



Office of Water (4601M)
Office of Ground Water and Drinking Water
Distribution System Issue Paper

Nitrification

August 15, 2002

PREPARED FOR:

U.S. Environmental Protection Agency
Office of Ground Water and Drinking Water
Standards and Risk Management Division
1200 Pennsylvania Ave., NW
Washington DC 20004

Prepared by:
AWWA
With assistance from
Economic and Engineering Services, Inc

Background and Disclaimer

The USEPA is revising the Total Coliform Rule (TCR) and is considering new possible distribution system requirements as part of these revisions. As part of this process, the USEPA is publishing a series of issue papers to present available information on topics relevant to possible TCR revisions. This paper was developed as part of that effort.

The objectives of the issue papers are to review the available data, information and research regarding the potential public health risks associated with the distribution system issues, and where relevant identify areas in which additional research may be warranted. The issue papers will serve as background material for EPA, expert and stakeholder discussions. The papers only present available information and do not represent Agency policy. Some of the papers were prepared by parties outside of EPA; EPA does not endorse those papers, but is providing them for information and review.

Additional Information

The paper is available at the TCR web site at:

http://www.epa.gov/safewater/disinfection/tcr/regulation_revisions.html

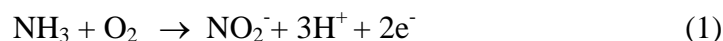
Questions or comments regarding this paper may be directed to **TCR@epa.gov**.

1.0 Introduction

The goal of this document is to review existing literature, research and information on the potential public health implications associated with Nitrification.

Nitrification is a microbial process by which reduced nitrogen compounds (primarily ammonia) are sequentially oxidized to nitrite and nitrate. Ammonia is present in drinking water through either naturally-occurring processes or through ammonia addition during secondary disinfection to form chloramines. The nitrification process is primarily accomplished by two groups of autotrophic nitrifying bacteria that can build organic molecules using energy obtained from inorganic sources, in this case ammonia or nitrite.

In the first step of nitrification, ammonia-oxidizing bacteria oxidize ammonia to nitrite according to equation (1).



Nitrosomonas is the most frequently identified genus associated with this step, although other genera, including *Nitrosococcus*, and *Nitrospira*. Some subgenera, *Nitrosolobus* and *Nitrosovibrio*, can also autotrophically oxidize ammonia (Watson et al. 1981).

In the second step of the process, nitrite-oxidizing bacteria oxidize nitrite to nitrate according to equation (2).



Nitrobacter is the most frequently identified genus associated with this second step, although other genera, including *Nitrospina*, *Nitrococcus*, and *Nitrospira* can also autotrophically oxidize nitrite (Watson et al. 1981).

Various groups of heterotrophic bacteria and fungi can also carry out nitrification, although at a slower rate than autotrophic organisms (Verstraete and Alexander 1973; Watson et al. 1981). Speciations of nitrifying bacteria in drinking water systems (Wolfe 1990 and 2001) suggest that the number of heterotrophic nitrifiers in drinking water systems may be negligible compared to autotrophic nitrifiers. In comparison, heterotrophic nitrification occurs in wastewater applications (Grady et al. 1980).

Chloramines are produced in a reaction between free chlorine and ammonia. Chloramination is commonly used for secondary disinfection purposes to control microbial growth in finished water. Chloramines include monochloramine, dichloramine, trichloramine, and organochloramines. For disinfection purposes, monochloramine is the preferential form.

Chloramine use is expected to increase in the near future as a result of more stringent disinfection by-product (DBP) maximum contaminant levels (MCLs) associated with the Stage I and Stage II Disinfectant/Disinfection By-Product Rule (DDBP Rule). Review of the Information Collection Rule (ICR) database indicates that 33% of 353 treatment plants use chloramines. The draft regulatory impact analysis prepared for the Stage 2 Microbial and

Disinfection Byproducts Federal Advisory Committee predicted that the use of chloramines could increase to as much as 65% of surface water systems (U.S. EPA M/DBP FACA Support Document, 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 to reduce DBP levels below the Stage I MCLs (U.S. EPA M/DBP FACA Support Document, 2000).

2.0 Description of Potential Water Quality Problems

Nitrification can have the adverse impacts of increasing nitrite and nitrate levels, reducing alkalinity, pH, dissolved oxygen, and chloramine residuals, and promoting bacterial regrowth (Wilczak et al. 1996). Table 1 provides a summary of water quality problems associated with nitrification.

