Nitrification Prevention and Control in Drinking Water

AWWA MANUAL M56

Second Edition





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Chapter 1

Introduction and Impact on Regulatory Compliance

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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 (or secondary) disinfection. The objectives of this manual 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 and overall water quality in tap water; and
- help utilities effectively prevent and mitigate nitrification episodes that may occur in their systems.

There are many sources that discuss the various aspects of nitrification. Several Water Research Foundation (WaterRF) reports discuss nitrification in conjunction with other topics, primarily drinking water disinfection and chloramination. Since the first writing of this manual, a better understanding of chloramination treatment, chloramine residual maintenance, and nitrification control within distribution systems has evolved. This understanding is a result of field experience, research, and pilot studies. For example, water utility personnel understand more fully how to form and monitor chloramine at carefully measured chlorine to ammonia ratios (usually 4.5 or 5.1 Cl₂:NH₃⁻N) with minimal excess ammonia.

Another improvement in the practice of nitrification control is the use and maintenance of a slightly higher chloramine residual level throughout the distribution system for effective nitrification detection and preventive monitoring and control. The understanding of chloramine decay and demand in distribution systems and factors that contribute to nitrification, such as water quality and system characteristics contributing to nitrification, has improved as well.

The passage of the Stage 2 Disinfectants and Disinfection By-Product Rule necessitates that utilities comply with locational disinfection by-products maximum contaminant levels (MCLs) (USEPA 2006).With a national trend toward consolidating water systems into larger systems overall (USEPA 2009), the use of a chloramine residual is seen by many utilities as a possible option for distribution system disinfection while controlling chlorinated disinfection by-products. Hence, there is a growing need for easy access to information related to nitrification occurrence, prevention, and control in drinking water distribution systems that use chloramines.

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. Experimental approaches are also discussed in some sections and are clearly identified as nonpeer reviewed results or as experimental, anecdotal, or emerging issues. The final product is a manual that can be used by chloraminating utilities, as well as utilities that are considering chloramination for use in their systems. This manual will also be useful to consulting engineers and researchers trying to control or mitigate nitrification through operational practices, engineering improvements, mitigating or eliminating conditions that promote biological growth, and treatment options for the inactivation of nitrifying bacteria. Readers are advised to work with their local authorities to make the best disinfection application and nitrification remediation decisions for their particular conditions.

The following is a brief summary of each chapter:

- Chapter 1 provides background information on disinfection practices, nitrification, and the impact of nitrification on regulatory compliance.
- Chapter 2 provides an overview of the potential for nitrification to develop, occurrences in drinking water and wastewater treatment facilities, and its impact on distribution system water quality. There is an expanded discussion of wastewater systems and innovations, as well as new material addressing drinking water biofiltration operations and impacts on nitrification.
- Chapter 3 summarizes mechanisms and factors related to nitrification occurrence in drinking water distribution systems. This second edition offers updated and expanded content based on recent literature.
- Chapter 4 provides an overview of water quality, operations, and maintenance conditions that contribute to or cause nitrification in the distribution system. This second edition offers updated and expanded content based on recent literature.
- Chapter 5 presents information on the morphology, taxonomy, growth, and detection of ammonia- and nitrite-oxidizing bacteria and the microbiology

of nitrifying and denitrifying bacteria. Modifications to this second edition include: the addition of information about the recently discovered archaea group, biodegradation of THMs, interactions between nitrifiers and other bacterial communities, and new molecular methods.

- Chapter 6 provides information on the growth characteristics and inactivation
 of ammonia-oxidizing and nitrite-oxidizing bacteria. This second edition offers
 an elaboration on Haldane kinetics that describes some ammonia-oxidizing
 bacteria found in drinking water, updated information on inactivation of nitrifiers by light and growth effects of phosphate and alkalinity, inactivation of
 THMs, and microelectrode data on chlorine and chloramine profiles in nitrifying biofilms.
- Chapter 7 discusses 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 describes treatment and operational practices designed to prevent nitrification and makes recommendations for best practices. This second edition provides more information on booster chloramination, impact of high pH and chlorite ion effects. A new section on the UV light to control nitrification in storage facilities was added.
- Chapter 9 provides guidelines to assess whether nitrification is occurring, including water quality indicators of nitrification. This chapter also provides recommendations on operational response to nitrification in the distribution system and finished water storage facilities and development of a nitrification response plan. This second edition covers shifts related to use an effectiveness of periodic free chlorine burn.
- 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.

