serve as a nutrient source for microbes in the distribution system. Flushing following a line break can minimize the potential for microbiological contamination of the distribution system.

As previously mentioned, flushing generally increases customer satisfaction as a result of enhanced water quality. However, this may not always be the case. A poorly implemented flushing program can result in water of poor quality being drawn into larger regions of the system and result in customer complaints. Further, even a well-planned and sequenced flushing program can disturb sediments in the system and result in short-term deterioration in water quality at the tap. Finally, depending on the location of hydrants at which flushing occurs, streets may temporarily be closed and large volumes of water may drain onto consumers' property. The inconvenience that results may be a source of customer complaints.

Steps can be taken to minimize the negative impacts associated with flushing. Where flushing is required in high-traffic areas, it is recommended that flushing occur during nonpeak hours. Also, AWWA offers several resources on flushing, including DVDs (*Unidirectional Flushing*, AWWA, 2002) and print materials (Kirmeyer et al., 2000).

Monitoring. Chapter 7 identifies the key nitrification monitoring parameters that a water utility should monitor for in the distribution system: total chlorine, nitrite-N, free ammonia-N, temperature, and pH (see Table 7-2). Those are the parameters that a water utility should monitor for during flushing activities in the distribution system. Utilities should make it a common practice to collect samples for the appropriate parameters before and after flushing activities. Hence, the water utility can determine the effectiveness of flushing as a response to nitrification.

Dechlorination. Dechlorination must occur where large volumes of chloraminated or chlorinated water are discharged into a storm drain or directly to the environment, which is basically the case when water is flushed out of a hydrant or a flush-out. Local regulatory agencies must be contacted to obtain discharge requirements and information regarding discharge permits that the utility must obtain before a discharge to the storm drain is allowed. Local regulatory agencies may require that only dechlorinated water with no detectable chlorine residual enter the storm drain.

Dechlorination is best performed by adding a controlled amount of dechlorination chemical to the flow of water that will be discharged to the storm drain. Dechlorination can be accomplished by a number of different dechlorination chemicals. Water utilities most frequently use sodium thiosulfate, sodium sulfite, and sodium bisulfite ($NaHSO_3$). Other dechlorination alternatives include sulfur dioxide, sodium metabisulfite, calcium thiosulfate, ascorbic acid (vitamin C), and sodium ascorbate (buffered form of vitamin C).

AWWA offers several resources on dechlorination. The AwwaRF guidance manual (Tikannen et al., 2001) discusses advantages and disadvantages of all dechlorination chemicals mentioned above.

The series of pictures in Figure 9-9 show an example of how dechlorination can be performed.

Increase Chloramine Residual

The process of increasing chloramine residual is mainly used as a nitrification prevention measure. A reduction in chloramine residual is typically caused in chloramined

Put on a safety vest and hardhat. Place "Flooded" signs and cones around work area.

Install the fire hose to the diffuser and then to the fire hydrant.

Prepare the dechlorination solution.

Dry dechlorination chemical is added to the container and then water is added to dissolve the chemcal.

Dechlorination container is placed between hydrant and nearest storm drain. Open valve on container to allow solution to drip out.

Dechlorination container is placed on the curb in a position such that the dechlorination solution will drip into the water stream.

Figure 9-9 Steps in the dechlorination procedure (continued on next page)

water systems through autodecomposition or consumption of chloramines by NOM or other substances in the water. A decrease in chloramine residual can also indicate the beginning of a nitrification event. During a nitrification episode, an abnormal decrease in chloramine residual should be investigated before any adjustments are made to the plant dose, because an increase in chloramine residual has never been demonstrated to be effective to correct a nitrification episode.

A reduction in chloramine residual may also originate from operational problems, e.g., the chloramine residual entering the system is too low or the Cl_2:NH_3-N is

Turn on the fire hydrant.

Check chlorine residual of hydrant water (at start up).

After adding the sodium thiosulfate at the appropriate application rate, you need to test the water for chlorine residual at approximately 10 ft downstream to allow for sufficient contact with sodium thiosulfate, for chlorine residual. The result of the chlorine residual test should be zero (water remains clear after adding the reagent). If there is a detectable residual, the solution application rate should be increased until no residual is detected in the water 10 ft downstream of the point of application.

Check chlorine residual of hydrant water (during and at end of flushing). Record all chlorine residual results.

Figure 9-9 Steps in the dechlorination procedure (continued)

less than the desired ratio. Consequently, the operator should review the following: chlorine and ammonia feed rates, free and total chlorine residual data (both dose set point and residual entering the system), free ammonia dose and concentration at the treatment plant and entering the distribution system, calibration of the chemical feed pumps, and chlorine and ammonia analyzers. If the operator determines that the chloramine residuals, ammonia measurements, and Cl_2:NH_3-N feed ratios appear to be within the targeted range, the chloramine residual and the Cl_2:NH_3-N ratio may not be the contributing factor for the nitrification event.

RESPONSES TO NITRIFICATION EPISODES IN DISTRIBUTION SYSTEM STORAGE FACILITIES

When nitrification is occurring in a storage facility or reservoir, the response may be significantly different than when nitrification is occurring in the distribution system. First, early detection of nitrification in a storage tank can prevent spread of nitrification to other areas of the distribution system. Second, when detected in a timely manner, the nitrification can be kept isolated in the storage facility, making the response more efficient. For these reasons, it is critical that distribution system storage facilities be included when developing a nitrification monitoring plan (see chapter 7). This section discusses responses to nitrification in distribution storage facilities.

Breakpoint Chlorination of Storage Tanks and Reservoirs

As previously described, breakpoint chlorination refers to the addition of chlorine to water at a concentration whereby all of the ammonia has been oxidized to nitrogen, resulting in a free chlorine residual. When nitrification is occurring in a storage tank or reservoir, breakpoint chlorination can be an effective response measure. Determining the appropriate free chlorine dose to achieve breakpoint chlorination in a storage tank or reservoir requires utilities to:

- Determine the volume of water in the tank/reservoir
- Determine the available volume in the tank/reservoir (for injection at the inlet)
- Measure the total chlorine concentration in the reservoir and tank inflow
- Measure the total ammonia in the reservoir and tank inflow
- Measure the nitrite in the reservoir and tank inflow
- Identify target free chlorine residual in the tank/reservoir after breakpoint

In poorly mixed tanks, it is recommended that the total chlorine, total ammonia, and nitrite concentrations be measured at multiple depths in the storage tank and the analytical results averaged. In such a case, mixing or recirculation equipment may be required to effectively breakpoint chlorinate the tank.

A free chlorine residual of 1.0 mg/L is an appropriate target for most storage tanks. The duration of the breakpoint period can vary depending on the ability of a system to isolate and remove a storage facility from service given pressure and emergency requirements. Where it is possible to remove a tank from service, a period of 12 to 24 hours is recommended. The Irvine Ranch Water District (2003) targets a free chlorine residual of 2.0 mg/L in nitrifying storage tanks and returns the tank to service within 12 to 30 hours if monitoring indicates breakpoint chlorination has occurred and nitrification has ceased. Lower target free chlorine residuals (e.g., 0.5 mg/L) have been used for large water storage facilities. These examples are merely guidelines, and the required duration is a function of free chlorine dose and time. A discussion of AOB inactivation by free chlorine is included in chapter 6.

The breakpoint dose can then be determined by (Guistino, 2004a):

$$Cl_{2\text{–}ResBP} = [(NH_{3\text{–}Res} \times 10) + (NO_{2\text{–}Res} \times 5) - Cl_{2\text{–}Res}] \times \left[\frac{3.78\frac{L}{gal} \times 1{,}000{,}000\frac{gal}{mil\ gal}}{454\frac{g}{lb} \times 1{,}000\frac{mg}{g}}\right] \times V_{Res} \quad (9\text{-}5)$$

$$Cl_{2\text{–}InfBP} = [(NH_{3\text{–}Inf} \times 10) + (NO_{2\text{–}Inf} \times 5) - Cl_{2\text{–}Inf}] \times \left[\frac{3.78\frac{L}{gal} \times 1{,}000{,}000\frac{gal}{mil\ gal}}{454\frac{g}{lb} \times 1{,}000\frac{mg}{g}}\right] \times V_{Inf} \quad (9\text{-}6)$$

$$Cl_{2\text{–}FreeBP} = Cl_{2\text{–}Free} \times \left[\frac{3.78\frac{L}{gal} \times 1{,}000{,}000\frac{gal}{mil\ gal}}{454\frac{g}{lb} \times 1{,}000\frac{mg}{g}}\right] \times (V_{Res} + V_{Inf}) \quad (9\text{-}7)$$

$$Cl_{2\text{–}BP} = (Cl_{2\text{–}ResBP} + Cl_{2\text{–}InfBP} + Cl_{2\text{–}FreeBP}) \times \frac{100}{\%} \times \frac{1}{8.34\frac{lb}{gal} \times SG} \quad (9\text{-}8)$$

Where:
- $Cl_{2\text{–}ResBP}$ = chlorine required to breakpoint reservoir/tank (lb Cl_2)
- $Cl_{2\text{–}InfBP}$ = chlorine required to breakpoint reservoir/tank inflow (lb)
- $Cl_{2\text{–}FreeBP}$ = chlorine required to achieve free chlorine residual (lb)
- $Cl_{2\text{–}Res}$ = total chlorine concentration in reservoir/tank (mg/L Cl_2)
- $Cl_{2\text{–}Inf}$ = total chlorine concentration in reservoir/tank inflow (mg/L Cl_2)
- $Cl_{2\text{–}Free}$ = desired free chlorine residual in reservoir/tank (mg/L Cl_2)
- $NH_{3\text{–}Res}$ = total ammonia concentration in reservoir/tank (mg/L N)
- $NH_{3\text{–}Inf}$ = total ammonia concentration in reservoir/tank inflow (mg/L N)
- $NO_{2\text{–}Res}$ = total nitrite concentration in reservoir/tank (mg/L N)
- $NO_{2\text{–}Inf}$ = total nitrite concentration in reservoir/tank inflow (mg/L N)
- V_{res} = volume of water in tank at start of breakpoint operation (mil gal)
- V_{Inf} = volume of water added during breakpoint (mil gal)
- % = trade percent of hypochlorite solution (%)
- SG = specific gravity of hypochlorite solution
- $Cl_{2\text{–}BP}$ = volume of hypochlorite required to achieve breakpoint (gal)
- 10 = mg Cl_2/mg NH_3-N needed in practice for reaction with ammonia
- 5 = mg Cl_2/mg NO_2-N needed in practice for reaction with nitrite

Exhibit 9-1 provides an example breakpoint dose calculation. There are two methods by which breakpoint chlorination can be achieved in a storage tank or reservoir: injection at the inlet while the tank is filling or addition through access hatches or recirculation/mixing system while the tank is isolated and mechanically mixed.

Injection of chlorine at the inlet while the tank is filling. Injection of chlorine into the tank inlet may be difficult if no facilities, such as an injection vault and/or in-line mixer, are available. Injection at the inlet generally requires a portable pump with a hose adapted to the pump discharge and injection port and a small generator for power. The pump suction can draw from buckets or carboys. Some utilities may have vehicles equipped with portable hypochlorite feed systems. Guistino (2004b) identified this as one of the easiest and most efficient means by which to breakpoint chlorinate a storage tank or reservoir.

The effectiveness of this method can be compromised if the mixing characteristics of the tank are such that the chlorine does not mix into all layers of the tank. Chapter

Exhibit 9-1. Example Breakpoint Dose Calculation

Big City operates at 1-MG storage tank and suspects nitrification is occurring in the tank. Total nitrate is 0.25 mg/L, well above the baseline concentration of 0.01 mg/L. Total ammonia is 0.04 mg/L, which is well below the baseline concentraiton of 0.15 mg/L. The total chlorine residual in the tank is 0.15 mg/L, which is well below the baseline concentration of 0.5–1.0 mg/L for this tank. The inflow has a total nitrite concentration of 0.08 mg/L, a total ammonia concentration of 0.4 mg/L, and a total chlorine concentration of 1.5 mg/L. Calculate the required breakpoint dose to achieve a 1.0 mg/L free chlorine residual in the tank. Assume the tank contains 500,000 gallons at the start of the breakpoint operation, 500,00 gallons will be pumped into the tank, and use of a 12% (trade percent) sodium hypochlorite solution (SG = 1.15).

$$[(0.04 \times 10) + (0.25 \times 5) - 0.15] \times \left[\frac{3.78 \times 1{,}000{,}000}{454 \times 1{,}000}\right] \times 0.5 = 6.25 \text{ lb } Cl_2 \text{ to breakpoint tank}$$

$$[(0.04 \times 10) + (0.08 \times 5) - 1.5] \times \left[\frac{3.78 \times 1{,}000{,}000}{454 \times 1{,}000}\right] \times 0.5 = 12.1 \text{ lb } Cl_2 \text{ to breakpoint inflow}$$

$$1.0 \times \left[\frac{3.78 \times 1{,}000{,}000}{454 \times 1{,}000}\right] \times (0.5 + 0.5) = 8.34 \text{ lb } Cl_2 \text{ to achieve 1.0 mg/L free chlorine residual}$$

$$(6.25 + 12.1 + 8.34) \times \frac{100}{12} \times \frac{1}{8.34 \times 1.15} = 23.2 \text{ gallons 12\% NaOCl required.}$$

10 provides more information on tank mixing and mixing systems. In storage tanks in which nitrification is occurring because of stratification in the storage tank (i.e., upper regions of the tank consist of much older water), sufficient tank volume must be drained to ensure complete mixing of the storage tank while filling. Therefore, the tank level must be lowered to allow for sufficient fill time to completely mix the storage tank. However, it is also important to minimize or eliminate the possibility that water of poor quality is drained into the distribution system—this could result in nitrification in other parts of the system or water of poor quality reaching customers. Guistino (2004b) recommended a minimum available volume of 50% to ensure adequate mixing. However, this level is tank specific and is dependent on the mixing characteristics of the storage facility. A lower tank level, such as 25%, is recommended, if possible. Figure 9-10 presents an example procedure to breakpoint chlorinate a storage tank or reservoir by addition of chlorine at the inlet while the tank is filling.

After breakpoint chlorination, water drawn from the tank will contain a free chlorine residual. This may result in Cl_2:NH_3-N greater than 5:1 at the interface of water from the tank and water in the distribution system. As a result, flushing is recommended, where practical, to simulate increased demand and quickly remove free chlorine-containing water from the tank and distribution system. In certain instances, distributing water to customers with free chlorine may be acceptable, provided the residual is not too high (greater than approximately 1.0 mg/L Cl_2).

The MWDSC experienced nitrification in two of its four finished water reservoirs in 1985 and 1986 (Wolfe et al., 1988). The Garvey and Orange County reservoirs are capable of storing 521 mil gal and 65 mil gal, respectively. In September 1985, operators at the Garvey Reservoir were having difficulty maintaining a chloramine residual in the reservoir effluent. This was accompanied by an increase in HPC (>1,000 cfu/mL) and nitrite (0.4 mg/L as N). The reservoir was subsequently removed from service and chlorinated to breakpoint by injecting 7.4 mg/L of chlorine (as Cl_2) in the reservoir influent. Within 1 week, HPC counts were less than 100 cfu/mL and all of the nitrite had been oxidized to nitrate. The following year, in August 1986, the Orange County Reservoir

Step 1.
Lower reservoir to 50% of total volume (or as low as possible).