Table 1	
Summary of Water Quality Problems Associated with Nitrification	
Chemical Issues	Biological Issues
Disinfectant Depletion	HPC Increase
Nitrite/Nitrate Formation	Ammonia Oxidizing Bacteria (AOB) Increase
Dissolved Oxygen Depletion	Nitrite Oxidizing Bacteria (NOB) Increase
Reduction in pH and Alkalinity	
DBP Formation due to Mitigation Techniques	

Various potential health impacts have been associated with issues identified in Table 1. The Chemical Health Effects Tables (U.S. Environmental Protection Agency, 2002a) provides a summary of potential adverse health effects from high/long-term exposure to hazardous chemicals in drinking water. The Microbial Health Effects Tables (U.S. Environmental Protection Agency, 2002b) provides a summary of potential health effects from exposure to waterborne pathogens.

While nitrification can degrade water quality, the formation of nitrite/nitrate and DBP formation during nitrification mitigation are the only water quality issue identified in the literature with the potential to impact public health directly. Other issues listed in Table 1 either are already regulated under provisions of the Safe Drinking Water Act, or were not identified within existing literature as posing direct public health impacts. However, more research may be needed to better understand interactions between these issues.

For example, reductions in pH and alkalinity can be a symptom of nitrification, as shown by hydrogen ion formation in equations (1) and (2). Although reductions in pH and alkalinity may not pose a direct public health threat, such reductions could theoretically lead to a violation of the USEPA Lead and Copper Rule (1991) either through failure to maintain designated optimal water quality parameters, or possibly through an action level exceedence at the tap. 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, so that there might be some linkage between the two phenomena within specific households (Murphy et al., 1997). System-wide Lead and Copper Rule violations due to nitrification were not cited in the literature.

Disinfection depletion and HPC increases are other examples of water quality impacts associated with nitrification that are addressed under provisions of the Safe Drinking Water Act. The loss of disinfectant residual does not necessarily pose a direct public health threat (many systems throughout the world are operated without use of a disinfectant residual). However, disinfectant decay can contribute to microbiological problems such 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 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 Surface Water Treatment Rule requires that a “detectable” disinfectant residual (or HPC measurements not exceeding 500/mL) be maintained in at least 95% of samples collected throughout the distribution system on a monthly basis. 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 that disinfect 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 total coliform regulation.

Nitrite/Nitrate Formation

Under the Safe Drinking Water Act (SDWA), primary MCLs have been established for nitrite-N, nitrate-N, and the sum of nitrite-N plus nitrate-N. The MCLs are 1 mg/L for nitrite-N, 10 mg/L for nitrate-N, and 10 mg/L for nitrite + nitrate (as N). The current nitrite and nitrate standards are measured at the point of entry to the distribution system so any subsequent elevated nitrite/nitrate levels resulting from nitrification within the distribution system are not identified by compliance monitoring.

Nitrite and nitrate are produced during nitrification through ammonia utilization by nitrifying bacteria. According to equations (1) and (2), for every mole of ammonia-N produced, a 1-mole equivalent of nitrite-N is produced. Subsequently, for every mole of nitrite-N produced, a 1-mole equivalent of nitrate-N is produced.

Ammonia can also be released from chloramines through a series of complex reactions. Reactions 2 through 6 in Table 2 describe five mechanisms of ammonia release presented by Wooschlager 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. Review of the equations presented thus far indicates that the greatest fraction of ammonia species is produced from Reaction 3 in Table 2.