DISTRIBUTION SYSTEM DISINFECTION PRACTICES

The practice of disinfecting drinking water and carrying a disinfectant residual throughout the distribution system began in the early 1900s to provide a barrier to 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. Chlorine dioxide is also approved for use but has not been used to a substantial extent within the distribution system (AWWA Disinfection Systems Committee 2008a: USEPA 2009). Free chlorine and chloramines are effective at destroying some pathogenic microorganisms and controlling the growth of microorganisms in the distribution system. Additionally, their presence and residual levels are used as an indicator of water quality integrity within the distribution system (Friedman et al. 2010).

Table 1	-1	Key	points	from	chapter	1
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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.

Secondary disinfection (disinfectant applied with the objective of providing a residual throughout the drinking water distribution system) is used 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 occur through external sources. Microbial contamination of the distribution system may occur through a cross-connection with a contaminated water supply and during main breaks and main repairs. Contamination may also occur from intrusion due to 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 taste good and have good 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. It should be noted, however, that chlorine, and to a lesser extent chloramines, also impart a taste and odor to the water that can be objectionable to customers who are not accustomed to that taste.
- 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 over time 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 regrowth problems, and chloramines were first used at a water treatment facility in Ottawa, Canada in 1918. Between 1920 and 1936, chloramines gained popularity in water treatment because 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 percent used chloramines. However, following the discovery of breakpoint chlorination in 1939 and due to an ammonia shortage during World War II in the 1940s, the use of chloramines dropped (White 1999). A survey of 11,500 municipal water supplies in 1962 indicated use dropped from 16 percent to 2.6 percent (Kirmeyer 2004).

Following the discovery of THMs, a group of halogenated DBPs, and the promulgation of the Total Trihalomethane Rule in 1979 (USEPA 1979), more water utilities began using chloramines, which form substantially lower levels of chlorinated DBPs compared to free chlorine. 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 percent 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.

The use of chloramines has become more popular due to the USEPA Stage 1 and Stage 2 Disinfectants/Disinfection Byproducts (D/DBP) Rules (USEPA 2001 and USEPA 2006). These rules reduce the levels of various DBPs in drinking water and base compliance on locational annual averages rather than system-wide averages. As a result of the Stage 1 and 2 DBP Rules, chloramination for secondary disinfection in the US is predicted to increase significantly.

The USEPA forecasts that as a result of Stage 2 implementation alone, 8 percent of surface water and 3 percent of groundwater community water systems will convert to chloramination (USEPA 2005). After implementation of both of these rules, up to

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57 percent of all surface and 7 percent of groundwater systems (USEPA 2005) will use chloramination as a secondary disinfectant. A recent survey reported that 30 percent of respondents currently chloraminate to maintain distribution system residuals and other recent surveys suggest that between 8 and 12 percent of drinking water utilities are contemplating a future switch to chloramination (AWWA Disinfection Systems Committee 2008b; Seidel et al. 2005).

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 $Cl_2:NH_3N$ (chlorine to ammonia-N) to form the preferred monochloramine species. This is further discussed in Chapter 9 as part of the description of breakpoint chlorination. 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 dry ammonium sulfate, liquid ammonium hydroxide, or by dissolving anhydrous ammonia gas into solution.