Step 2.
Measure water quality inside tank/reservoir. Calculate required breakpoint chlorination dose.

Step 3.
Begin filling the tank as quickly as possible and add hypochlorite as quickly as possible during the fill cycle.

Step 4.
Isolate the tank or reservoir and let sit for 24 hours (if possible).

Step 5.
Measure chlorine residual to ensure the target free chlorine residual was achieved prior to returning to service.

Step 6.
As long as free chlorine residual is not too high (> ~1.0 mg/L), return tank/reservoir to service.

Figure 9-10 Example of storage tank breakpoint chlorination procedure

experienced similar problems. It, too, was chlorinated to breakpoint and nitrite and bacterial levels returned to normal within several days.

Addition through hatches or recirculation system. In instances where the inlet configuration will not accommodate chlorine injection, chlorine can be added through access hatches or through recirculation equipment. Recirculation or mixing equipment (see chapter 10) may be necessary if the shape of the facilities is such that it is not possible to disperse the chlorine over the entire surface area of the facility.

There are several methods by which chlorine can be added through access hatches each with its own advantages and disadvantages as described in Table 9-5. The drag-the-bag and broadcast spray methods are generally not recommended unless the storage facility configuration is such that the pour-in-the-hatch method is not likely to be effective, i.e., very large reservoirs. With the pour-in-the-hatch method, it is critical that the sodium hypochlorite be well mixed within the tank. Sodium hypochlorite is more dense than water and it has been reported that slug doses will settle to the bottom of the tank or reservoir (pers. commun., San Francisco Public Utilities Commission, 2004). Carlomagno et al. (2005) describes a similar occurrence and the need for a mixer to disperse the sodium hypochlorite throughout the storage tank. Personal protective equipment (PPE) is required with all of the identified methods. However, the broadcast spray and drag-the-bag methods present an increased risk of chlorinous vapor production and require breathing protection.

For those methods in Table 9-5 that require storage tank or reservoir levels to be dropped, Guistino (2004b) recommends that reservoirs be dropped to a minimum level of at least 50% of the tank volume. In tanks or reservoirs with poor mixing characteristics, it may be necessary to use recirculation equipment to ensure adequate dispersion of the chlorine added. As listed in Table 9-5, it is not necessary to remove a tank or reservoir from service when the broadcast spray method is used. However, in those instances where the reservoir or tank level is not lowered with this method, the tank should be at least temporarily removed from service to allow for adequate settling of the sodium hypochlorite solution through the water column.

Table 9-5 Comparison of breakpoint chlorination methods for storage tanks and reservoirs by addition through access hatches

Method	Procedure	Advantages	Disadvantages
Pour-in-the-hatch while the tank is filling	1. Measure water quality and calculate required chlorine dose. 2. Drop reservoir to low/target level. 3. Confirm positive/inflow into reservoir. 4. Pour sodium hypochlorite solution into hatch. 5. Wait until high/target level is achieved. 6. Take reservoir out of service and let sit for 24 hours (if possible) 7. Measure free chlorine residual. 8. Return reservoir to service if OK.	• Quick and easy • Good for small tanks	• Requires good tank mixing • Only good when hatch is directly over inlet • May be difficult if the hatch is not easily accessible
Broadcast spray	1. Measure water quality and calculate required chlorine dose. 2. Drop reservoir to low/target level (if applicable). 3. Isolate reservoir (if practicable). 4. Broadcast sodium hypochlorite over surface of reservoir. 5. Fill reservoir (if applicable). 6. Measure free chlorine residual. 7. Return to service if OK.	• Good for medium-sized tanks and below-grade reservoirs • Broadcasts high chlorine dose over entire surface of reservoir or tank • Good mixing as higher density water (containing free chlorine) drops through water column • No need to take reservoir out of service (but recommended) • Use of “spray sticks” can minimize exposure to hypochlorite • Venturi nozzles can eliminate need for pumps	• Need nozzle with sufficient pressure to spray over entire surface of reservoir or use a boat if reservoir allows access • May require chemical-resistant pump that can pump into high-pressure supply • Requires PPE • Not recommended in most cases
Drag-the-bag	1. Measure tank/reservoir water quality and calculate required chlorine dose. 2. Take reservoir out of service (if possible). 3. Use 65–75% calcium hypochlorite tablets. 4. Use mesh bag (attached to boat for large reservoirs). 5. Drag bag for several hours. 6. Measure free chlorine residual. 7. Repeat as necessary to achieve desired free chlorine residual. 8. Return reservoir to service.	• Low chance of overdosing • Use of granular calcium hypochlorite eliminates chlorine fumes	• Awkward • Not very efficient • Time consuming • Need to disinfect boat • Not recommended in most cases

Source: Guistino, 2004b.

In 1992, the Fort Worth (Texas) Water Department (FWWD) experienced severe drops in chloramine residual at two of its finished water reservoirs as a result of nitrification. The Westland (5 mil gal) and Caylor (5 mil gal) reservoirs had been sized based on future demands, resulting in excessive detention times within the reservoirs. FWWD opted to install rechlorination and recirculation equipment at the reservoirs. In this case, chlorine was introduced in the bottom of the tank and rechlorinated water was drawn off the top of the tank for distribution. The recirculation equipment provided a small, continual vortex in the tank, allowing a chlorine residual to be maintained. Total cost of the equipment was approximately $73,000 (Kirmeyer et al., 1995). It was reported that this was an effective means of controlling nitrification.

Depending on the degree of nitrification and the chlorine dose used, it is recommended to isolate the tank from the system during breakpoint chlorination. If rechlorination is practiced, as in the FWWD example previously discussed, it may also be necessary to add ammonia to the tank discharge prior to the distribution system to maintain the Cl_2:NH_3-N ratio and prevent di- and trichloramine formation.

Deep Cycling of Storage Tanks and Reservoirs

A number of utilities implement deep cycling of storage tanks and reservoirs to increase turnover and prevent or respond to nitrification. However, the ability of a utility to implement deep cycling of storage facilities is dependent upon system pressure and emergency flow requirements. In 1987, the Philadelphia Water Department lowered tank levels to improve turnover and prevent nitrification. This strategy was effective for several years, until system pressure requirements necessitated higher operating levels (Odell et al. 1996). The Irvine Ranch Water District (2003) and the San Francisco Public Utilities Commission (Smith 2003) both include deep cycling of storage tanks as a level 2 response in their nitrification action plans. The effectiveness of deep cycling also depends on storage tank configuration. Kirmeyer et al. (2004) reported that deep cycling is only effective in well-mixed storage tanks.

Draining and Disinfection of Storage Facilities

When other responses to nitrification are ineffective, draining and disinfection may be an appropriate response to nitrification in small storage facilities (i.e., less than 1 mil gal). Much like flushing, draining a storage facility to waste simply removes the nitrification problem from the system. The ability to use this approach is dependent upon the ability of the utility to maintain adequate system pressures and meet emergency flow requirements with the affected tank off line. Draining the tank without disinfection usually will not be effective for the control of nitrification. In fact, some states require that drained storage facilities be disinfected prior to returning them to service. AWWA Standard C652, *Standard for Disinfection of Water Storage Facilities,* (latest edition) provides guidelines for disinfection of all equipment used to clean storage facilities. Chapter 8 discusses routine cleaning and tank maintenance as a nitrification prevention measure in greater detail.

Impact on Water Quality, Regulatory Compliance, and Customer Notification

Introduction of free chlorine into a chloraminated distribution system may result in an increase in DBP concentrations, specifically THMs and HAAs. At the chlorine–chloramine water interface, the Cl_2:NH_3-N ratio is likely to be in excess of 5:1. As a result, systems may experience short-term taste and odor problems.

Targeted free chlorine burnout and breakpoint chlorination of a storage tank or reservoir may be considered maintenance activities and not require notification in

some states. Contact the state regulatory agency to determine when it is necessary to seek approval for breakpoint chlorination activities.

Monitoring

Utilities should monitor free chlorine during breakpoint chlorination of storage tanks to assure target residual levels are maintained for the duration of the breakpoint activity. Upon returning the tank to service, the tank should be resampled within 24 to 48 hours for key nitrification parameters to determine if the response was effective. Chapter 7 identifies key nitrification monitoring parameters and discusses the relevance of each during breakpoint chlorination periods.

CONCLUSIONS

Nitrification is most likely to occur in distribution system dead-ends, storage facilities, and other low-flow areas. Indicators that nitrification may be occurring include low total chlorine, high nitrite, and low free ammonia concentrations. Other observations, such as high nitrate concentrations, high HPC R2A counts, and depressed pH, can also be indicative of nitrification.

After it has been determined that nitrification is occurring, it is important to determine the cause of the nitrification episode. Determining the cause of nitrification and preventing recurring nitrification requires an assessment of the impacts of distribution monitoring, finished water quality, treatment plant operation, distribution system and storage tank operation, and distribution piping on nitrification. Prevention of nitrification, either by operational or physical system improvements, is the preferred method of dealing with nitrification. However, when nitrification is occurring in a distribution system or storage facility, it is critical that a timely and effective response be initiated. Developing a nitrification response plan is critical to achieving this objective. A well-coordinated response plan should include both alert levels and action levels requiring varying degrees of response. Alert levels and action levels should be developed based on system-specific baseline concentrations of critical nitrification monitoring parameters (e.g., total chlorine, total and free ammonia, nitrite, and HPC).

The levels of operational response to nitrification vary depending on the alert level or action level and the degree to which nitrification is occurring in the distribution system. The most basic response includes increased monitoring and verification of chlorine and ammonia feed rates at the treatment plant or booster disinfection stations. The next level of response typically includes targeted flushing, breakpoint chlorination of the affected tank or area, increased tank cycling (lower tank operating levels), and cleaning and disinfecting storage tanks. For widespread nitrification, breakpoint chlorination of the entire distribution system may be necessary.

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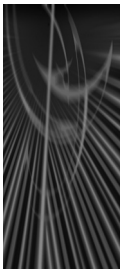


Chapter 10

Capital Improvements for Nitrification Prevention

Andrzej Wilczak

INTRODUCTION

When operational practices are not sufficient and/or not cost effective for nitrification prevention, utilities may consider capital improvements, such as:

- improvements to storage reservoir mixing and reducing water age,
- changes to pressure zones,
- changes to engineering design standards for storage volume and piping diameters, and
- chloramine residual boosting stations in the system to provide a more stable disinfectant residual.

The key points of this chapter are summarized in Table 10-1. Many of the capital improvements discussed here have minimizing water age as a goal, and published resources are available that provide engineering solutions to controlling water age in the drinking water distribution systems. As with operational practices discussed in chapters 8 and 9, several of these solutions have been developed for a general water quality maintenance strategy that is not exclusively used for controlling nitrification. Excessive water age has been identified as one of the root causes of nitrification; therefore, eliminating water stagnation zones and decreasing average water age should have a direct and positive impact on nitrification prevention.

IMPROVEMENTS TO RESERVOIR MIXING AND DECREASING OF WATER AGE

One of the most important aspects from a water quality standpoint is deciding whether a storage facility will be mixed to preclude dead zones or whether it will operate in a plug-flow mode. Due to the fact that the rate of disinfectant decay is concentration dependent, the tank operating under plug-flow conditions will generally lose more disinfectant than one operated under mixed-flow conditions. Therefore, the water storage facility should be designed to encourage good mixing rather than plug-flow behavior (Grayman et al., 2000). Complete mixing results in elimination of stagnant water zones

Table 10-1 Key points from chapter 10

Improvements to Reservoir Mixing and Water Age	• Plug-flow conditions for reservoirs with separate inlet/outlet are difficult to achieve and undesirable, except for clearwells with $C \times T$ requirements. • Completely mixed conditions are relatively easier to achieve than plug flow. Complete mixing will eliminate dead spots and even out the water age and disinfectant residuals. • Separation of common inlet and outlet, change in their orientation, or mechanical mixing can be selected to improve mixing conditions within storage reservoirs. Separation of inlet and outlet is usually expensive so other means to achieve good mixing conditions may be considered. • Inlet and outlet orientation is important. Typically the inlet should not be directed at walls or along the walls but at an angle toward the longest reservoir dimension. A reduction in inlet size can promote mixing within a reservoir without generating excessive hydraulic loss. Outflow rate (fire-flow requirement) is most important for common inlet/outlet. • Baffling within reservoirs should not be used except for $C \times T$ compliance. • A variety of proprietary mixers are available on the market. • Recirculation loops have been installed by some utilities. The recirculation rate and locations of intake/discharge are important design considerations. • Using tracer studies and CFD models may help optimize mixing and provide better understanding of the hydraulics of the reservoirs and layout proper improvements. Nitrification monitoring within the reservoir will determine the benefits of improved mixing and reduced water age.
Redesign of Pressure Zones and Piping	• Opportunities exist to modify fire-flow requirements through the increased use of alternate fire suppression technologies. This will help reduce water system infrastructure overdesign needs and lead to smaller pipeline sizes, cleaning and relining existing pipelines, and lower storage volumes for fire-flow demands. • Some utilities have recently reduced water storage planning and design guidelines from 1.5 days to 1 day of MDD. Many utilities do not have storage even close to 1 MDD. • The two strategies about pressure zones are: (1) bypassing lower zones when pumping to upper zones, and (2) installing bypass piping and valves to allow controlled "bleeding" of water back into lower pressure zones when upper zone water becomes stagnant. Care should be taken not to distribute old water and spread nitrification while using bleeding to lower pressure zones.
Chlorine and Chloramine Residual Boosting in the Distribution System	• Boosting chloramine residuals combines free ammonia and increases biocide (chloramine) to food (ammonia) ratio. When boosting chloramine with chlorine alone, it must be applied at a point where sufficient free ammonia is present. Ammonia addition is used much less frequently in chloramine boosting. • Monitoring of chlorine and ammonia is necessary for successful boosting, preferably with on-line combined chlorine analyzers, supplemented with grab samples, as well as nitrite, pH and possibly on-line free ammonia analyses. • Manual feed, flow-paced, or flow-paced feed with combined chlorine residual feedback can be used for chemical dose control. Operators should be able to fine-tune the chemical doses depending on water quality. Feeding both chlorine and ammonia may require good on-line instrumentation. • Boosting in the distribution system typically reduced the incidences of nitrification but may not eliminate them completely, especially at the ends of the distribution system. • Large transmission reservoirs and water mains with high water age and smaller tanks within the distribution system are potential locations for booster stations. • Recirculation (external or internal) with manual or automatic chlorine addition (and possibly also ammonia feed in some cases) appears to be the best method for nitrification control in reservoirs located within distribution system.