Table 2
Overview of Nitrification and Chloramine Reactions

Reaction Description	Overall Reaction
1. Ammonium and nitrite utilization	$\text{NH}_3 + \text{O}_2 \rightarrow \text{NO}_2^- + 3\text{H}^+ + 2\text{e}^-$ $\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}^+ + 2\text{e}^-$
2. Release of ammonia through chloramine decay (autodecomposition)	$3\text{NH}_2\text{Cl} \rightarrow \text{N}_2 + \text{NH}_3 + 3\text{Cl}^- + 3\text{H}^+$
3. Release of ammonium through oxidation of organic matter by chloramine	$1/10 \text{C}_5\text{H}_7\text{O}_2\text{N} + \text{NH}_2\text{Cl} + 9/10\text{H}_2\text{O} \rightarrow 4/10\text{CO}_2 + 1/10\text{HCO}_3^- + 11/10\text{NH}_4^+ + \text{Cl}^-$
4. Release of ammonium through reaction of chloramine with corrosion products at pipe surfaces*	$1/2\text{NH}_2\text{Cl} + \text{H}^+ + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1/2\text{NH}_4^+ + 1/2\text{Cl}^-$
5. Release of ammonia through catalysis reactions of chloramine at pipe surfaces	$3\text{NH}_2\text{Cl} \rightarrow \text{N}_2 + \text{NH}_3 + 3\text{Cl}^- + 3\text{H}^+$
6. Release of ammonia through oxidation of nitrite by chloramine*	$\text{NH}_2\text{Cl} + \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{NO}_3^- + \text{HCl}$

Source: Adapted from Wooschlager et al. 2001

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

In this case, ammonium is released through oxidation of organic matter by chloramine. Greater than one mole of ammonium is produced (11/10 mole), all of which can be converted to nitrate, based on the molar ratios presented in Reaction 1. Many of these reactions can occur simultaneously; however, a conservative approach for predicting *maximum* nitrite/nitrate formation would be to use Reaction 3 in Table 2. Based on this approach, Table 3 was developed to assess the impact of Cl₂:NH₃-N ratio, total chloramine dose, and chloramine decay on theoretical nitrite/nitrate-N formation through nitrification.

Table 3
Theoretical Nitrite/Nitrate Production Based on Chloramine Decay Stoichiometry

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

* Assumes: (1) 100% of chloramine decay according to reaction: $1/10 \text{C}_5\text{H}_7\text{O}_2\text{N} + \text{NH}_2\text{Cl} + 9/10\text{H}_2\text{O} \rightarrow 4/10\text{CO}_2 + 1/10\text{HCO}_3^- + 11/10\text{NH}_4^+ + \text{Cl}^-$, (2) 100% conversion of ammonia to nitrite/nitrate.

The results in Table 3 show that using the most conservative chloramine decay reaction, 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 $\text{Cl}_2:\text{NH}_3\text{-N}$ ratio is less than 5:1. As the chlorine to ammonia-N ratio decreases, more ammonia becomes available for the nitrification process. This calculation is quite conservative as it is unlikely that 100% of chloramine decay will occur according to one single pathway.

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 decay species.

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 and nitrate levels may increase on the order of 0.005 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 $\text{NO}_2^- \text{-N}$, with levels more frequently ranging from 0.015 to 0.1 mg/L (Wolfe et al. 2001). Figure 1 compares treatment plant effluent and distribution system nitrite concentrations in nine chloraminating utilities (Kirmeyer et al. 1995). This figure demonstrates that nitrite levels during nitrification events can vary from as little as 0.05 mg/L to as much as 1 mg/L.