The following are generalized inorganic chloramine formation reactions:

Monochloramine (NH_oCl)*

$$NH_{2} + HOCl \rightarrow NH_{2}Cl + H_{2}O$$
 (Eq. 1-1)

Dichloramine (NHCl₂)

$$NH_{2}Cl + HOCl \rightarrow NHCl_{2} + H_{2}O$$
 (Eq. 1-2)

Trichloramine (NCl₂)

$$\text{NHCl}_2 + \text{HOCl} \rightarrow \text{NCl}_3 + \text{H}_2\text{O}$$
 (Eq. 1-3)

Monochloramine is the desired inorganic chloramine species for 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). After entering the distribution system, the chloramine residual starts to decay (autodecompose) as a result of water age and physical conditions, such as temperature and pH. A chloramine demand can be exerted due to water quality conditions, such as presence of NOM, biofilm, corrosion by-products, and nitrification by-products. Chapter 4 contains a detailed discussion of chloramine decay and demand. As discussed in the following sections, during these processes, free ammonia is released into the water. Free ammonia may also enter the distribution system from the treatment plant due to an excess dose of ammonia or incomplete reaction with free chlorine, or may be present in the source water.

^{*} It should be noted that the speciation of ammonium ion and hypochlorous acid are pHdependent. For 7.5 < pH < 9.3, NH₄⁺ and OCl⁻ are the dominant species.

NITRIFICATION BASICS

The Nitrogen Cycle

All biological growth processes require nitrogen for the synthesis of cellular proteins and nucleic acids. Microorganisms, such as ammonia-oxidizing bacteria (AOB), archaea (AOA), and nitrite-oxidizing bacteria (NOB) can use a range of nitrogen compounds under a variety of conditions; in some cases, the oxidation state of nitrogen is changed while in others it is not. The microbiological process of converting free ammonia (NH₃) into nitrite (NO₂⁻) and then nitrate (NO₃⁻) is called nitrification. The main biological 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 nitrogen gas (anaerobic ammonium oxidation or anammox conversion) is a recent addition to our understanding of the biological nitrogen cycle (Kuenen et al. 2001; Strous et al. 1999). 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 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 NOB into nitrate. Nitrite can also act as a dechlorination agent due to chemical reaction with either free chlorine or chloramines. The following are approximate equations for nitrification reactions by the AOB *Nitrosomonas* and the NOB *Nitrobacter* (Morel and Hering 1993):

Nitrosomonas reactions:

$$NH_{3} + 3/2O_{2} \rightarrow NO_{2}^{-} + H_{2}O + H^{+}$$
 (Eq. 1-4a)

$$NH_4^+ + 3/2O_2 \rightarrow NO_2^- + H_2O + 2H^+$$
 (Eq. 1-4b)

Nitrobacter reaction:

$$NO_{2}^{-} + 1/2O_{2} \rightarrow NO_{3}^{-}$$
 (Eq. 1-5)

More information on nitrification reactions by AOB, AOA, and NOB is provided in Chapter 5. The overall reaction for complete nitrification (Grady et al. 1999) is shown in equation 1-6.

Overall reaction for complete nitrification:

$$\label{eq:NH4+} \begin{split} & \mathrm{NH_4^+} + 3.300 \ \mathrm{O_2} + 6.708 \ \mathrm{HCO_3^-} \rightarrow \\ & 0.129 \ \mathrm{C_5H_7O_2N} + 3.373 \ \mathrm{NO_3^-} + 1.041 \ \mathrm{H_2O} + 6.463 \ \mathrm{H_2CO_3} \end{split} \tag{Eq. 1-6}$$

As shown by the reactants and products of equation 1-6, complete nitrification results in the consumption of alkalinity (HCO_3^-) , reduced pH (formation of carbonic acid, H_2CO_3), production of nitrate (NO_3^-) , and increased biomass $(\text{C}_5\text{H}_7\text{O}_2\text{N})$. Both complete (to nitrate) and incomplete (to nitrite) nitrification have been frequently observed in chloraminated drinking water distribution systems. Nitrate metabolism

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Figure 1-1 Main biological processes involving nitrogen transformation

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 electron acceptor to oxygen). Denitrification, an important wastewater treatment process, is a special case of dissimilation in which gaseous N_{a} and/or $N_{a}O$ are the end products.