NOTE: CFD, computational fluid dynamics; $C \times T$, product of disinfectant concentration and the corresponding disinfectant contact time; MDD, maximum day demand.

and evening out an average water age within a facility. It is easier to achieve good mixing than plug flow. For fill-and-draw operation, particularly for elevated circular tanks, it is not clear how true plug-flow conditions can be maintained. On the other hand, some storage tanks have no problem achieving close to complete mix conditions without the use of special structural additions or mixing devices. The main deterrents to achieving well-mixed conditions in tanks appear to be improper placement, orientation, and size of I/O pipes, and the possibility of temperature differences between the inflow and tank contents. Both of these factors can be dealt with through minor structural or operational changes (Grayman et al., 2000).

Changing Required Water Storage Engineering Criteria

Planning of distribution reservoirs and pumping stations should consider features with operational flexibility to achieve a minimum uniform water age using techniques such as the following:

- synchronized pumping (bypassing intermediate zones and pumping directly by two or more sets of pumps to higher zones) and minimization of pumping during highest demand;
- seasonal operating ranges;
- seasonal removal of reservoirs from service;
- regulating water down to lower pressure zones from higher zones; and
- remotely controlled valves for reservoir operation.

One California utility recently revised its Distribution Reservoir and Pumping Plant Planning Criteria to reduce water storage from 1.5 days to 1 day of maximum day demand (MDD). This criterion also includes provisions to allow storage to fall as low as 12 hours if there is sufficient pumping capacity or above-zone storage available through a pressure regulator (pers. commun., J.S. Hurlburt, 2003). The impact of these changes on nitrification has not been quantified yet; however, they reflect a significant change in planning criteria.

Modeling for Improvement of Storage Reservoir Mixing and Water Age

Hydraulic modeling can provide information on mixing patterns and water age in an existing, modified, or proposed facility under a range of operating situations. Physical scale models are constructed from materials such as wood or plastic and dyes or chemicals are used to trace the movement of water through the model. Equivalence with full-scale operation is achieved by maintaining the same Froude numbers in the scale model as full-scale. In mathematical models, equations are written to simulate the behavior of water in a reservoir. These models range from detailed finite-element representation of the hydraulic mixing phenomena in the facility, called computational fluid dynamics (CFD) models, to simplified conceptual representations of the mixing behavior, called systems models (Grayman et al., 2000). For complex design situations, CFD or scale models can be applied to study the mixing patterns associated with alternative design options. Grayman et al. (2000) presented a summary of modeling options available. Many commercial CFD packages are available. The use of these packages requires a significant investment in training prior to any productive use of the software. Grayman and Arnold (2003) present a further overview of CFD methods in analysis of distribution system tanks and reservoirs. Examples of model utilization to improve reservoir mixing and decrease water age are presented in the subsequent sections of this chapter. Simpler models are also available, such as EPANET and H_2ONET, and may provide satisfactory information.

Some utilities opt to implement improvements without the use of models, e.g., installation of mechanical mixers, which may provide a direct answer as to whether nitrification can be stopped. The engineering solution implemented may not be the most efficient but nevertheless acceptable, especially if the costs are relatively low and additional modifications are possible, depending on gained field experience. Modern modeling technology appears ideally suited for more expensive capital improvements where substantial construction costs are incurred. The report by Grayman et al. (2000) provides many easy-to-use modeling equations.

Reservoir I/O configuration and modifications. The primary variable in operation of tanks and reservoirs is whether the facility is operated in a "fill-and-draw" or in a "flow-through" mode. These operational modes are determined by the design configuration of the facility: combined or separate inlets and outlets.

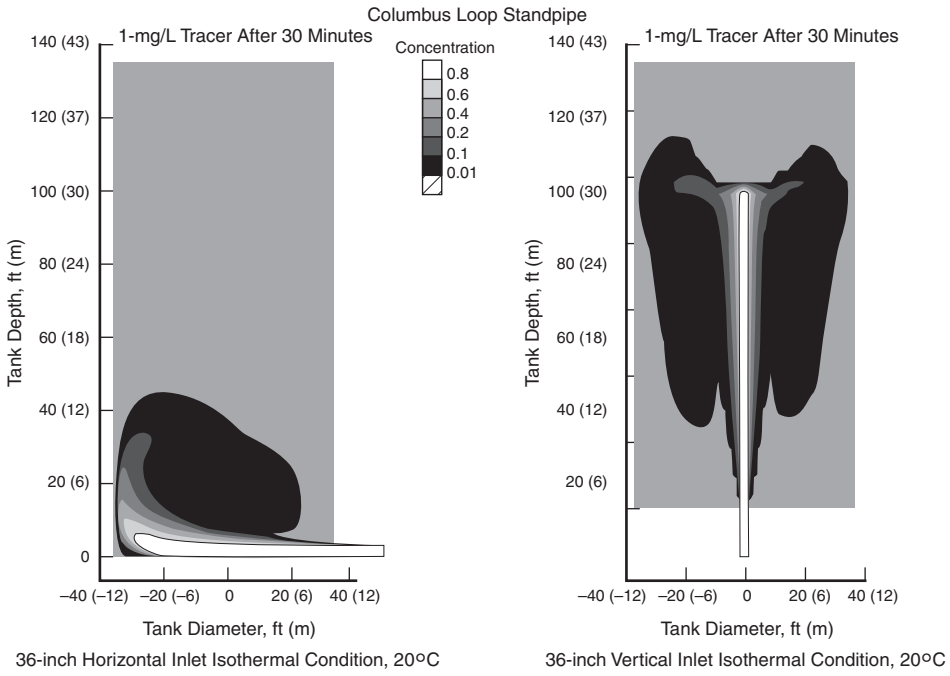
A survey of 892 finished water storage facilities conducted by Kirmeyer et al. (1999) indicated that 80% of the surveyed facilities in the United Kingdom had separate inlets and outlets, while only 38% of the US and Canadian facilities had separate inlets and outlets. Separate inlets and outlets are required for plug flow reactors, allow for better flow rate monitoring in and out of the storage facility, and facilitate the application of chlorine. Combined inlets/outlets in storage facilities are also acceptable provided good mixing within the storage tank is achieved. Separate inlets/outlets can have the advantage of high-velocity inflow and low head loss outflow, especially considering fire-flow requirements.

Reservoir I/O modifications may include: (1) altering the orientation of the I/O pipe (horizontal versus vertical discharge, turning the pipe and pointing it at an angle); (2) extending the I/O pipe to spatially separate reservoir influent and effluent; (3) distributing the influent/effluent through several diffusers; (4) separating inlet and outlet by placing a tee and check valves on existing I/O piping; and (5) physically separating the inlet and outlet. Case studies of these modifications are discussed below.

Changing inlet and outlet orientation. The key design parameters of inlet pipe diameter and orientation should produce an inlet momentum adequate to completely mix the water in the tank within the fill time. At a tank in Virginia, an inflow of 2,000 gpm through a horizontal 24-in. inlet pipe could not provide adequate momentum to mix the bulk water within 3 hours of fill time. When the inlet diameter was reduced to 12 in., the entire tank was well mixed by 1 hour of filling (Mahmood et al., 2003).

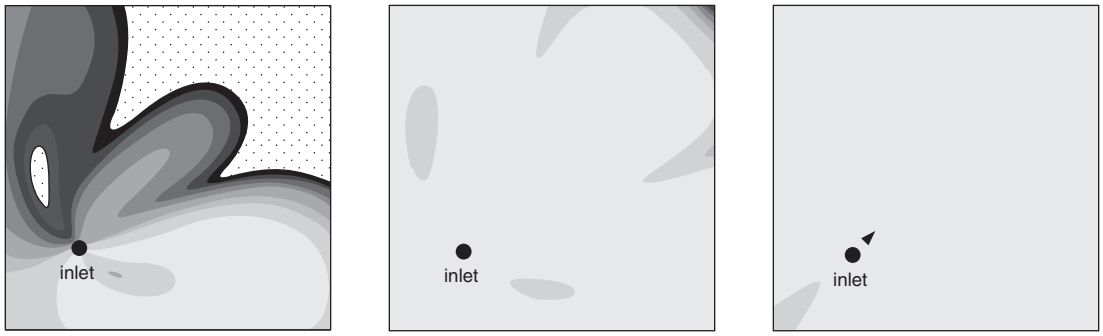
Mahmood et al. (2003) studied the effect of inlet orientation on mixing characteristics, shown in Figure 10-1, using output from a CFD model after 30 minutes of fill time for a 4-mil gal standpipe (Figure 10-1). The tank was modeled with a 36-in. diameter horizontal inlet near the bottom of the tank versus a 36-in. vertical inlet. When the inlet orientation is horizontal, the path of the jet is in the direction of minimum tank dimension. The water jet hits the far wall of the tank within 15 minutes and is thus unable to mix the stored water in the top portion of the tank. However, when the inlet orientation is vertical, the path of the jet is in the direction of the maximum water length. In this case, mixing extended to the upper regions of the water column.

Hannoun and Miller (2003) used CFD modeling to evaluate water circulation patterns of a large balancing reservoir in California. The current inlet includes a 7-ft diameter pipeline that runs parallel to the floor and ends at a sump below the reservoir. The walls of the sump form a 15-ft by 21-ft concrete riser box that extends vertically 6 ft above the reservoir floor. The velocities in the riser are typically very low, about 0.2 fps at 40 mgd inflow rate. The proposed modifications of the inlet/outlet included demolition of the riser box and replacing it with: (A) a 90° elbow attached to the end of the 84-in inlet/outlet, resulting in a 1.6-fps inflow velocity at 40 mgd; (B) addition of an 84-in. by 48-in. nozzle on the end of the elbow, resulting in a 4.9-fps velocity; and (C) a 60° elbow, instead of 90°, directed at the far corner of the reservoir.



Source: Mahmood et al., 2003.

Figure 10-1 CFD modeling of water standpipe mixing for horizontal and vertical inlet pipe orientation after 30 minutes of fill time at 2,000 gpm

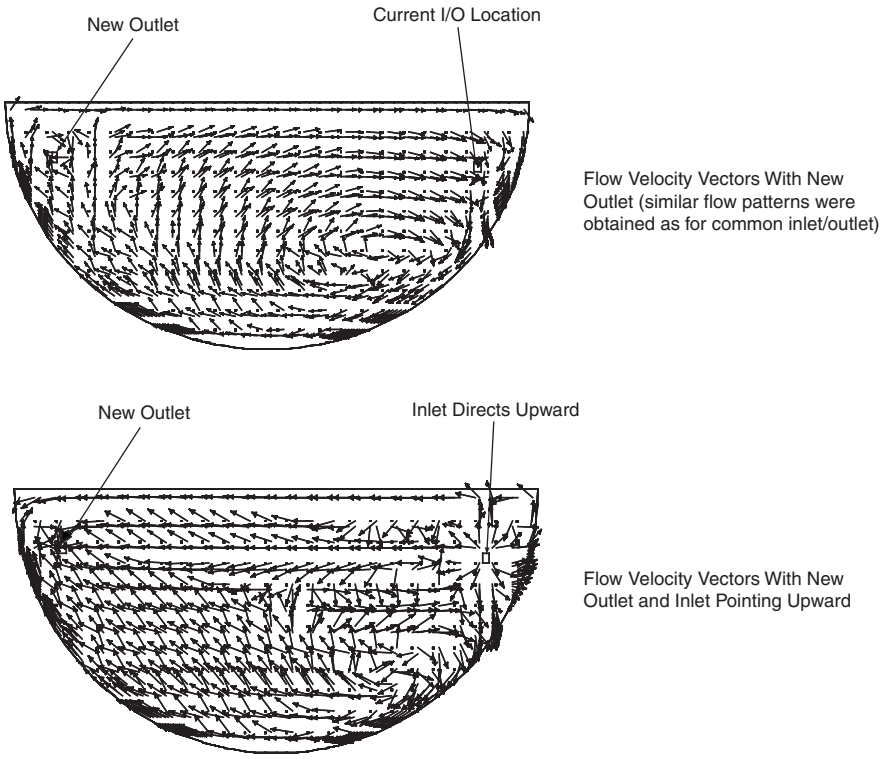


Source: Hannoun and Miller, 2003.

Figure 10-2 CFD modeling of large reservoir water age and mixing for different inlet configurations. Plan view; older water is shown with dark shades.

The results of CFD modeling for these three engineering options show the distribution of water age within the reservoir after 45 days (Figure 10-2).

With the concept A design, which directs the flow vertically in the reservoir, there are low water ages near the inlet and in the middle of the reservoir, but higher ages of 40 to 45 days around the edges of the reservoir. With concept B, which included a 48-in. diameter nozzle, more mixing occurs and water ages of 40 to 45 days are



Source: Ta, 2003.

Figure 10-3 CFD modeling of large reservoir mixing patterns with separated inlet and outlet and for different inlet configurations

limited to the far corner of the reservoir. Concept C, with the nozzle oriented at 60° rather than 90° and directed to the far corner of the reservoir, shows that only very small pockets of the reservoir at the far corner and the corner near the inlet have water ages that exceed 40 days. Most of the water in the reservoir is between 35 and 40 days old (Hannoun and Miller, 2003).

Separation of inlet and outlet. Ta (2003) reviewed the operation and CFD modeling for water storage reservoirs in the United Kingdom and discussed the issue of separating the inlet and outlet for some of their facilities. The reservoirs in the city have an average depth of 14 ft and capacity of 3.4 mil gal. Most reservoirs have multiple inlets/outlets but are normally operated in a fill/draw mode. If reservoirs fill and empty 50% of their volumes within 24 hours, the reservoirs are in reasonably mixed condition.

The elevated storage facility consists of two identical half-circular sections, each with a 215-ft radius, maximum height of 18 ft, 238 supporting columns, and a total capacity of 10 mil gal (Ta, 2003). Only one half was therefore considered in the analysis. The tank has a common inlet/outlet located at one end of the tank, with the pipe at a 10° angle from the floor directed toward the curved wall of the tank. An option of moving the outlet to the opposite side of the existing I/O sump was considered. Figure 10-3 shows the velocity vectors in the reservoir when the outlet was relocated to the other side of the reservoir, while the existing inlet was employed.

The general flow circulation around the reservoir did not change as compared with a common inlet/outlet. Short-circuiting was observed as large portions of the water exited the reservoir at the new outlet. Additionally, the inlet was modified to

direct the water upward, which resulted in short-circuiting and stagnation in some areas. It was concluded that sufficient mixing was achieved with the existing I/O arrangement and that the relocation of the outlet was not beneficial (Ta, 2003).

Extension of an I/O line to separate inlet and outlet. If an existing storage facility with a single service pipe is modified to separate the inlet and outlet, the modification usually can be installed inside the facility to avoid making a new wall penetration; however, the access to check valves and piping for maintenance and upkeep is more difficult.