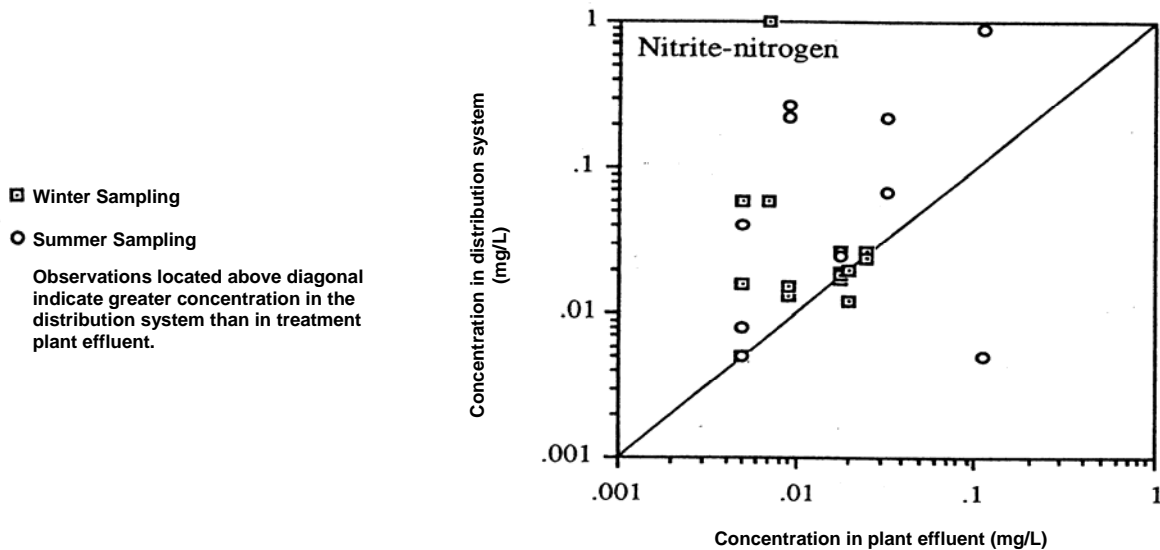


Figure 1
Comparison Between Plant Effluent and Distribution System Concentrations of Nitrite
 Source: Kirmeyer et al. 1995

3.0 Prevention/Mitigation Methods

Both groups of nitrifying bacteria are obligate aerobic organisms commonly found in terrestrial and aquatic environments (Holt et al. 1995, Watson et al. 1981). Their growth rates are controlled by:

- Substrate (ammonia-N) concentration,
- Temperature,
- pH,
- Light,
- Oxygen concentration, and
- Microbial community composition.

Water quality and environmental factors affecting nitrification are discussed below.

3.1 Source Water Treatment

3.1.1 Sources of Ammonia, Nitrate, and Nitrite

Excess nitrogen in the form of ammonia in finished water can be the principal cause of nitrification since ammonia serves as the primary substrate in the nitrification process. Ammonia, nitrate and nitrite can typically be found in surface water supplies as a result of natural processes. These natural sources of nitrogen generally have minimal impacts on water supply distribution systems because the concentration of nitrite nitrogen in surface and ground waters 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 agriculture runoff percolates into aquifers. A survey of 67 large utilities (greater than 50,000 customers) found that average levels of raw water nitrate ranged from 0 to 5.7 mg/L (Kirmeyer et al. 1995). To protect public health, any system with source water that exceeds the inorganic contaminant MCLs for nitrate and nitrite of 10 mg/L and 1 mg/L (as Nitrogen), respectively, must treat the water to below those levels (USEPA 2001). However, if a water treatment plant removes nitrate and nitrite levels to just meet the MCLs, and the water system uses chloramine for disinfection, there is a potential for nitrate and nitrite values during a nitrification event to exceed the numeric values of their respective MCLs.

Ammonia is deliberately added to a chloraminated water supply. In these systems, the concentration of free ammonia present in the distributed water will be a function of the chlorine to ammonia-N ($\text{Cl}_2:\text{NH}_3\text{-N}$) ratio. Free ammonia is almost completely eliminated when a 5:1 weight ratio of $\text{Cl}_2:\text{NH}_3\text{-N}$ is used (Kirmeyer et al. 1993). Nitrate/nitrite-N formation results presented previously in Table 3 showed that the lowest amount of nitrate/nitrite-N is formed when a 5:1 ratio is used.

3.1.2 Removal of Natural Organic Matter (NOM)

Song (1999) documented the impact of NOM on chloramine decay by altering NOM concentrations through GAC adsorption of the test water. Figure 2 shows the impact of NOM on chloramine decay rates.