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. The soluble microbial products produced by active bacteria also exert a chloramine demand. A decrease in relative concentrations of inorganic chloramines and an increase in organic chloramines have 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 (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 toxic sediments of the lake, and their activity is likely inhibited by anoxia during 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. This discharge produces seeding of the receiving water body with nitrifying bacteria that can be more pronounced with untreated sewage than with 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).

Ammonia, nitrate, and nitrite can typically be found in surface water supplies as a result of natural processes. Other sources of nitrogen can include agricultural runoff from fertilization or livestock wastes, contamination from sewage, and industrial discharges. Ammonia also occurs naturally in some groundwater supplies, and groundwater can become contaminated with nitrogen as agricultural runoff percolates into aquifers. The concentration of nitrite nitrogen in surface water and groundwater is normally far below 0.1 mg/L (Sawyer and McCarty 1978). As described in Chapter 8, the level can vary rapidly and dramatically due to watershed events. Seasonal highs in surface water ammonia concentrations typically occur in winter when nitrification rates decline. Groundwater generally contains relatively low concentrations of ammonia because of the cation exchange capacity of soil, unless there have been anthropogenic inputs (Bouwer and Crowe 1988).

No organism has been identified that is capable of fully oxidizing ammonia to nitrate. Consequently, the classification of nitrifying bacteria is based primarily on 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). A new ammonia-oxidizing microorganism belonging to the *Archaea* domain has recently been identified and is described in Chapter 5.

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)
- Primary MCL for nitrate and nitrite and Phase II Inorganic Contaminant Rule
- Stage 1 and Stage 2 DBP Rules

Over the past few years, federal efforts to identify and prioritize distribution system water quality issues have included considering nitrification as a possible public health issue. The National Research Council's (NRC) assessment of distribution system risks determined that "the most important problem exacerbated by both nitrification and by long retention times is loss of disinfectant residuals (NRC 2006)." The NRC designated this to be a medium priority concern due to indirect health impacts caused by the loss of residual, which may result in compromising biological integrity of the system and promoting microbial regrowth (NRC 2006). Additionally, the NRC (2006) determined that the formation of nitrate and nitrite by nitrification is a low priority relative to other distribution system water quality issues. Finally, the NRC also noted that nitrification in low alkalinity waters can cause pH to decrease and affect lead and copper release.

The Total Coliform Rule/Distribution System Advisory Committee recommended that a Research and Information Collection Partnership (RICP) be formed to inform and support the drinking water community in developing future national risk management decisions pertaining to drinking water distribution systems. The advisory committee recommended seven priority areas for research and information collection, one of which was nitrification. The document entitled *Priorities of the Distribution System Research and Information Collection Partnership* (USEPA 2010b) states that adverse public health impacts are suspected to be associated with nitrification, although available information is more anecdotal in nature and additional research and information collection are necessary to better define public health risks. Several projects identified in the *Priorities* document propose to further explore the occurrence and impacts of nitrification and associated public health risks (USEPA 2010b).

Table 1-2 provides a summary of water quality and possible compliance issues as they relate to nitrification.

Surface Water Treatment Rule

Disinfectant depletion and heterotrophic bacteria 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 loss can allow growth and/or survival of microbial organisms within the bulk water, in biofilms, or on 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 percent of samples collected throughout the distribution system on a monthly basis (or HPC measurements not

	Water Quality Issues	Compliance Issues
Chemical	Disinfectant depletion	Surface Water Treatment Rule, Total Coliform Rule, Revised Total Coliform Rule
	Nitrite/nitrate formation	Elevated nitrite/nitrate levels*
	Dissolved oxygen depletion	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	Total Coliform Rule, Revised Total Coliform Rule
	Increase in AOB and NOB	Cause increases in nitrate and nitrite, can contrib- ute to disinfectant demand
Aesthetic	Taste and odor, color, turbidity	

Table 1-2	Water quality	and compl	iance issues	caused by	^{<i>v</i>} nitrification
	1 2				

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. Systems with elevated source water nitrate/nitrite concentrations could experience levels within the distribution system that exceed the MCL during nitrification events.