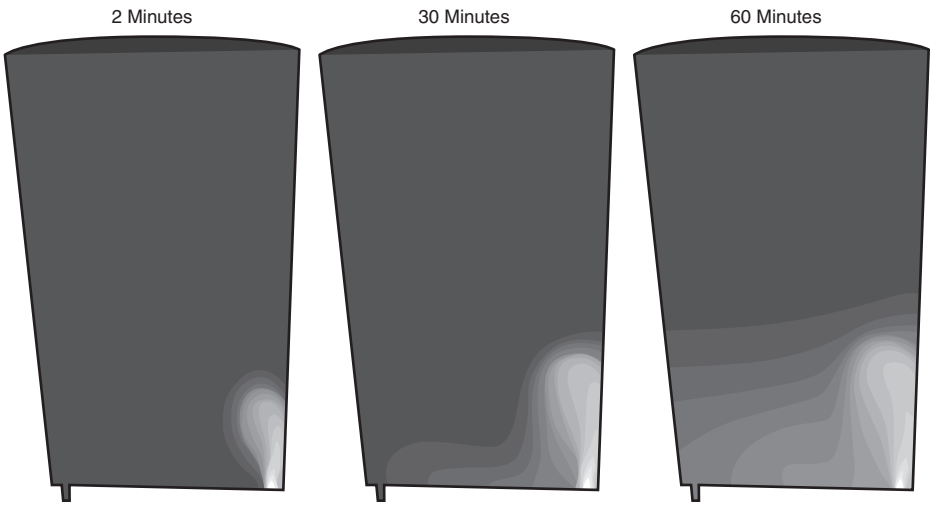
Kirmeyer et al. (1999) evaluated a company that provides drinking water service to approximately 240,000 service connections in 75 cities. In some cases, reservoir inlet and outlet configurations worsened the problem of low chlorine residuals and sediment reaching the distribution system. To alleviate the problem, several reservoirs were upgraded when they were removed from service for cleaning. Common inlet and outlet piping was reconfigured to provide better mixing in the reservoirs by splitting the influent and effluent pipes and piping the influent to the opposite end of the reservoir from the effluent. Reservoir outlet piping located in the flooring of the concrete reservoirs was raised 1 ft to avoid draining sediment into the distribution system. An aggressive valve maintenance program was implemented to ensure all distribution system valves were operating and were in an open position to avoid unnecessary dead-ends in the distribution system.

Standpipes and reservoirs with thermal stratification. In standpipes, the depth exceeds the diameter of the storage facility, and due to this configuration, standpipes are more susceptible to stratification. Also, tall tanks and tanks with large-diameter inlets have a greater tendency toward stratification (Grayman et al., 2000). Standpipes, almost always fabricated from steel and located above ground, can experience a wide variation of water temperature inside the tank throughout the year (Duer, 2003).

Water has its maximum density at about 39°F (4°C), and its density decreases with increasing temperature above this temperature and decreases below 4°C. A temperature gradient is established between the warmer (less dense) water and cooler water within the tank. Whenever there is a temperature difference between the contents of a tank and its inflow, the potential for poor mixing and stratification exists. An inflow jet with excessive buoyancy (either positive or negative) relative to its momentum will lead to ineffective mixing and cause stable, stratified conditions within the tank (Grayman et al., 2000; Duer, 2003). A buoyant jet will either rise or fall (positive or negative buoyancy). This provides a secondary turbulent motion that also entrains ambient water. Mixing and dilution will increase provided the movement of the jet is away from the inlet port. A buoyant jet that falls back on itself results in re-entrainment, with the influent resulting in reduced mixing efficiency (Duer, 2003). Even temperature differences of less than 1°C between the bulk tank water and the inflow can affect mixing characteristics.

Duer (2003) modeled mixing in a 1.5-mil gal standpipe, 53 ft in diameter and with a maximum water depth of 94 ft and a combined inlet and outlet. Figure 10-4 illustrates a case of negative influent buoyancy when the inlet water temperature is 2°F lower than the tank water and the water jet directed upward is overcome by negative buoyancy (second case in Table 10-2 described below). Since the freshest water remains in the bottom of the standpipe after the fill cycle, this will be the first water drawn from the tank during the following draw cycle, i.e., last-in, first-out.

Table 10-2 presents the results of several CFD modeling cases for the standpipe described above and shown in Figure 10-4. CFD modeling suggested that the thermal stratification due to even 12°F negative buoyancy can be overcome by high-momentum pumping (cases 3 and 5 in Table 10-2). Many tanks have inlet pipe sizes that result in a 2- to 4-fps inlet velocity at average flow rates. By simply placing a reducer or duckbill valve on the inlet, the mixing efficiency can be improved without a



Source: Duer, 2003.

Figure 10-4 CFD modeling of water standpipe stratification due to temperature gradient (bottom inlet: 60°F inlet, 62°F tank, low flow velocity of 2 fps)

severe head loss penalty (8-fps jet velocity only yields 1 ft (0.43 psi) of exit loss) (Duer, 2003). Locating the inlet toward the top of the standpipe (cases 6, 7, and 8 for inlet placed mid-depth at 45 ft) resulted in a better mixing throughout the entire tank volume, except when the buoyancy was extremely large (12°F temperature difference). The use of the multiport inlet diffusers (cases 9 and 10) has been shown to mix and disperse influent water throughout the tank faster than a single inlet with the same momentum.

Check valve and piping configuration can also be used for elevated tanks and standpipes when the existing service is a single riser pipe. The riser service pipe entering the tank bottom can be extended inside the tank almost up to the maximum water level, with a tee outlet and a check valve near the bottom. The pipe extension at the top fills the tank (Kirmeyer et al., 1999).

Some large reservoirs with large inlets can also be thermally stratified. Table 10-3 presents the results of a depth sample monitoring study of a large reservoir (150 mil gal with a combined I/O tower containing five rectangular 3 ft by 5 ft gate openings) (Wilczak, 1998). A temperature difference was observed inside the reservoir in August 1998 when the colder water residing in the lower layers below 30 ft depth, which did not mix well, was lower in chlorine and higher in free ammonia. This study was conducted just a few months after chloramine conversion. Subsequently, this reservoir completely nitrified with low chlorine and no free ammonia in the water samples.

Stratified reservoirs will pose the greatest challenge to water quality. The examples of smaller and large temperature-stratified storage reservoirs point out that nitrification is expected to occur there unless the stratification is broken. Fortunately, several design tools are available, including CFD modeling, to remedy these conditions.

Reservoir Baffling and Pillars

Baffling to enhance plug flow and reduce short-circuiting is undesirable in distribution storage facilities and should only be used where CT (disinfectant concentration multiplied by disinfectant contact time) is an issue (Kirmeyer et al., 1999). In distribution system tanks and reservoirs where mixed flow is preferable to plug flow, introduction

Table 10-2 Results of CFD modeling of mixing for various inlet configurations for a water standpipe (1.5 mil gal, 53-ft diameter, 94-ft water depth)

Case Number	Inlet Number × Diameter (inches)	Inlet Location	Discharge Direction	Inlet Velocity (fps)	Inlet Temperature (°F)	Tank Temperature (°F)	Inlet Jet Buoyancy	CFD Modeling Results
1	**1 × 16-in.**	**Floor**	**Vertical**	**2**	**60**	**60**	**Neutral**	**Tank mixed from top to bottom**
2	1 × 16-in.	Floor	Vertical	2	60	62	2° Negative	Only 40% lower volume mixed
3	**1 × 16-in.**	**Floor**	**Vertical**	**4**	**60**	**62**	**2° Negative**	**Higher momentum improved mixing**
4	1 × 16-in.	Floor	Vertical	2	60	72	12° Negative	Only 20% lower volume mixed
5	**1 × 16-in.**	**Floor**	**Vertical**	**8**	**60**	**72**	**12° Negative**	**Tank mixed from top to bottom**
6	**1 × 16-in.**	**Middle 45 ft**	**45° Upward**	**2**	**70**	**72**	**2° Negative**	**Relatively good mixing everywhere**
7	1 × 16-in.	Middle 45 ft	45° Upward	2	60	72	12° Negative	Poor mixing in the upper portions
8	1 × 16-in.	Middle 45 ft	45° Upward	2	72	60	12° Positive	Poor mixing in the lower portions
9	**4 × 8-in.**	**Every 22.5 ft**	**Horizontal**	**2**	**60**	**60**	**Neutral**	**Good mixing everywhere**
10	**4 × 8-in.**	**Every 22.5 ft**	**Horizontal**	**2**	**60**	**72**	**12° Negative**	**Good mixing up to the top inlet**

Source: Adapted from Duer, 2003.
NOTE: Cases of relatively good mixing shown in bold.

Table 10-3 Results of depth sampling indicating thermal stratification of a large water storage reservoir in California (150 mil gal)

Sample Location	Depth (ft)	Temperature (°C)	Total Chlorine (mg/L Cl_2)	Free Ammonia (mg/L NH_3-N)
North	5	18	1.73	0.07
North	15	18	1.68	0.09
North	25	19	1.64	0.12
Center	5	18	1.67	0.11
Center	20	17	1.61	0.10
Center	32	14	0.98	0.17
South entrance	5	18	1.73	0.11
South entrance	20	16	1.64	0.11
South entrance	35	14	0.76	0.20
Sample tap		21	1.73	0.09

Source: Wilczak (1998).

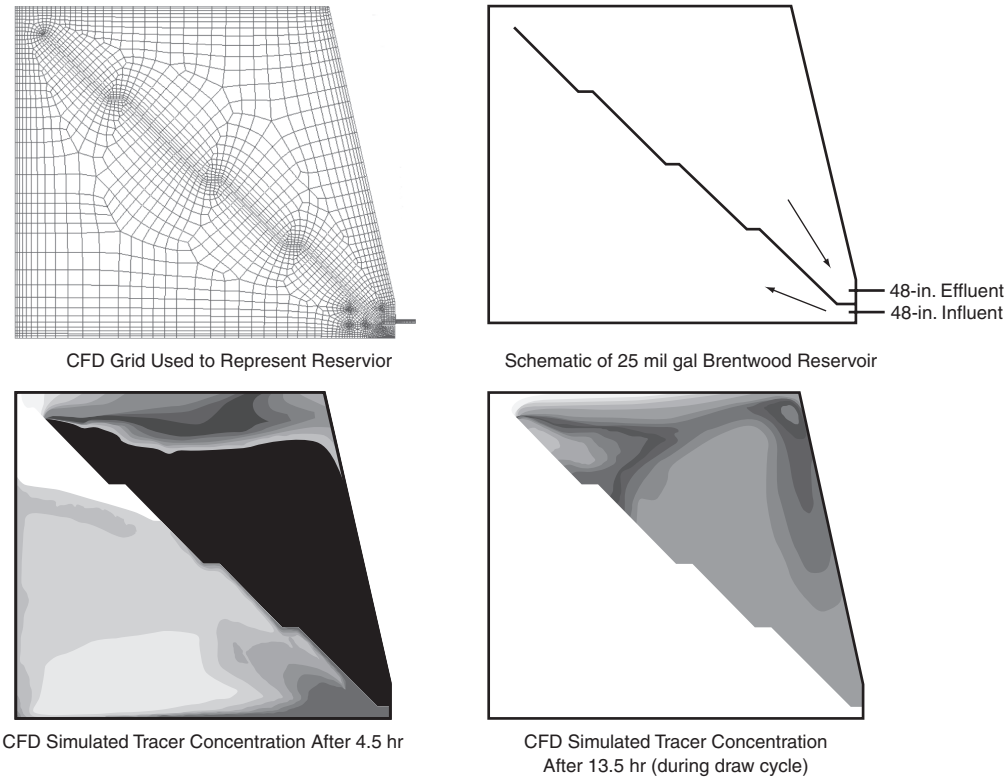
of baffles inhibits mixing and, especially in fill-and-draw operation, can produce stagnant zones and zones of poor mixing. Therefore, under most circumstances in distribution system storage facilities, baffles should not be used (Grayman et al., 2000). Modeling of clearwells indicates that dead space areas develop even with relatively good baffling, whereas good mixing typically eliminates all dead spaces.

Grayman and Arnold (2003) presented a case of modeling the impacts of baffling on mixing within a large reservoir. This 25-mil gal ground storage reservoir has separate 48-in. inlet and outlet pipes located at the bottom of the reservoir. The height of the reservoir is approximately 30 ft. A 28.5-ft tall baffle wall divides the reservoir into two sections. CFD modeling was applied to study an alternative configuration in which the three 16-ft panels were removed from the baffle wall (Figure 10-5). The results of the modeling presented in the lower portion of Figure 10-5 show faster mixing with portions of the baffle wall removed.

Mixing Alternatives

Hydraulic circulation systems or some method to mix the water may be needed for reservoirs with dead zones. Mixing will eliminate dead zones and increase chloramine concentrations and lower free ammonia levels in these areas.

Mixing the storage facility contents could be accomplished by momentum mixing, using the energy from inlet streams, mechanical mixing, or air sparging, or by circulating storage facility contents by pumping. Momentum mixing requires special attention to size and location of inlets and outlets (velocity and inlet direction), configuration, and the depth of water. Whenever a fluid flows through an orifice into a large body of water, a jet is formed. The diameter of the jet increases with distance from the orifice and significant amounts of the surrounding fluid are entrained into the jet. The jet needs to be turbulent to promote the entrainment of ambient water with water inside the jet (Grayman et al., 2000). Grayman et al. (2000) listed guidelines for recirculation mixing and mixing time formulas (see chapter 8). A tank's mixing time increases with increasing tank volume and decreases with increasing inflow rate or decreasing inlet diameter. The inlet jet should not be pointed directly toward nearby



Source: Grayman and Arnold, 2003.

Figure 10-5 CFD modeling of large reservoir mixing patterns with separated inlet and outlet and different baffling configurations

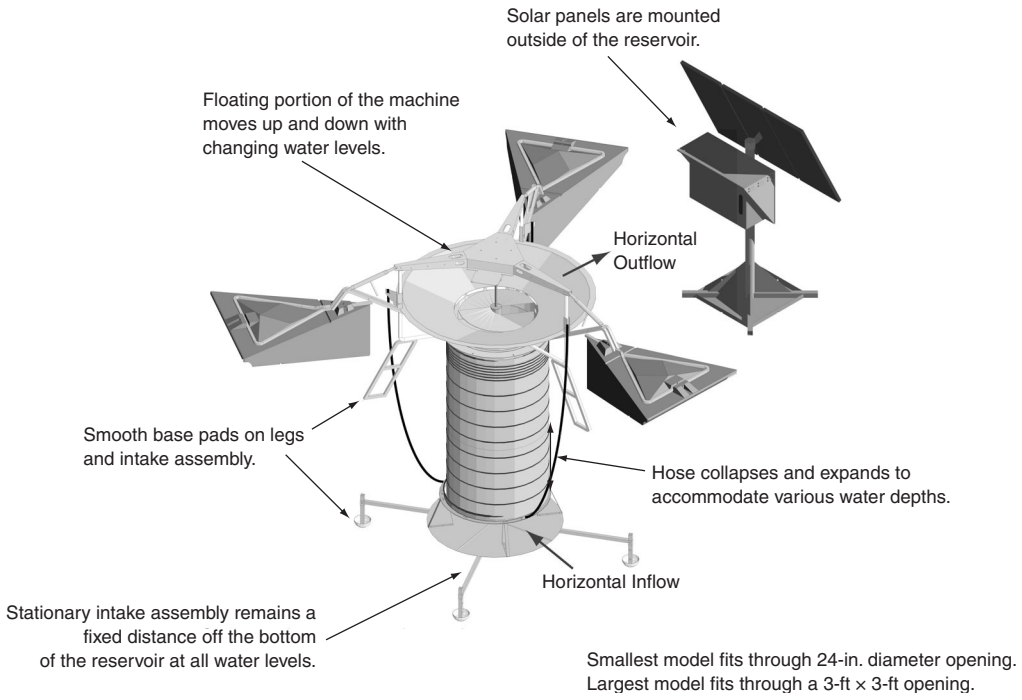
impediments, such as a wall, the reservoir floor, or deflectors, to allow for the path of the jet to be long enough to promote mixing. A turbulent, rather than laminar, jet is necessary to entrain ambient water into the jet (Grayman et al., 2000). Momentum mixing has been discussed in detail in chapter 8.