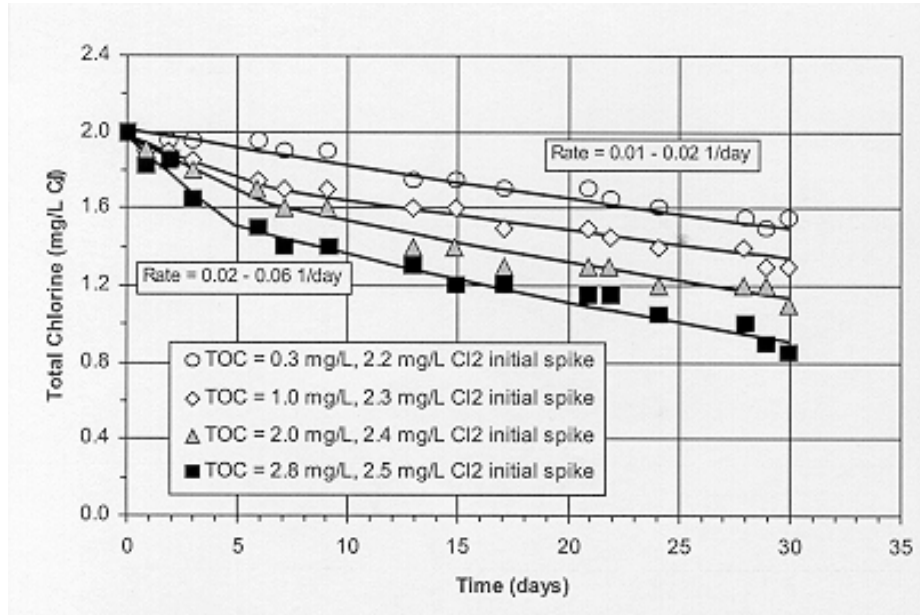


Figure 2
Elimination of Chloramine-NOM Reaction by TOC Removal with GAC Adsorption in USL WTP
Filtered Water at pH = 8.5
Source: Song 1999.

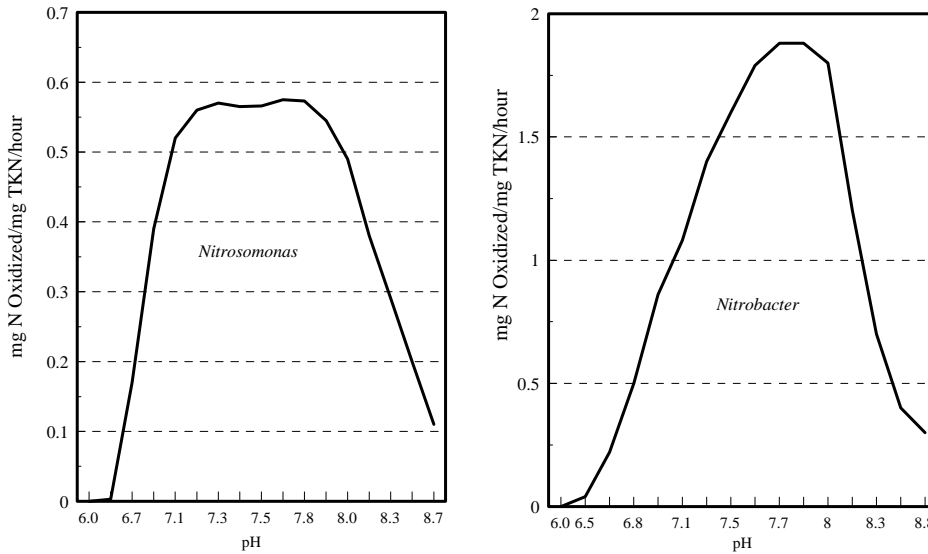
For the lowest TOC condition, only the autodecomposition pathway occurred. Bone et al (1999) hypothesized that the NOM oxidation mechanism is the dominant pathway for chloramine decay early in the decay process (i.e., within 24 hours), and that autodecomposition is the dominant cause of chloramine decay later.

3.1.3 pH and Alkalinity

Bulk water pH value is an important factor in nitrification activity for two reasons. First, a reduction of total alkalinity may accompany nitrification because a significant amount of bicarbonate is consumed in the conversion of ammonia to nitrite. A model developed by Gujer and Jenkins (1974) indicates that 8.64 mg/L of bicarbonate (HCO_3^-) will be utilized for each mg/L of ammonia-nitrogen oxidized. While reduction in alkalinity does not impose a direct public health impact, reductions in alkalinity can cause reductions in buffering capacity, which can impact pH stability and corrosivity of the water toward lead and copper. The relationships between pH, alkalinity, corrosivity, and metals leaching are addressed in a separate White Paper.

Secondly, nitrifying bacteria are very sensitive to pH as shown in Figure 3. *Nitrosomonas* has an optimal pH between approximately 7.0 and 8.0, and the optimum pH range for *Nitrobacter* is approximately 7.5 to 8.0. Some utilities have reported that an increase in pH (to greater than 9)

can be used to reduce the occurrence of nitrification (Skadsen et al. 1996). However, many other factors contribute to the viability of nitrifying bacteria and as a result, nitrification episodes have been observed at pH levels ranging from 6.6 to 9.7 (Odell et al. 1996).



Source: Grady and Lim 1980

Figure 3
Effects of pH on *Nitrosomonas* and *Nitrobacter* enrichment cultures

According to Wilczak (2001) pH appears to be the most important factor controlling the rate of chloramine autodecomposition. Thomas (1987) stated that the rate of chloramine decay approximately doubles for a drop in pH of 0.7 units.