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. 2005; Harp 2002). 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. It should be noted, however, that systems relying on chloramines for secondary disinfection typically aim to maintain a distribution system residual of 1.0 to 4.0 mg/L (USEPA 1999) due to the relatively weak disinfecting properties of chloramines and to prevent nitrification from developing. As discussed in Chapter 8, residual levels of >1.5–2 mg/L are recommended for reducing risk of nitrification. Thus, operating a chloraminated distribution system with only a "detectable" disinfectant residual level is not advisable.

Total Coliform Rule and Revised Total Coliform Rule

Nitrification can have an indirect effect on TCR compliance in three ways: disinfectant depletion caused by nitrification can theoretically allow for the increased growth of coliform bacteria; implementation of nitrification control practices can cause biofilm detachment from pipes and introduction to the bulk water; and the resulting growth of heterotrophic bacteria during nitrification events can interfere with the detection of coliform bacteria. However, as described in several case studies presented in Friedman et al. (2009), the presence of disinfectant residual level alone is not an adequate indicator of microbial water quality or TCR compliance status.

The Revised Total Coliform Rule (RTCR) Draft Assessments and Corrective Actions Guidance Manual (USEPA 2010a) recommends that systems collect and evaluate disinfectant residual levels, as well as nitrite/nitrate levels at high water-age locations (for chloraminating systems) during level 1 & 2 assessments. The manual identifies water-age management as a potential corrective action for systems experiencing nitrification and coliform occurrences. Additionally, maintenance of a disinfectant residual, which can be affected by nitrification, is identified as a treatment technique. Although nitrification is not specifically identified as a cause of coliform treatment technique violations, systems with coliform problems will likely need to resolve nitrification should it be identified during the assessment process.

Lead and Copper Rule

Nitrification can have an indirect effect on LCR compliance. Nitrification can cause reduced pH, alkalinity, and dissolved oxygen, which can result in lead and copper release from lead and/or copper bearing materials in the distribution system (Boyd et al. 2008; Zhang et al 2010; Zhang et al. 2009a & b, USEPA 2007; NRC 2006). Although reductions in pH and alkalinity may not pose a direct public health threat, such reductions could theoretically result in enough elevated lead or copper samples to contribute to an exceedance of the LCR action levels (USEPA 2007) as well as failure to maintain optimal water quality parameters such as pH.

As reported by Zhang et al. (2009b), the magnitude of the change in pH depends on the initial alkalinity, extent of nitrification, and acid production. The researchers used lead pipes that were exposed to synthesized water for one year without nitrification and then exposed to water with ammonia (and resulting nitrification) for 15 months. No disinfectant had ever been added to the pipes.

Groups of pipes were exposed to different levels of orthophosphate-P and some of the pipes were exposed to high levels of free chlorine (to a final concentration of 10 mg/L total chlorine), which reacted with existing ammonia (2 mg/L ammonia-N) and formed monochloramine; some were exposed to 1 mg/L chlorite; and some were used as the control (no nitrification inhibitor such as chloramine or chlorite). At 100 mg/L alkalinity as $CaCO_3$ and pH values of greater than 7.5, complete nitrification did not reduce pH or increase lead release from lead piping, but at 15 mg/L alkalinity as $CaCO_3$, nitrification at the elevated chloramine dosages used in the study caused a pH reduction of approximately 1.5 units (to less than 6.5) and an increased soluble lead release by 65 times.

These results are presented in Figure 1-2. Note that nitrification was abruptly halted in the control when no alkalinity was present. The researchers concluded that although some inorganic carbon is required for autotrophic nitrification, it will not be a limiting factor unless alkalinity is below 15 mg/L as $CaCO_3$ (Zhang et al. 2009b). The researcher's overall conclusion is that serious problems with lead leaching from nitrification are not expected at the alkalinities and initial pHs encountered at a majority of water utilities. However, utilities operating at pH values near 8.3 (the point of minimum buffering capacity) and low alkalinities could be very susceptible to elevated soluble lead from nitrification.