Mechanical mixing requires special precautions to avoid water contamination by mixer lubricants. The use of food-grade lubricants is recommended in submerged electromechanical devices such as mixers. Air sparging is rarely used and not recommended because it can cause a change in water quality characteristics (pH, temperature, carbon dioxide or oxygen concentration, dechlorination). Nozzles, as well as the air filtration blower system, need to be maintained and noise must be controlled. Pumped circulation systems, which provide good mixing without potential contamination or maintenance, can easily be designed and allow for rechlorination processes.

Mechanical Mixers

Several mixer technologies are available on the market. The SolarBee (Pump Systems, Inc., Dickinson, ND) (Figure 10-6) is a floating solar-powered reservoir circulator that has been used in the past for aeration of wastewater, open reservoirs, and lakes, as well as in covered potable storage tanks. Solar panels are installed on top of a reservoir and connected to a battery supplying the mixer motor with a direct current supply.

The largest unit is 16 ft in diameter and is constructed of stainless steel. The SolarBee draws flow from below the machine and spreads it gently across the top of the



Source: SolarBee, Div. of Pump Systems, Inc., 2003.

Figure 10-6 Schematic of SolarBee mechanical mixer

reservoir. SolarBee models are equipped with photovoltaic solar modules. A chemical injection kit can also be added to the SolarBee to disperse and mix chemicals. The manufacturer recommends it for tanks 0.2 to 80 mil gal in size per single unit (SolarBee, 2003). Several water utilities have recently installed these mixers to help control nitrification; however, no published reports exist yet as to the effectiveness of these devices for that purpose. It is likely that the numbers of mechanical mixers installed inside water storage reservoirs will increase in the future.

Severn Trent Services, Inc. provides the ClorTec Reservoir Management System™ (RMS) to manage the internal water quality of storage tanks and reservoirs (SevernTrent, 2003). The RMS uses a pump to move the body of water within the reservoir in an upward fashion, providing the residual chlorine analyzer with the water sample stream and allowing for the injection of chemicals directly into the water jet. Each RMS is typically configured to include the following support components:

- programmable logic controller system with operator interface,
- chlorine residual analyzer,
- submersible pump and mixer assembly,
- associated valves and tank level controls, and
- optional equipment, which includes ammonia feed system and/or a chlorine feed and generation system.

RMS output is up to 150 gpm, and the manufacturer recommends installation of the unit on up to 10-mil gal tanks. The application of RMS for reservoir residual boosting is also discussed at the end of this chapter.

A large water utility in California has installed five RMS mixers at their distribution water storage reservoirs ranging in capacity from 0.8 to 7 mil gal. No continuous

chemical feed or automation equipment was installed, instead the utility relies on improved mixing and periodic breakpoint chlorination for reservoir water quality maintenance. The operational experience gained in the last few years suggests that improved mixing allows the tanks to maintain total chlorine residuals longer between nitrification episodes (for a few months instead of 1 month prior to installation of the mixers). Therefore, only one seasonal breakpoint chlorination is needed in the summer. Breakpoint chlorination is also easier because the mixer provides efficient chemical delivery and dispersion. Reservoir water levels do not need to be lowered prior to chlorination and filled to achieve mixing once the chlorine has been added. Following breakpoint chlorination, the reservoir is isolated for 24 hours, checked for adequate free chlorine, and put back in service (pers. commun., J. Guistino, 2003).

There are other mechanical mixers on the market. The two technologies briefly described above appear to be gaining popularity currently in the United States. Again, at this point there are no published studies verifying the benefits of mechanical mixers for nitrification control. The number of applications is increasing and operators feel that mixers are helpful in managing water quality. A large utility in Australia operates a vast distribution system serving 4.2 million customers and consisting of 260 water storage reservoirs with approximately 50% of them having installed mechanical mixers (pers. commun., J. Broad, 2005).

Custom-built Pump Recirculation Systems

Circulation systems for water storage facilities have been used less frequently and there is little history of performance data indicating what level of velocity gradient is sufficient for good mixing. An energy gradient of 10 sec^{-1} has been used in the design of recirculation systems and it may be used as a guideline (Kirmeyer et al., 1999). Retrofitting a circulation and mixing system into an existing storage facility is fairly straightforward; a single wall penetration is required.

An external pump recirculation system is an option in lieu of an internal mechanical mixer. The benefits of this approach are: (1) easy access to mechanical equipment; (2) possibly lower cost, especially for smaller tanks; (3) avoidance of potential lubricant contamination from an internal mixer; and (4) allowance for chemical addition. The disadvantages are: (1) requirement for wall or roof penetration and (2) higher power requirements than for mechanical mixers.

A Washington State utility has installed or completed design for several pump recirculation systems on reservoirs ranging in capacity from 1 mil gal to 60 mil gal. The pumps recirculate water back to the reservoir and provide mixing energy via dedicated discharge piping equipped with a series of nozzles. The systems are designed to provide reservoir mixing and to boost disinfectant residuals. The recirculation systems have also been configured to provide a source of high-pressure water for periodic interior washdown and cleaning. The utility has found that required pump sizes are on the order of 1.0 to 1.25 hp/mil gal of water stored (CDM, 2002).

Monitoring for Reservoir Mixing

Sampling the inlet or outlet water may not indicate what is happening inside the storage facility. Short-circuiting or lack of use may cause water quality to vary widely throughout the storage facility. On-line continuous monitoring, especially on the outlets of storage facilities, should be considered for tracking water quality. In addition to access hatches, design considerations should include strategically placed ports that would facilitate adding chlorine to the facility and sampling locations distributed within the reservoir (Kirmeyer et al., 1999).

One utility installed water quality cabinets in several of its water storage reservoirs to allow for better sampling of the stored water and to assist in reservoir cleaning

and periodic chemical treatment (e.g., chlorination). Previously, the only sampling taps and chemical injection ports were available on the I/O line.

The facility contains sampling, aeration, dispersion, injection, and vacuum connection piping; sinks for draining water samples; electrical connections; and space for future total chlorine analyzer and chemicals (if needed). The cabinet is locked and accessible only to utility staff. The aeration and chemical dispersion piping runs across the entire diameter of the reservoir to better mix and disperse the chemical, while a chemical injection line allows for optional injection directly to the centerline of the inlet/outlet. Vacuum line connections provide penetration through the wall for periodic reservoir cleaning.

The sample tap from the side of the tank provided in the cabinet is frequently used to collect water quality data; this location is preferred to the sample tap located on the I/O line. Most chlorine analyzers are still installed at the pumping plants and analyze the I/O water sample, but future installation of analyzers at the cabinets is possible if a disinfectant residual booster station is installed. The aeration line for sparging and mixing the reservoir contents has not been used extensively, and pumping is still the primary way to mix the reservoirs. Chemical dispersion lines have been useful for faster and better hypochlorite delivery during breakpoint chlorination.

Uncovered Reservoirs

Uncovered finished water storage facilities have a high potential for direct contamination and should be replaced or covered (Kirmeyer et al. 1999). Providing a cover for a facility may be the single most effective means of avoiding water quality problems. Uncovered reservoirs make up only 3% of all storage facilities in the United States, and many are being replaced or covered (Kirmeyer et al., 1999), as required under the US Environmental Protection Agency Interim Enhanced Surface Water Treatment Rule. Covering a reservoir, especially large-volume facilities, may lead to nitrification, because nitrifying bacteria grow better in the dark conditions. Therefore, nitrification considerations should be taken into account while designing reservoir covers.

Kirmeyer et al. (1996) described the experience in Pennsylvania with covering and placing the reconstructed storage reservoir into service. Redesign and construction involved a new Hypalon cover, a cover drainage system, a geotextile liner, modified slope walls, new inlet piping, and an inlet structure. This 150-mil gal finished water reservoir replaced an open finished water reservoir. The utility had determined that a maximum hydraulic detention time of 5 days (based on plug-flow calculations) was desired in all finished water storage facilities to ensure satisfactory water quality. A minimum total chlorine residual goal of 1.0 mg/L was selected. Options identified to minimize chloramine residual loss included increased hydraulic turnover and, in extreme cases, boosting the total chlorine residual by chemical addition (sodium hypochlorite and ammonia) to the reservoir influent. Disinfectant was not added to the reservoir on a regular basis. About 6 weeks after the reservoir was put into service, the stored water's total chlorine residual decreased to 1.15 mg/L. The operating level was lowered from 27 ft to 20 ft, effectively increasing its hydraulic turnover. This action resulted in boosting the chloramine residual leaving the reservoir to acceptable levels. The new reservoir eliminated several water quality problems associated with the open reservoir, such as problems with algae and bacterial growth. It also reduced the potential for direct contamination, accumulation of sediment, and formation of disinfection by-products (DBPs) associated with seasonal chlorination of the open reservoir. Nevertheless, covered reservoirs are not free of water quality problems and are susceptible to contamination if the cover is torn or when the roof begins to leak. Current chloramine residual goals are: 2.0 mg/L Cl_2 at the entry to the distribution system and to maintain 1.0 mg/L Cl_2 or more in the system (Burlingame et al. 2003).

MODIFICATIONS TO PIPING AND PRESSURE ZONES

Piping replacement and/or improvements are generally associated with the best management practices regardless of the presence of nitrification, especially regarding corroded pipes. Nitrification would be generally a minor driver for pipeline replacement.

Sizing Water Mains

Piping has a much greater surface area to water volume ratio compared to storage facilities, and water in the pipes may have comparably lower disinfectant residual than bulk water in storage tanks. Currently, fire flows govern the sizing of the distribution system but not transmission mains.

A recent study (Snyder et al., 2002) has shown that the basis of current fire-flow standards (i.e., needed fire flow) is not clear, potentially outdated, and definitely not consistent with new potable water quality regulations. Further, the study concludes that opportunities exist to modify these requirements through the increased use of alternate fire suppression technologies. These methods include automatic fire sprinklers; automatic mist suppression systems; non-water–based suppression systems; additives (surfactants/foams); small droplet technologies; use of nonpotable water supplies; and the increased use of water tankers. The increased use of these methods will help reduce the need to overdesign potable water systems, thereby reducing water system infrastructure needs (such as smaller pipeline sizes and lower storage volumes for fire-flow demands) and costs, while balancing the need for providing adequate fire flows and maintaining water quality because both affect public health and safety (pers. commun., J.L. Rios, 2003). Utilities need to coordinate with local fire officials and consider their International Organization for Standardization ratings and insurance costs. In the future, if fire agencies require sprinklers for all homes and structures, fire-flow requirement and therefore mains sizes could be reduced. The use of alternate fire suppression technologies can help reduce costs of new potable water systems. Where infrastructure is in place, replacing pipes and reservoirs is a very costly undertaking.

Line or Replace Corroded and Old Water Mains

Deteriorated pipelines, especially unlined cast iron lines, can create water quality problems such as rusty or red water, reduce secondary disinfectant levels, and support excessive biofilm growth, including nitrifiers. Pipeline replacement or rehabilitation programs, which are costly and should be carefully planned to be efficient and cost effective, are usually part of a capital improvement program (Kirmeyer et al., 2000).

Eliminate Dead-ends to Avoid Stagnation

Design pipelines with adequate blow-offs. A Virginia utility installed automatic flushers that go off at a specific time at some key areas. The concept of automatic flushers, or “bleed stations,” is a potentially cost-effective tool for residual maintenance.

Pressure Zone Modifications

In water distribution systems containing multiple pressure zones, excessive water age can build in the upper zones if the zone transfer pumps take suction from the lower zone’s storage facilities. In such pumping configuration, the water passes through each pressure zone’s storage facility before getting pumped to an upper zone, thus accumulating water age. Instead, zone transfer pumps should bypass storage facilities and take suction from the nearest transmission pipeline in the lower zone. This will

not reduce average water age but will avoid concentrating older-age water to the upper pressure zones and encouraging nitrification.

Pressure zone boundaries are often created by closing an isolation valve on a water main. This creates a dead-end main that will lead to stagnation and possible nitrification. In addition to automated and manual flushing, the isolation valve can be bypassed by a much smaller-diameter pipe to allow water from the upper zone to bleed back to the lower zone. One utility that follows this practice uses only a 1-in. diameter pipe, which moves enough water to keep the water in an upper-zone pipeline fresh, without wasting water. Again, this will not reduce average water age but will move water from stagnant areas to the more active lower zone where the water will be consumed sooner (pers. commun., J. Anderson, 2005).

BOOSTING COMBINED CHLORINE RESIDUAL IN CHLORAMINATED DISTRIBUTION SYSTEMS

Chloramines are typically more stable than free chlorine, and elimination of booster stations has been one of the benefits of chloramine conversion for some utilities. However, in cases where chloramine demand/decay is high or for larger systems with longer water age, boosting chloramine residuals may be used for nitrification prevention or disinfectant maintenance. Boosting combined chlorine residual in chloraminated distribution systems is still relatively uncommon and only a limited number of cases have been reported. The majority involve boosting the combined residual at a point of entry to a consecutive distribution system, for example, for systems purchasing water from a wholesaler. The number of boosting stations in reservoirs within distribution systems is gradually increasing. Typically, boosting chloramine would be considered after other operational or engineering options not requiring chemical additions in the system have been implemented. Kirmeyer et al. (2000) state that the causes of disinfectant loss within the distribution system should be determined prior to installing booster facilities. Operational or maintenance practices may improve chloramine residuals without the expense of installing and operating booster disinfection facilities.

Cohen (1998) stated that operating a chloramine boosting station could be expensive and labor intensive. Boosting chloramine is more difficult due to the fact that two different chemicals may have to be added at different dosage rates and at a specific ratio to the water flow rate. Also, day-to-day variation of water quality in the distribution system, based on factors such as demand, temperature, type of pipes, and variable water flow and chemical strength, requires constant adjustment of the chemical dosage. Other measures discussed earlier in this manual need to be considered prior to installing booster stations in the distribution system. The following measures are aimed at increasing chloramine residual by attempting to reduce distribution system water age and chloramine demand in distribution system pipes and reservoirs:

- Establish a water quality monitoring program and baseline levels for water quality parameters, such as chloramine residual, total ammonia, and nitrite.
- Follow up on all customer complaints with comprehensive investigations.
- Establish a program to turn over reservoir contents as quickly as possible.
- Implement a specific flushing program to address problem areas.
- Establish a valve maintenance program to ensure appropriate valves are open and minimize system dead-ends.
- Optimize corrosion control.
- Improve chloramine stability in bulk water and consider increasing chloramine dosage at the source or treatment plant.