3.1.4 Disinfection Practices

Chemical control or treatment of nitrifying bacteria typically involves either the maintenance of high distribution system disinfectant residuals (greater than 2 mg/L) or periodic breakpoint chlorination. Analytical survey results of ten U.S. utilities showed that greater than 90% of distribution system samples with increased nitrite and nitrate levels, indicative of nitrification, occurred in water with disinfectant residuals less than 2 mg/L (Wilczak et al. 1996). Many utilities have found that increasing disinfectant residuals by increasing chemical doses or managing water age has helped to control nitrification.

Utilities can use booster chlorination in the distribution system to increase disinfectant residuals. This practice is generally not employed in chloraminated distribution systems because chloramines are normally more stable than free chlorine (Woolschlager et al. 2001, Valentine et al. 1998). In addition, uncontrolled blending of chlorinated and chloraminated water could occur near a chlorine booster station; in some cases uncontrolled blending has been shown to cause unintended breakpoint chlorination, increases in DBP levels, or decreases in disinfectant residuals (Mahmood et al. 1999 and Muylwyk et al. 1999). In 2001, one utility installed a chloramine booster station that adds both sodium hypochlorite and aqueous ammonia to increase residuals in a remote area of a distribution system (Potts et al. 2001). The booster station was

designed to carefully control the chlorine to ammonia ratio and avoid excess ammonia in the downstream system. The effects of the booster station on nitrification have not yet been fully assessed (Potts et al. 2001).

Free chlorine is more effective at inactivating ammonia-oxidizing bacteria colonies than chloramines (Wolfe et al. 1990). As a result, breakpoint chlorination is also used by utilities to treat nitrifying bacteria. According to Schrempp et al. (1994), mechanically cleaning pipelines; draining and cleaning reservoirs; and dead-end, unidirectional and continuous flushing; were not sufficient to control nitrification at one mid-western utility. When these strategies were replaced with breakpoint chlorination, nitrification was controlled and target residuals could be maintained. Some systems using breakpoint chlorination have reported an initial increase in HPC bacteria and total coliform levels immediately following treatment that is probably attributable to biofilm sloughing (Odell et al. 1996, Wilczak et al. 1996).

3.2 Absence of Sunlight

Although monochloramine will degrade when exposed to the atmosphere at varying rates depending on the amount of sunlight, wind, and temperature (Wilczak, 2001), nitrifiers are very sensitive to near UV, visual, and fluorescent light; consequently, nitrification episodes in distribution systems occur in the dark (in covered reservoirs, pipelines, taps, etc.) (Wolfe et al, 2001). Wolfe et al (2001) also report that nitrifiers do have an excision repair mechanism for DNA repair; therefore low levels of nitrifiers may be recovered from partially shaded reservoirs or channels.

The Long-Term 2 Enhanced Surface Water Treatment Rule will require utilities to either cover uncovered finish water reservoirs or treat reservoir discharge to the distribution system to achieve a 4-log virus inactivation, unless the State/Primacy Agency determines that existing risk mitigation is adequate. The potential increase in nitrification episodes associated with covering uncovered storage facilities within chloraminated systems was not addressed within the literature.

3.3 Operations Activities

Nitrifying bacteria are slow growing organisms, and nitrification problems usually occur in large reservoirs or low-flow sections of the distribution system. According to Kirmeyer et al (1995), operational practices that ensure short residence time and circulation within the distribution system can minimize nitrification problems. Low circulation areas of the distribution system such as dead-ends and reservoirs are prime areas for nitrification occurrence since detention time and sediment buildup can be much greater than in other parts of the system.

Water temperature has a strong effect on the growth rate of nitrifying bacteria. Numerous researchers have documented that nitrification episodes are more common during the warmer months. Most strains of nitrifiers grow optimally at temperatures between 25 and 30°C (Watson, Valos, and Waterbury, 1981) but nitrification has occurred over a wide range of temperatures (8-26°C) (Kirmeyer et al. 1995). Operations activities that lead to decreased water age may also result in decreased bulk water temperatures.

The blending of distribution system waters containing different disinfectants may also have an impact on nitrification. Typically, the blended $\text{Cl}_2:\text{NH}_3\text{-N}$ ratio will increase after blending. Most often this is due to dilution of the ammonia fraction in the chloraminated water. The impact on the blended total chlorine residual will be a function of the initial chlorine and chloramine residuals.