Zhang et al. (2009b) also conducted a bench-scale test to investigate nitrification in PVC pipes in comparison to copper piping. For the experiment, the researchers simulated homes with PVC or copper plumbing and leaded brass faucets by placing a brass rod inside a PVC or copper pipe. In the test, complete nitrification occurred in the PVC pipes after two months. However, this did not occur in the copper pipes, presumably due to copper toxicity. At an alkalinity of 35 mg/L as $CaCO_3$, nitrification resulted in a pH drop of 1.4 units (pH 8.2 to 6.8) and leached 45 percent more lead and 81 percent more zinc from leaded brass inserted into to the PVC pipes compared to the leaded brass inserted into the copper pipes. The pH increased in the copper piping (8.15 to 9.96) possibly due to corrosion.

The researchers pointed out that the results indicate that when nitrification has occurred and leaded brass faucets are in use, homes with PVC piping will demonstrate higher lead levels in first-draw samples than homes with copper piping. The researchers also determined that lead leaching was not significantly impacted by production of nitrite and nitrate, or by reductions in inorganic carbon or dissolved oxygen via nitrification (Zhang et al. 2009b).

Zhang et al. (2009b) pointed out that copper can have both an inhibitory effect on nitrification or may promote nitrification. The researchers indicated that this may depend on the free copper concentration, copper complexes present, and purity of the nitrifying culture. Zhang et al. (2008) found that levels of copper of 1–10 ppb might stimulate nitrification while levels greater than 100 ppb might prohibit nitrification.

Nitrite and Nitrate Primary MCLs and Phase II Inorganic Contaminants

According to 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 one year following any one routine sample in which the measured concentration is greater than 50 percent of the MCL (USEPA 2001). 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.



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Figure 1-2 Ammonia loss % and final pH, versus time when initial alkalinity was reduced in stages from 100 to 0 mg/L as CaCO₂.

However, in some states if any drinking water sample is analyzed using certified methods and a regulated contaminant is found above its MCL, 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) and Vikesland et al. (1998). Three of the demand reactions (3, 4, and 6) essentially release one mol of ammonia for one mol of monochloramine. Comparatively, the autodecomposition reaction (major pathway) releases only one mol of ammonia for every three mols of monochloramine. This

Reaction Description		Overall Reaction		
1.	Ammonia and nitrite utilization	$\begin{array}{l} \mathrm{NH_3} + \mathrm{O_2} \rightarrow \mathrm{NO_2} + 3\mathrm{H^+} + 2\mathrm{e} \\ \mathrm{NO_2} + \mathrm{H_2O} \rightarrow \mathrm{NO_3} + 2\mathrm{H^+} + 2\mathrm{e} \end{array}$		
2.	Release of ammonia through chloramine decay (autodecomposition)	$3NH_{2}Cl \rightarrow N_{2} + NH_{3} + 3Cl + 3H^{+} (Major)^{1}$ $4NH_{2}Cl + 3H_{2}0 \rightarrow 4Cl + 3NH_{3}NO_{3} + 5H^{+} (Minor)^{1}$		
3.	Release of ammonia through oxidation of organic matter by chloramine	$1/10C_5H_7O_2N + NH_2CI + 9/10H_2O \rightarrow 4/10CO_2 + 1/10HCO_3 + 11/10NH_4^+ + CI$		
4.	Release of ammonia through reaction of chlora- mine with corrosion products at pipe surfaces*	$1/2\mathrm{NH_2Cl} + \mathrm{H^+} + \mathrm{Fe_2} + \rightarrow \mathrm{Fe^{3+}} + 1/2\mathrm{NH_4^+} + 1/2\mathrm{Cl}$		
5.	Release of ammonia through catalysis reactions of chloramine at pipe surfaces	$3\mathrm{NH_2Cl} \rightarrow \mathrm{N_2} + \mathrm{NH_3} + 3\mathrm{Cl^{+}} + 3\mathrm{H^{+}}$		
6.	Release of ammonia through oxidation of nitrite by chloramine*	$\mathrm{NH_2Cl} + \mathrm{NO_{2^{*}}} + \mathrm{H_2O} \rightarrow \mathrm{NH_3} + \mathrm{NO_{3^{*}}} + \mathrm{HCl}$		
Ada	oted from Woolschlager et al., 2001			