- Make hydraulic modifications to increase circulation within the distribution system.
- Establish a main replacement or recoating program to replace old and deteriorated pipelines with high disinfectant demand.

Nomenclature, Potential Benefits, and Disadvantages

Booster chlorination typically refers to the addition of chlorine at an appropriate location in the distribution system. In the case of a chloraminated system, "booster chlorination" would also apply to the addition of chlorine only. However, the desired outcome would be to bind the available free ammonia and any nitrite present to raise the combined chlorine residual without developing a free chlorine residual. "Booster chloramination" in a chloraminated system refers to the addition of both chlorine and ammonia at a distribution system location, typically where free ammonia would not be present in sufficient quantities and the desired outcome would be to raise the combined chlorine residual.

The benefits of boosting chloramine residual can be summarized as follows:

- Boosting chloramine minimizes free ammonia available to the nitrifying bacteria and helps in reducing nitrite levels. Chloramine demand is increased in the presence of nitrifying bacteria and nitrite; therefore, boosting improves chloramine stability and residual maintenance. This is the main objective of boosting in a chloraminated system.
- Boosting chloramine allows for lower chloramine concentrations to enter the distribution system, thus minimizing the decay rate. The rate of chloramine loss is concentration dependent: the higher the concentration, the faster it decays and more free ammonia is released. Uber et al. (2003) referred to this as the "chemical kinetic effect." For example, as is the case with free chlorine, a lower disinfectant dose applied at the treatment plant may also lower the levels of DBPs produced and improve the taste and odor of water in the service areas near the plant.
- Boosting chloramine residual reduces disinfectant use by better matching the dose to the unique ultimate residence time of the water, rather than dose large flows near the treatment plant to levels that may only be required by relatively smaller flows with long residence times (Uber et al., 2003). So far, the tendency has been to increase chloramine residuals in treatment plant effluents to help maintain the disinfectant in the distribution system, but the use of booster stations offers an alternative with more efficient chemical use.

The main disadvantages of boosting chloramine residual are:

- The mixing of free chlorine with chloramines, if not controlled properly, can result in loss of some residual, breakpoint chlorination, increased DBP production at breakpoint, and the potential for bacteriological regrowth, Total Coliform Rule violations, and customer complaints related to taste and odor. A utility practicing chloramination must carefully operate and monitor the rechloramination process.
- The need for remote chemical storage, feeds, increased maintenance, and monitoring associated with boosting. If insufficient ammonia is present, it must be added along with chlorine. Storing and handling chemicals off site, often in residential areas, is considered undesirable; utility staff have expressed concerns about the safety to workers associated with chemical handling. For these reasons, utilities have been reluctant to employ booster stations.
- The operational challenges of adding two different chemicals at different dosages.

- Ammonia addition, if overdosed, will promote nitrification. Boosting chloramines should not be used as a measure to control existing nitrification episodes but rather as a preventive measure only.
- Distribution system operation and maintenance (O&M) crews are often different from the water treatment plant O&M crews and are completely untrained in the use of water treatment chemicals, and, in some cases, union contracts preclude chemical handling activities.
- Chlorine and ammonia cannot be added as preformed chloramine to mitigate many of the concerns. In spite of what is stated in some textbooks, addition of preformed chloramine is not an option due to the potential explosion hazard from combining two strong chemicals. Preforming of chloramine should only be attempted in a laboratory setting with proper safeguards and by trained personnel, typically only for research purposes.

Cohen (1998) and Kirmeyer et al. (2004) offered several comments on distribution system chloramine booster stations:

- Proper mixing of the chemicals needs to be allowed prior to the distribution system; 10 or even 20 pipe diameters distance was not enough for proper mixing. Static mixers may need to be installed.
- Ammonia stock concentrations should not be too high (<20%) to minimize evaporation in hot climate areas. Ammonia tanks need to be designed with proper pressure relief to allow for trouble-free tank filling. Ammonia lines should be buried 1 ft below grade to minimize chemical pump vapor-locking and to maintain constant ammonia dose.
- In the case of flow-through reservoirs, add chlorine at the reservoir influent in proportion to available free ammonia and nitrite and, if necessary, boost chlorine and ammonia at the effluent. This will minimize nitrification inside the reservoir.
- Consistently maintaining a 5:1 Cl_2:NH_3-N weight ratio is difficult. A set of guidelines for operators and use of a supervisory control and data acquisition (SCADA) system and computers to control the ratio may help.
- If an attempt to automatically control the dosage is made, set the chlorine analyzer to control the chlorine pump to achieve the total chlorine residual goal. Then, phase the ammonia pump at a 5:1 ratio to the chlorine pump and prevent the ammonia pump from running without the chlorine pump being on.
- Hook up alarms to warn of chlorine chemical pumps out of service, chlorine residual out of range, and low chemical storage levels.

Kirmeyer et al. (2000, 1999) list the following criteria in selecting the location of booster stations:

- The total chlorine residual in the water has begun to decrease but has not totally dissipated.
- Chlorine can be applied uniformly into the water.
- The location is acceptable to neighbors and is easily accessible for chemical delivery vehicles, with room for chemical storage and feed equipment.
- Power is readily available.
- Communications systems are readily available for SCADA system.
- Flow and/or residual pacing can be used.
- Safety concerns can be addressed.
- For a common I/O line, chlorine should be injected as the storage facility is filling, although mixing the chlorine throughout the reservoir may be difficult.

A large Australian utility has extensively used booster chlorination in their vast, 85% chloraminated system, which supplies over 4.2 million customers. The system consists of 9 water treatment plants, 260 water supply tanks, and 21,000 km of water mains. Chlorine is dosed at many tanks to try and maintain a 5:1 chlorine to ammonia ratio. Dosing is done either manually or by automatic booster plants. Nitrification is an ongoing problem, although major episodes are rare. The utility has also tried manual booster chloramination (addition of chlorine and ammonia) on a limited scale, with mixed success (pers. commun., J. Broad, 2005).

Booster Station Survey

Wilczak et al. (2003) conducted a survey of 10 chloramine booster stations. A variety of booster station locations and process controls were applied depending on the case and funds available. Overall, several utilities have successfully boosted at their flow-through transmission facilities with careful monitoring with both on-line or grab samples. A great deal of operator attention is required to operate these facilities since the success of boosting combined chlorine residual impacts the entire downstream distribution system. The applications at the smaller reservoirs or pumping stations are typically newer, and a significant amount of experimentation is still occurring to optimize the process. However, these attempts have been successful in maintaining higher total chlorine residuals in storage facilities served by the booster stations. The number of booster stations at storage facilities in the farther ends of the distribution system is likely to increase significantly in the near future as more systems convert to chloramines and the practice of seasonal (annual) breakpoint of the entire distribution system becomes less attractive due to more stringent DBP regulations and concerns regarding DBP formation.

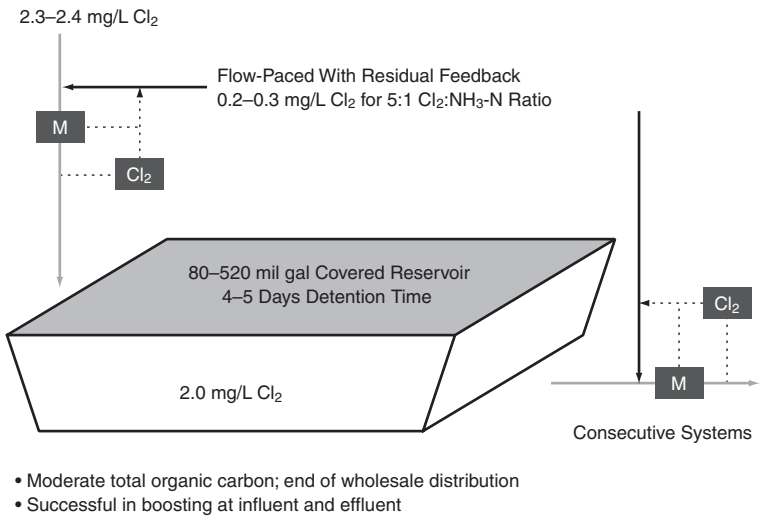
Flow-through Booster Stations at the Entry to a Distribution System: Case Studies

Several utilities have been operating flow-through booster stations for many years. These include large wholesale utilities boosting the residual prior to the entry to the member agencies' distribution systems and utilities boosting the residual close to the beginning of the distribution system. Examples of these practices are shown graphically in Figures 10-7 to 10-10 (Wilczak et al., 2003). The large water storage reservoirs in California are represented in Figure 10-7. Chlorine is fed only to combine free ammonia at the entry and exit of several of the large water storage and transmission reservoirs. Chlorine is flow-paced (flowmeter denoted as "M" in Figure 10-7 and subsequent figures) with total chlorine residual analyzer feedback (denoted as "Cl_2" in Figure 10-7 and subsequent figures). The goal of boosting is to maintain 5:1 Cl_2:NH_3-N weight ratio at the influent and effluent. Ammonia feeds (manual control) are also available at the influent and effluent; they are only used after reservoir outages.

Figure 10-8 depicts continuous chlorine boosting at an outlet of a large flow-through reservoir in Oregon to increase residual. Chlorine is fed flow-paced to twin 30-in. effluent pipes flowing at 3 to 15 mgd (the existing influent feeds are not used). A total chlorine residual analyzer is located upstream of the chemical feed point for monitoring only. Operators make careful dose adjustments based on the Cl_2:NH_3-N ratio at the outlet and free NH_3 measurement downstream.

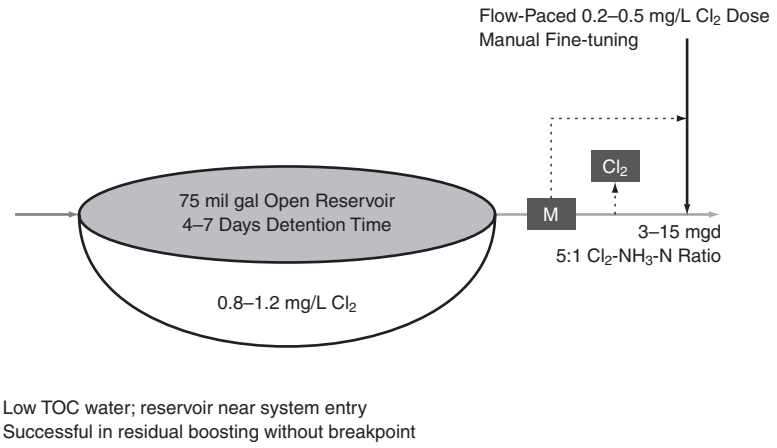
Continuous boosting of total chlorine is conducted in Florida to tie up free ammonia and to increase total chlorine residual in a blend of surface and groundwater to meet the target residual set point of 4.25 mg/L after boosting (see Figure 10-9).

Prior to boosting, the treated surface water and treated groundwater are blended together in the transmission main (see Figure 10-9). Then the final product residual is boosted before delivery to the customers. The total Cl_2 analyzer controls



Source: Wilczak et al., 2003.

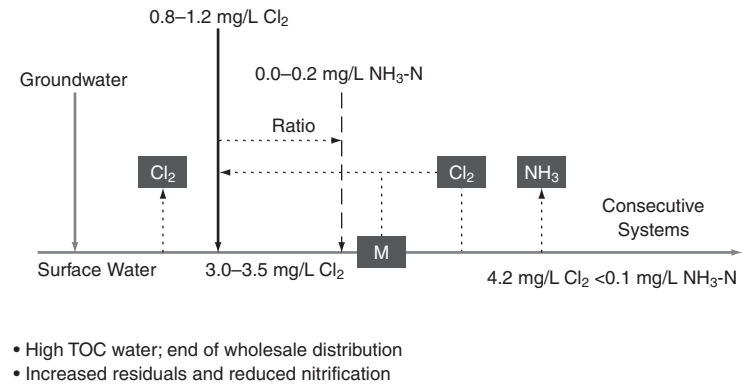
Figure 10-7 Booster station at a large water transmission reservoir operated in California near the entry to consecutive distribution systems: chlorine feed at reservoir influent and effluent



Source: Wilczak et al., 2003.

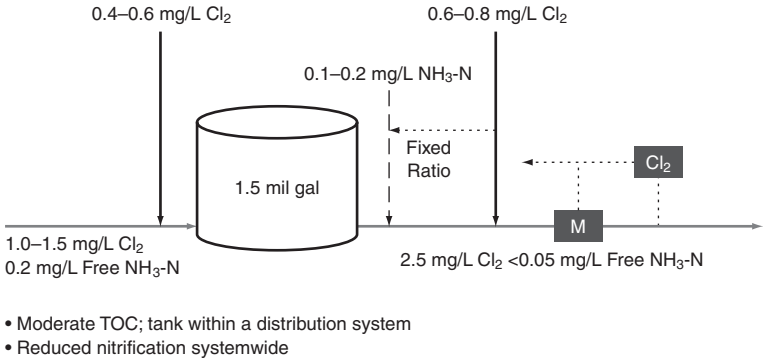
Figure 10-8 Booster station at a large water transmission reservoir at the beginning of a distribution system in Oregon: chlorine feed at reservoir effluent

the output of 12.5% hypochlorite metering pumps (variable speed and fixed stroke). Free NH_3 is monitored via a Hach APA 6000 analyzer (Hach Company, Loveland, Colorado). Feed control for 19% NH_3 pumps is based on total Cl_2 analyzer value and programmable logic controller (PLC) calculation, which maintains a fixed ratio for the injection of hypochlorite and NH_3. The fixed ratio value is adjustable via a SCADA system, based on free NH_3 in the finished water. The booster NH_3 dose can be adjusted from 2:1 to 6:1 Cl_2:NH_3-N ratio. This provides the flexibility to optimize free NH_3 in the blend. Manual override capability is available for all metering pumps, and all flow, pressure, and water quality data are collected and stored in the SCADA system.



Source: Wilczak et al., 2003.

Figure 10-9 Booster station at a large water transmission pipeline/blending facility in Florida near the entry to consecutive distribution systems: chlorine and ammonia feeds

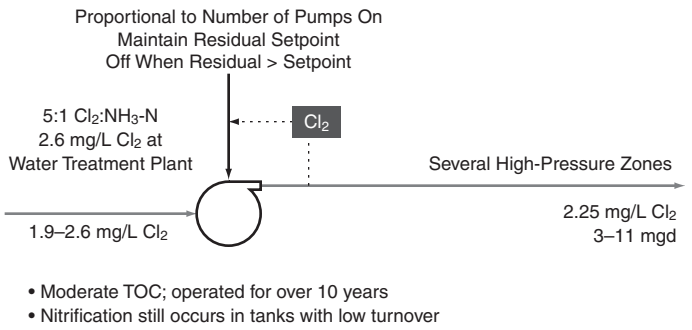


Source: Wilczak et al., 2003.