 Table 1-3
 Overview of nitrification and chloramine reactions

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

Source: Vikesland et al. (1998).

indicates that some demand reactions release significantly more ammonia than the major autodecomposition (decay) reaction.

Nitrite and nitrate are produced during nitrification through ammonia utilization by nitrifying bacteria. According to Table 1-3, reactions 1 and 2, for every mol of ammonia-N produced through chloramine decay, a 1-mol equivalent of nitrite-N is produced by AOB. Subsequently, for every mol of nitrite-N produced by AOB, a 1-mol equivalent of nitrate-N is produced by NOB. Figure 1-3 shows that by using reaction 3 in Table 1-3, which is the most conservative chloramine demand reaction in terms of quantity of ammonia produced per mol of monochloramine present, the nitrite-N MCL of 1 mg/L as N could theoretically be exceeded if the chloramine dose greater than approximately 3 mg/L (as total chlorine) and the Cl₂:NH₂-N ratio is less than 5:1. As the chloramine dose increases and 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.:NH.-N ratio of 3.9:1. The pilot train represented conventionally coagulated Lake Mendota (Madison, Wisc.) 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 percent, and for all but three cases the amount was less than 10 percent. The authors concluded that although nitrate is an important decomposition product of monochloramine decay, it is not the major nitrogen-containing species of decomposition.

Using data from a survey of 40 utilities that use chloramine as a disinfectant and an previous survey by Hack (1984), Wilczak et al. (1996) indicated that nitrite-N and nitrate-N levels may increase by 0.05 to 0.5 mg/L as N although increases of greater than 1 mg/L are possible. Nitrite levels during nitrification episodes have been reported ranging from 0.005 to 0.5 mg/L as N, with levels more frequently ranging from 0.015 to 0.1 mg/L as N (Wolfe and Lieu 2001). As discussed previously, the amount of nitrite produced is a function of the amount of ammonia present.



Figure 1-3 Theoretical nitrite/nitrate production based on chloramine decay stoichiometry as a function of chlorine:ammonia-N ratio. Assumes: (1) 100% decay according to Reaction 3 in Table 1-3; (2) 100% conversion of ammonia to nitrite/nitrate-N.

High nitrite levels could be observed in systems with high source water ammonia concentrations, regardless of whether or not disinfection is practiced. Rezania (2010) reported ammonia levels ranging from 1.7 mg/L up to 7 mg/L in a study of 39 public water supply wells in Minnesota. In addition, it was reported that samples taken in the distribution system had nitrite levels ranging from 0.0 to 2.1 mg/L. Lytle et al. (2007; 2009) reported that levels of nitrite greatly exceeded the maximum contaminant level (MCL) of 1.0 mg/L in the distribution systems of several communities in Illinois that had elevated ammonia in their source water.

As previously discussed, the NRC's assessment of distribution system health risks determined that formation of nitrate and nitrite in the distribution system was a relatively low priority compared to other potential distribution system health risks (NRC 2006). The report indicates that an increase of nitrite in the distribution system due to nitrification would likely be less than 10 percent of the MCL. Therefore, nitrite and nitrate formation from nitrification could be of most serious concern in systems with high source water ammonia concentrations. The additional nitrate and nitrate could cause an MCL exceedance.

Disinfection Byproducts

Nitrification in and of itself is not known to form DBPs, however certain practices to prevent or respond to nitrification, such as breakpoint chlorination, can form increased levels of regulated DBPs. As previously described, utilities often use chloramines for secondary disinfection to substantially reduce the formation of regulated DBPs present in the drinking water. However, other DBPs have been linked to the use of chloramines. Nitrosamines, including *N*-nitrosodimethylamine (NDMA), are another type of DBP that can form during chloramination of waters containing some organic nitrogen precursors and are considered to be carcinogenic (Schreiber and Mitch 2006).

For utilities monitoring NDMA as part of the second Unregulated Contaminant Monitoring Rule, one in four detected the presence of NDMA (Roberson 2010) and two-thirds of those utilities detecting NDMA reported the use of chloramines (Russell et al. 2012). Other nitrosamines monitored as part of this effort appear to occur less frequently and in smaller quantities. It appears likely that the USEPA will propose regulation of nitrosamines in the near future with a Maximum Contaminant Level Goal of zero due to their carcinogenic nature (Roberson 2010). California has established notification levels for NDMA and two other nitrosamines of 10 ng/L.

Speitel et al. (2010) conducted an assessment of how THMs can impact nitrification in chloraminated distribution systems. AOB can biodegrade THMs through cometabolism, an enzymatic process in which a specific microbial enzyme causes biodegradation of a chemical with no significant benefit to the microorganism. With respect to AOBs, this cometabolism produces by-products that are toxic to the microorganism (especially THMs with bromine). The research suggested that THM concentration and length of exposure could delay nitrification. In reactors fed with the concentrations of $400-600 \mu g/L$ of THM (much higher than levels that would be found in drinking water distribution systems), nitrification was delayed by 5–8 days in comparison to reactors receiving no THMs. The researchers also found that THMs in the presence of monochloramine also delayed the onset of nitrification in comparison with reactors that received only monochloramine.

Figure 1-4 presents the results of an experiment conducted by Speitel et al. (2011) in which reactors were fed with a water quality meant to promote nitrifying conditions. The THMs concentration for the two reactors receiving THMs was 56 μ g/L and the control reactor had no THMs present (note: one of the two control reactors failed). For the control reactor, nitrification was initially indicated at about 300 hours as shown by the increase in nitrite. Over the next 350 hours, the ammonia concentration decreased steadily with complete nitrification. Reactors receiving THMs started to show signs of nitrification, but full nitrification was not observed even after 650 hours.

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 resulting presence of free ammonia from dosing procedures and/or chloramines decomposition) and the presence of nitrifying bacteria in the distribution system are the main causes of nitrification in water distribution systems. Because 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 can be present in drinking water through naturally occurring processes, through ammonia addition during secondary disinfection to form chloramines, and when it is released into the water due to chloramine degradation (e.g. decay and demand reactions). Because the use of chloramine is expected to increase in the near future as a response to more stringent DBP MCLs associated with the Stage 2 D/DBP Rules, the occurrence and impacts of nitrification are expected to increase.

There are several impacts of nitrification that can affect distribution system water quality. Of the water quality issues identified in the literature and summarized



NH3-ammonia, NO2-nitrite, THM-trihalomethane

Source: Speitel et al. 2011

Figure 1-4 THM inhibition of nitrification during bench-scale studies

in Table 1-2, most impacts on regulatory compliance are indirect, such as loss of disinfectant residual or reduction in pH. Only the formation of nitrite and nitrate within the distribution system poses a potential direct public health threat, but nitrite and nitrate are not addressed within the distribution system through current provisions of SDWA. It should be noted, however, that a nitrite or nitrate MCL violation within the distribution system is unlikely in most chloraminated distribution systems, unless treated water nitrite and nitrate levels are already near their respective MCLs or source waters contain elevated levels of ammonia. Although compliance with current regulations may not 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 an essential water quality maintenance practice because 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 heterotrophic bacteria prevalent during nitrification episodes. Maintenance of a disinfectant residual and the biological integrity of the distribution system are important from a customer point of view as well as from a distribution system security point of view, because a disinfectant residual is commonly used as one *indicator* of distribution system integrity and overall water quality (National Research Council Committee on Public Water Supply Distribution Systems 2006; Friedman et al. 2010).

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