Figure 10-10 Booster station at a small water transmission reservoir at the beginning of a consecutive distribution system in California: chlorine feed at reservoir influent and effluent, ammonia feed at reservoir effluent

Figure 10-10 depicts continuous chlorine boosting at the influent to a consecutive system to tie up free NH_3 (water is 1 to 2 days old) and boosting Cl_2 and NH_3 at the effluent of 1.5-mil gal flow-through reservoirs. Boosting is conducted at this location in the distribution system to prevent nitrification within these facilities and to increase total residual for the rest of the system. Ammonia was added to reservoir influent in the initial trials, which resulted in nitrification within the reservoir. Subsequently, the addition point was moved to the effluent. Operators make manual dose adjustments based on results of grab samples. Manual adjustments are needed due to multiple chemical feeds. The guidelines for inlet and outlet Cl_2, NH_3, and NO_2 ranges, and corrective actions if these ranges are not met are provided to the operators.

In summary, chlorine can be boosted at the influent or effluent of a transmission reservoir, while ammonia feed is recommended at the effluent only. Operator care is required to maintain chemical ratios.



Source: Wilczak et al., 2003.

Figure 10-11 Booster station at a transfer pumping plant in a California distribution system: chlorine feed to pump suction

Flow-through Booster Station at a Transfer Pumping Station: Case Study

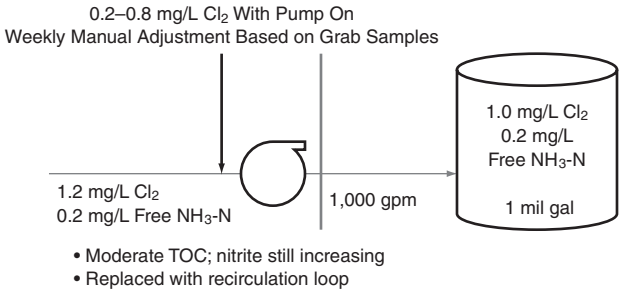
Year-round chlorine boosting (primarily in winter when demands drop off) at a 3- to 11-mgd pumping station partway in a California distribution system (water is 1 to 7 days old) is depicted in Figure 10-11. The goal is to produce consistent total Cl_2 residual and reduce microbial growth and nitrification in upper pressure zones. Sodium hypochlorite is fed to the intake of four pumps; metering pump speed is based on the number of pumps on (no flowmeter). Pump stroke is based on residual feedback to maintain a constant residual set point of 2.25 mg/L. If the residual is greater than the set point, the pump stroke goes down to zero. The booster station is effective and has been operated and maintained for 10 years. Nitrification still occurs in tanks with insufficient turnover. However, residuals entering the tanks are as high as 2.0 mg/L due to the booster station, which has contributed to delaying the onset of nitrification.

Booster Station at a Reservoir Pumping Station: Case Study

The schematic of a booster station feeding chlorine (May through November) at a distribution pumping station supplying water to a 1-mil gal standpipe and a portion of a Maine distribution system is shown in Figure 10-12 (water is several days old). A sodium hypochlorite metering pump turns on automatically with 1,000-gpm pumps (constant pumping rate). The dose is set based on grab total Cl_2 and free NH_3-N samples to combine free ammonia; no on-line chlorine analyzers are used. Nitrification in the standpipe was reduced, but nitrite was still increasing. The utility felt that a recirculation loop would be better because it would allow more free ammonia to be combined inside the standpipe than at the pumping station.

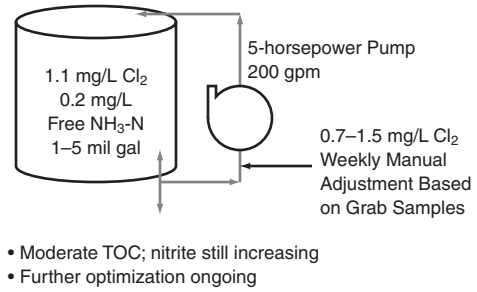
Booster Station at a Reservoir Recirculation Loop: Case Studies

The two cases shown in Figures 10-13 and 10-14 represent booster chlorination at a storage reservoir. Recirculation loops, as shown in Figure 10-13, with continuous (May through November) chlorine boosting at three 1- to 5-mil gal distribution system



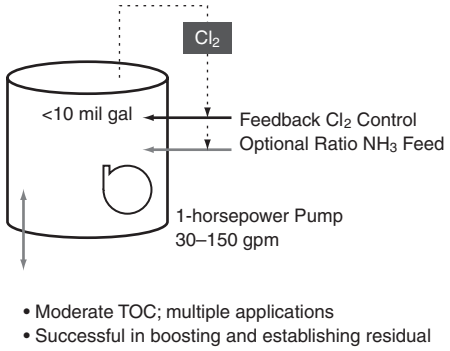
Source: Wilczak et al., 2003.

Figure 10-12 Booster station at a reservoir pumping plant within a Maine distribution system: chlorine feed to pump suction



Source: Wilczak et al., 2003.

Figure 10-13 Booster station at a reservoir recirculation loop in Maine: chlorine feed to the loop



Source: Wilczak et al., 2003.

Figure 10-14 Booster station at a reservoir internal mixer in California: chlorine and ammonia feeds directly to the mixing zone at the discharge of the mixing pump

standpipes were installed to increase residual, minimize nitrification, and stabilize pH. The boosters are started in the spring at a rate of 200 gpm (0.3 mgd) when there is no nitrification and discontinued in the fall. Water is taken from the standpipe I/O line and returned to the top of the standpipe below the water surface. The sodium hypochlorite dose is adjusted manually on a weekly basis based on grab total chlorine and free ammonia concentrations to combine free ammonia in the recirculated stream. No on-line total chlorine analyzers were installed originally. Metering pump and NaOCl scale readings are used for daily dose calculations. Smaller standpipes with larger turnover are monitored more frequently. Nitrification was reduced in standpipes with good turnover without DBP formation; however, nitrite concentration was still increasing and further optimization is ongoing.

The ClorTec Reservoir Management System™ (including chlorine and ammonia feeds with mixing pump inside a 10-mil gal storage tank) is schematically depicted in Figure 10-14. On-line combined chlorine residual analyzer and PLC control the addition of chlorine and ammonia (the installation may be also equipped with the on-site brine generator and sodium hypochlorite generator). A target 2.3-mg/L total chlorine residual is maintained inside the tank, whereas before booster installation, only traces of the residual were measured.

Proposed Controls and Water Quality Sampling for a Chloramine Booster Station

Several different process controls and water quality sampling schedules are applied by utilities depending on the location of the booster station, boosting objectives, variation in water quality, water flows, funds, and staff availability. Therefore, it is not possible to recommend an "ideal" process control and water quality testing configuration that would fit every case. However, based on information gathered (Wilczak et al., 2003), five alternative approaches are summarized below:

- Compound loop (flow-paced with residual feedback) control for a transmission pipeline boosting one chemical only (chlorine). This control scenario provides a consistent total chlorine residual downstream, which is a significant benefit where influent residuals are highly variable. This application is possible where enough free ammonia is always present to combine with the added chlorine. Adequate mixing conditions must be provided to allow for the chlorine to mix with the ammonia at the booster station. In many cases, this can be achieved by adding hypochlorite at a pump inlet. Too much chlorine may cause breakpoint.
- A water recirculation loop for a water storage reservoir with residual feedback control for chlorine or chlorine and ammonia feeds. An external water recirculation loop or an internal mixer can be applied to deliver the chemicals and mix the reservoir contents. A total chlorine residual analyzer sends a feedback signal to the chemical feed pump(s) controller. Typically, the ammonia feed rate is based on a set ratio of the chlorine feed rate.
- Flow-paced with dose set-point control for a transmission pipeline boosting of one or two chemicals (chlorine only or chlorine and ammonia) with manual adjustments based on grab or on-line water quality measurements. Typically, the ammonia feed rate is based on a set ratio of the chlorine feed rate.
- A water recirculation loop for a water storage reservoir with dose set-point control. For single chlorine feed applications, enough free ammonia must be available to combine with the chlorine added at the booster station. Complete mixing of the reservoir contents is essential for boosting.

Table 10-4 Summary of booster station operating conditions for 10 surveyed cases

Operating Component	Number Used in 10 Surveyed Cases
Chlorine feed	7—liquid hypochlorite
	2—on-site NaOCl generation
	1—tablet chlorination
Ammonia feed	5—installed facilities (3 used)
Water flowmeter	6—(4 assumed pump output)
Flow-paced feed only	4
Flow-paced + residual set-point feedback	4
Manual feed control	2
Manual fine-tuning based on water quality	10
On-line total chlorine analyzer	5—before booster; 7—after booster
On-line free ammonia analyzer	1—after booster
Grab total chlorine sampling	10—before and after
Grab ammonia sampling	8—before and after
Grab nitrite sampling	4—before and after

Source: Wilczak et al., 2003.

- Conceivably, one could control the process with the use of the on-line total chlorine residual, free ammonia, and nitrite analyzer. Ever-increasing applications of chloramine boosting will tell whether total chlorine analyzers are going to be sufficient for the purpose of disinfectant residual boosting within chloraminated systems or whether more expensive and sophisticated instruments capable of performing several analyses at once will be needed or preferable for some applications.

Table 10-4 presents a summary of chemical feeds, process controls, and water quality parameters for 10 cases of full-scale booster stations in chloraminated systems, located in California, Oregon, Florida, and Maine. The following observations and comments from the survey are emphasized (Wilczak et al., 2003):

- Nitrification still occurred at far ends of the distribution systems in spite of boosting at transmission reservoirs and/or transmission pumping stations. However, the onset of nitrification occurred later and areas impacted were smaller.
- Boosters located on a recirculation loop at a storage facility were more effective for that facility than boosters located at a pumping station because they allowed more free ammonia to be combined inside a tank than was available for boosting at a pumping station.
- Boosting is successful in tanks with good turnover or induced mixing. Simply adding chlorine to combine with free ammonia in a booster loop may not be sufficient to control nitrification long term. Breakpoint chlorination at the tank influent may be needed to control nitrification, as discussed in chapter 9.
- Three boosting applications where ammonia was continuously added were successful. More instrumentation was needed and more operator attention seems necessary. Dose set-point control was needed, whereas residual set point was too difficult.

- Residual total chlorine leaving the treatment plant was successfully lowered in one instance after the booster station was placed in service.
- On-line total chlorine analyzers, liquid hypochlorite feed systems with remote chemical inventory measurement, and connection to a SCADA system were preferred for booster operation.
- Reverse water flows require a meter that can measure flow in both directions. A downstream on-line total chlorine analyzer was needed in reverse-flow cases to prevent breakpoint chlorination.
- No accidents or safety violations associated with the remote booster stations were reported in the survey. Small chemical leaks were taken care of with proper maintenance and safety measures. Booster stations should have the same safety and redundancy measures as any chemical storage and feed facilities, including dual piping with check valves.

Tablet Chlorination

Tablet chlorination can be the first step in booster chlorination. Tablet chlorinators or floating chlorinators have been used in the past in Oregon and Australia. Tablet booster stations have been either replaced with automatic hypochlorite stations or the utilities would like to replace tablet chlorination in the future because tablet systems are not accurate and are labor intensive.

CONCLUSIONS

Capital improvements to resolve long-term or reoccurring nitrification episodes are likely to provide significant savings of operation's staff time; for example with improved reservoir mixing, which would not require breakpoint chlorination, or with improved pipeline circulation, which may decrease the frequency of flushing. Capital improvements will have a goal of either: (1) reducing water age or (2) improving chloramine residual. Therefore, customers will be provided fresher and/or more biologically stable drinking water.

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Abbreviations and Acronyms

AMO	ammonia mono-oxygenase
AOB	ammonia-oxidizing bacteria
APHA	American Public Health Association
AT	amperometric titration
ATP	adenosine triphosphate
AWWA	American Water Works Association
AwwaRF	Awwa Research Foundation
BAC	biological activated carbon
BDOC	biodegradable dissolved organic carbon
BOD	biological oxygen demand
BOM	biodegradable organic matter
CFD	computational fluid dynamics
cfu	colony forming unit
Cl_2:NH_3-N	chlorine-to-ammonia-nitrogen weight ratio
cm	centimeter
CO_2	carbon dioxide
$C \times T$	concentration × contact time
CT (credit)	concentration × contact time
DAPI	4,6-diamidino-2-phenylindole
DBP	disinfection by-product
D/DBP	Disinfectants/Disinfection By-product (Rule)
DNA	deoxyribonucleic acid
DNaR	nitrate reductase enzyme
DO	dissolved oxygen
DOC	dissolved organic carbon
DPD	N,N-diethyl-p-phenylenediamine
EBCT	empty bed contact time
EBMUD	East Bay Municipal Utility District
EES	Economic and Engineering Services, Inc.
EPANET	distribution system hydraulic and water quality behavior model
FACA	Federal Advisory Committee Act
FAD	flavin adenine dinucleotide

FISH	fluorescence in-situ hybridization
fps	feet per second
GAC	granular activated carbon
H^+	hydrogen
H_2	hydrogen gas
HAA	haloacetic acid
HEPES	4-(2-hydroxyethyl)-1-pipeazineethanesulfonic acid
HNO_2	free nitrous acid
H_2O	water
H_2ONET	AutoCADD-based water analysis program provided by MWH
HOS	hypolimnetic oxygenation system
hp	horsepower
HPC	heterotrophic plate count
HPLC	high performance liquid chromatography
HRT	hydraulic residence time
ICR	Information Collection Rule
I/O	inlet/outlet
ISE	ion selective electrode
LCR	Lead and Copper Rule
m	meter
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
MDD	maximum day demand
mgd	million gallons per day
mg/L	milligrams per liter
mil gal	million gallons
mL	milliliter
m/h	meter per hour
MPN	most probable number
MRDL	maximum residual disinfectant level
MWDSC	Metropolitan Water District of Southern California
µg/L	micrograms per liter
N	nitrogen
N_2	dinitrogen
NAD	nonreduced nicotinamide adenine dinucleotide
NADH	reduced nicotinamide adenine dinucleotide
Nb.	*Nitrobacter*

NCl_3	trichloramine
NDMA	n-dimethyl nitrosamine
NF	nanofiltration
NH_2Cl	monochloramine
$NHCl_2$	dichloramine
NH_3	ammonia
NH_4^+	ammonium ion
NHOH	intermediate compound formed and consumed during the oxidation of ammonia to nitrite
NH_2OH	hydroxylamine
NiR	nitrite reductase enzyme
Nm.	*Nitrosomonas*
NO	nitric oxide
N_2O	nitrous oxide
N_2OR	nitrous oxide reductase enzyme
NO_2^-	nitrite ion
NO_3^-	nitrate ion
NOB	nitrite-oxidizing bacteria
NOM	natural organic matter
O_2	oxygen
O&M	operations and maintenance
PCR	polymerase chain reaction
PLC	programmable logic controller
PO_4^{3-}	phosphate ion
PPE	personal protective equipment
PVC	polyvinyl chloride
R2A	agar growth medium
RMS	reservoir management system
RNA	ribonucleic acid
RO	reverse osmosis
SCADA	supervisory control and data acquisition
SDWA	Safe Drinking Water Act
SFPUC	San Francisco Public Utilities Commission
16S rDNA	molecular method through gene sequencing of the rDNA by speciating bacteria including nitrite-oxidizing and ammonia-oxidizing bacteria
16S rRNA	molecular method through gene sequencing of the rRNA by speciating bacteria including nitrite-oxidizing and ammonia-oxidizing bacteria
SMP	soluble microbial product

SOP	standard operating practice
SPU	Seattle Public Utilities
SRT	sludge retention time
SWTR	Surface Water Treatment Rule
SYTO9	fluorescent nucleic acid stain used in the *Bac*Light bacterial viability test kit
TCR	Total Coliform Rule
THM	trihalomethane
TOC	total organic carbon
UF	ultrafiltration
USEPA	United States Environmental Protection Agency
USL	Upper San Leandro (California) Water Treatment Plant
VAC	volt alternating current
VSS	volatile suspended solids
WTP	water treatment plant
WWII	World War II

Units of Measure With Metric Conversions

Linear Measurement

inch (in.)	× 25.4	= millimeters (mm)
inch (in.)	× 2.54	= centimeters (cm)
foot (ft)	× 304.8	= millimeters (mm)
foot (ft)	× 30.48	= centimeters (cm)
foot (ft)	× 0.3048	= meters (m)
yard (yd)	× 0.9144	= meters (m)
mile (mi)	× 1,609.3	= meters (m)
mile (mi)	× 1.6093	= kilometers (km)
millimeter (mm)	× 0.03937	= inches (in.)
centimeter (cm)	× 0.3937	= inches (in.)
meter (m)	× 39.3701	= inches (in.)
meter (m)	× 3.2808	= feet (ft)
meter (m)	× 1.0936	= yards (yd)
kilometer (km)	× 0.6214	= miles (mi)

Area Measurement

square meter (m^2)	× 10,000	= square centimeters (cm^2)
hectare (ha)	× 10,000	= square meters (m^2)
square inch ($in.^2$)	× 6.4516	= square centimeters (cm^2)
square foot (ft^2)	× 0.092903	= square meters (m^2)
square yard (yd^2)	× 0.8361	= square meters (m^2)
acre	× 0.004047	= square kilometers (km^2)
acre	× 0.4047	= hectares (ha)
square mile (mi^2)	× 2.59	= square kilometers (km^2)
square centimeter (cm^2)	× 0.16	= square inches ($in.^2$)
square meters (m^2)	× 10.7639	= square feet (ft^2)
square meters (m^2)	× 1.1960	= square yards (yd^2)
hectare (ha)	× 2.471	= acres
square kilometer (km^2)	× 247.1054	= acres
square kilometer (km^2)	× 0.3861	= square miles (mi^2)

Volume Measurement

cubic inch ($in.^3$)	× 16.3871	= cubic centimeters (cm^3)
cubic foot (ft^3)	× 28,317	= cubic centimeters (cm^3)
cubic foot (ft^3)	× 0.028317	= cubic meters (m^3)
cubic foot (ft^3)	× 28.317	= liters (L)
cubic yard (yd^3)	× 0.7646	= cubic meters (m^3)
acre foot (acre-ft)	× 123.34	= cubic meters (m^3)
ounce (US fluid) (oz)	× 0.029573	= liters (L)
quart (liquid) (qt)	× 946.9	= milliliters (mL)
quart (liquid) (qt)	× 0.9463	= liters (L)
gallon (gal)	× 3.7854	= liters (L)
gallon (gal)	× 0.0037854	= cubic meters (m^3)
peck (pk)	× 0.881	= decaliters (dL)
bushel (bu)	× 0.3524	= hectoliters (hL)
cubic centimeters (cm^3)	× 0.061	= cubic inches ($in.^3$)

cubic meter (m^3)	× 35.3183	= cubic feet (ft^3)
cubic meter (m^3)	× 1.3079	= cubic yards (yd^3)
cubic meter (m^3)	× 264.2	= gallons (gal)
cubic meter (m^3)	× 0.000811	= acre-feet (acre-ft)
liter (L)	× 1.0567	= quart (liquid) (qt)
liter (L)	× 0.264	= gallons (gal)
liter (L)	× 0.0353	= cubic feet (ft^3)
decaliter (dL)	× 2.6417	= gallons (gal)
decaliter (dL)	× 1.135	= pecks (pk)
hectoliter (hL)	× 3.531	= cubic feet (ft^3)
hectoliter (hL)	× 2.84	= bushels (bu)
hectoliter (hL)	× 0.131	= cubic yards (yd^3)
hectoliter (hL)	× 26.42	= gallons (gal)

Pressure Measurement

pound/square inch (psi)	× 6.8948	= kilopascals (kPa)
pound/square inch (psi)	× 0.00689	= pascals (Pa)
pound/square inch (psi)	× 0.070307	= kilograms/square centimeter (kg/cm^2)
pound/square foot (lb/ft^2)	× 47.8803	= pascals (Pa)
pound/square foot (lb/ft^2)	× 0.000488	= kilograms/square centimeter (kg/cm^2)
pound/square foot (lb/ft^2)	× 4.8824	= kilograms/square meter (kg/m^2)
inches of mercury	× 3,376.8	= pascals (Pa)
inches of water	× 248.84	= pascals (Pa)
bar	× 100,000	= newtons per square meter
pascals (Pa)	× 1	= newtons per square meter
pascals (Pa)	× 0.000145	= pounds/square inch (psi)
kilopascals (kPa)	× 0.145	= pounds/square inch (psi)
pascals (Pa)	× 0.000296	= inches of mercury (at 60°F)
kilogram/square centimeter (kg/cm^2)	× 14.22	= pounds/square inch (psi)
kilogram/square centimeter (kg/cm^2)	× 28.959	= inches of mercury (at 60°F)
kilogram/square meter (kg/m^2)	× 0.2048	= pounds per square foot (lb/ft^2)
centimeters of mercury	× 0.4461	= feet of water

Weight Measurement

ounce (oz)	× 28.3495	= grams (g)
pound (lb)	× 0.045359	= grams (g)
pound (lb)	× 0.4536	= kilograms (kg)
ton (short)	× 0.9072	= megagrams (metric ton)
pounds/cubic foot (lb/ft^3)	× 16.02	= grams per liter (g/L)
pounds/million gallons (lb/mil gal)	× 0.1198	= grams per cubic meter (g/m^3)
gram (g)	× 15.4324	= grains (gr)
gram (g)	× 0.0353	= ounces (oz)
gram (g)	× 0.0022	= pounds (lb)
kilograms (kg)	× 2.2046	= pounds (lb)
kilograms (kg)	× 0.0011	= tons (short)
megagram (metric ton)	× 1.1023	= tons (short)
grams/liter (g/L)	× 0.0624	= pounds per cubic foot (lb/ft^3)
grams/cubic meter (g/m^3)	× 8.3454	= pounds/million gallons (lb/mil gal)

Flow Rates

gallons/second (gps)	× 3.785	= liters per second (L/sec)
gallons/minute (gpm)	× 0.00006308	= cubic meters per second (m^3/sec)

gallons/minute (gpm)	× 0.06308	= liters per second (L/sec)
gallons/hour (gph)	× 0.003785	= cubic meters per hour (m^3/hr)
gallons/day (gpd)	× 0.000003785	= million liters per day (ML/day)
gallons/day (gpd)	× 0.003785	= cubic meters per day (m^3/day)
cubic feet/second (ft^3/sec)	× 0.028317	= cubic meters per second (m^3/sec)
cubic feet/second (ft^3/sec)	× 1,699	= liters per minute (L/min)
cubic feet/minute (ft^3/min)	× 472	= cubic centimeters/second (cm^3/sec)
cubic feet/minute (ft^3/min)	× 0.472	= liters per second (L/sec)
cubic feet/minute (ft^3/min)	× 1.6990	= cubic meters per hour (m^3/hr)
million gallons/day (mgd)	× 43.8126	= liters per second (L/sec)
million gallons/day (mgd)	× 0.003785	= cubic meters per day (m^3/day)
million gallons/day (mgd)	× 0.043813	= cubic meters per second (m^3/sec)
gallons/square foot (gal/ft^2)	× 40.74	= liters per square meter (L/m^2)
gallons/acre/day (gal/acre/day)	× 0.0094	= cubic meters/hectare/day (m^3/ha/day)
gallons/square foot/day (gal/ft^2/day)	× 0.0407	= cubic meters/square meter/day (m^3/m^2/day)
gallons/square foot/day (gal/ft^2/day)	× 0.0283	= liters/square meter/day (L/m^2/day)
gallons/square foot/minute (gal/ft^2/min)	× 2.444	= cubic meters/square meter/hour (m^3/m^2/hr) = m/hr
gallons/square foot/minute (gal/ft^2/min)	× 0.679	= liters/square meter/second (L/m^2/sec)
gallons/square foot/minute (gal/ft^2/min)	× 40.7458	= liters/square meter/minute (L/m^2/min)
gallons/capita/day (gpcd)	× 3.785	= liters/day/capita (L/d per capita)
liters/second (L/sec)	× 22,824.5	= gallons per day (gpd)
liters/second (L/sec)	× 0.0228	= million gallons per day (mgd)
liters/second (L/sec)	× 15.8508	= gallons per minute (gpm)
liters/second (L/sec)	× 2.119	= cubic feet per minute (ft^3/min)
liters/minute (L/min)	× 0.0005886	= cubic feet per second (ft^3/sec)
cubic centimeters/second (cm^3/sec)	× 0.0021	= cubic feet per minute (ft^3/min)
cubic meters/second (m^3/sec)	× 35.3147	= cubic feet per second (ft^3/sec)
cubic meters/second (m^3/sec)	× 22.8245	= million gallons per day (mgd)
cubic meters/second (m^3/sec)	× 15,850.3	= gallons per minute (gpm)
cubic meters/hour (m^3/hr)	× 0.5886	= cubic feet per minute (ft^3/min)
cubic meters/hour (m^3/hr)	× 4.403	= gallons per minute (gpm)
cubic meters/day (m^3/day)	× 264.1720	= gallons per day (gpd)
cubic meters/day (m^3/day)	× 0.00026417	= million gallons per day (mgd)
cubic meters/hectare/day (m^3/ha/day)	× 106.9064	= gallons per acre per day (gal/acre/day)
cubic meters/square meter/day (m^3/m^2/day)	× 24.5424	= gallons/square foot/day (gal/ft^2/day)
liters/square meter/minute (L/m^2/min)	× 0.0245	= gallons/square foot/minute (gal/ft^2/min)
liters/square meter/minute (L/m^2/min)	× 35.3420	= gallons/square foot/day (gal/ft^2/day)

Work, Heat, and Energy

British thermal units (Btu)	× 1.0551	= kilojoules (kJ)
British thermal units (Btu)	× 0.2520	= kilogram-calories (kg-cal)
foot-pound (force) (ft-lb)	× 1.3558	= joules (J)
horsepower-hour (hp·hr)	× 2.6845	= megajoules (MJ)
watt-second (W-sec)	× 1.000	= joules (J)

watt-hour (W·hr)	× 3.600	= kilojoules (kJ)
kilowatt-hour (kW·hr)	× 3,600	= kilojoules (kJ)
kilowatt-hour (kW·hr)	× 3,600,000	= joules (J)
British thermal units per pound (Btu/lb)	× 0.5555	= kilogram-calories per kilogram (kg/cal/kg)
British thermal units per cubic foot (Btu/ft^3)	× 8.8987	= kilogram-calories/cubic meter ($kg\text{-}cal/m^3$)
kilojoule (kJ)	× 0.9478	= British thermal units (Btu)
kilojoule (kJ)	× 0.00027778	= kilowatt-hours (kW·hr)
kilojoule (kJ)	× 0.2778	= watt-hours (W·hr)
joule (J)	× 0.7376	= foot-pounds (ft-lb)
joule (J)	× 1.0000	= watt-seconds (W-sec)
joule (J)	× 0.2399	= calories (cal)
megajoule (MJ)	× 0.3725	= horsepower-hour (hp·hr)
kilogram-calories (kg-cal)	× 3.9685	= British thermal units (Btu)
kilogram-calories per kilogram (kg-cal/kg)	× 1.8000	= British thermal units per pound (Btu/lb)
kilogram-calories per liter (kg-cal/L)	× 112.37	= British thermal units per cubic foot (Btu/ft^3)
kilogram-calories/cubic meter ($kg\text{-}cal/m^3$)	× 0.1124	= British thermal units per cubic foot (Btu/ft^3)

Velocity, Acceleration, and Force

feet per minute (ft/min)	× 18.2880	= meters per hour (m/hr)
feet per hour (ft/hr)	× 0.3048	= meters per hour (m/hr)
miles per hour (mph)	× 44.7	= centimeters per second (cm/sec)
miles per hour (mph)	× 26.82	= meters per minute (m/min)
miles per hour (mph)	× 1.609	= kilometers per hour (km/hr)
feet/second/second (ft/sec^2)	× 0.3048	= meters/second/second (m/sec^2)
inches/second/second ($in./sec^2$)	× 0.0254	= meters/second/second (m/sec^2)
pounds force (lbf)	× 4.44482	= newtons (N)
centimeters/second (cm/sec)	× 0.0224	= miles per hour (mph)
meters/second (m/sec)	× 3.2808	= feet per second (ft/sec)
meters/minute (m/min)	× 0.0373	= miles per hour (mph)
meters per hour (m/hr)	× 0.0547	= feet per minute (ft/min)
meters per hour (m/hr)	× 3.2808	= feet per hour (ft/hr)
kilometers/second (km/sec)	× 2.2369	= miles per hour (mph)
kilometers/hour (km/hr)	× 0.0103	= miles per hour (mph)
meters/second/second (m/sec^2)	× 3.2808	= feet/second/second (ft/sec^2)
meters/second/second (m/sec^2)	× 39.3701	= inches/second/second ($in./sec^2$)
newtons (N)	× 0.2248	= pounds force (lbf)

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NOTE: *f.* indicates a figure; *t.* indicates a table.

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AWWA Manuals

M1, *Principles of Water Rates, Fees, and Charges,* Fifth Edition, 2000, #30001PA

M2, *Instrumentation and Control*, Third Edition, 2001, #30002PA

M3, *Safety Practices for Water Utilities,* Sixth Edition, 2002, #30003PA

M4, *Water Fluoridation Principles and Practices,* Fifth Edition, 2004, #30004PA

M5, *Water Utility Management Practices,* First Edition, 2005, #30005PA

M6, *Water Meters—Selection, Installation, Testing, and Maintenance,* Fourth Edition, 1999, #30006PA

M7, *Problem Organisms in Water: Identification and Treatment,* Third Edition, 2004, #30007PA

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