A few studies have assessed the feasibility of blending chloraminated and chlorinated water in distribution systems (Mahmood et al. 1999; Muylwyk et al. 1999; and Barrett et al. 1985). Documented problems related to blending chlorinated and chloraminated water include the loss of disinfectant residuals, increases in tastes and odors, and increases in disinfection by-products, all of which are related to uncontrolled breakpoint chlorination that occurs in disinfectant blending zones (Barrett et al. 1985; and Mahmood et al. 1999). However, a few utilities do successfully blend their own chlorinated supplies with purchased chloraminated water. This is primarily accomplished when the chloraminated supply has excess ammonia that, when blended with the chlorinated supply, serves to form chloramines (Wolfe et al. 1988). In those cases, the blending ratios, and chlorine to ammonia ratios are strictly controlled to prevent breakpoint chlorination (Barrett et al. 1985).

A new AwwaRF Report which updates the 1993 report *Optimizing Chloramine Treatment* (Kirmeyer et al. 1993) includes an international survey of chloraminating utilities and is expected to provide additional information on blending multiple disinfectants.

3.4 Monitoring

The EPA Phase II Inorganic Contaminant regulations require water systems to sample for nitrite and nitrate at each entry point to the distribution system on at least an annual basis. 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 (EPA 2001). The MCLs are 1 mg/L for nitrite-N, 10 mg/L for nitrate-N, and 10 mg/L for nitrite + nitrate (as N).

Monitoring distribution system water quality can help to predict the on-set of a nitrification event. According to Wilczak et al, (1996), nitrification is often indirectly identified by one or more symptoms including:

- Loss of chloramine residual,
- Increase in water temperature,
- Decrease in dissolved oxygen,
- Drop in pH and alkalinity, and
- Increase in HPC population.

Individual utilities use combinations of the indicators listed based on their system's experience managing nitrification to initiate nitrification control measures. Example criteria reported in the literature as triggers for breakpoint chlorination include nitrite action levels of 0.05 mg/L and falling chloramine residuals (Odell et al. 1996, Wilczak et al. 1996, Wolfe 1988).

Nitrification occurrence can be confirmed by monitoring for nitrite or nitrate. Wilczak et al (1996) suggest that an accurate nitrogen balance and specific biological monitoring for ammonia-oxidizing bacteria and nitrite-oxidizing bacteria are the best ways to determine whether nitrification is occurring.

4.0 Summary

Nitrification is a microbial process by which reduced nitrogen compounds (primarily ammonia) are sequentially oxidized to nitrite and nitrate. Ammonia is present in drinking water through either naturally-occurring processes or through ammonia addition during secondary disinfection to form chloramines. Chloramine use is expected to increase in the near future as a result of more stringent disinfection by-product (DBP) maximum contaminant levels (MCLs) associated with the Stage I and Stage II Disinfectant/Disinfection By-Product Rule (D/DBP Rule). 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, 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 Safe Drinking Water Act. The findings of this paper suggest that a nitrite or nitrate MCL violation with the distribution system is unlikely, unless treated water nitrite and nitrate levels are near their respective MCLs. Additional research may be warranted to determine if nitrification episodes can cause direct violations of the Lead and Copper Rule. The causes of nitrification and prevention and mitigation approaches have been thoroughly documented within the literature.

5.0 Secondary Considerations

5.1 Increased Disinfection By-Products during Mitigation

Nitrification mitigation techniques such as break-point chlorination or temporarily switching from chloramines to free chlorine can result in increased levels of disinfection by-products. Disinfection by-products are regulated under the Stage 1 Disinfectants and Disinfection By-Product Rule. Under the Disinfectants and Disinfection By-Product Rule compliance monitoring samples are collected under routine operating conditions. Thus, disinfection by-product samples collected during a nitrification mitigation episode are not typically included in MCL compliance calculations. It would also be possible to exceed a Maximum Residual Disinfectant Level (MRDL) under the Disinfection By-Product Rule during a nitrification mitigation episode. However, the USEPA specifically allows short-term exceedence of MRDLs to control microbiological contamination problems.

5.2 Source Water Nitrification

Under certain circumstances nitrification can have a beneficial impact on drinking water quality. This would be true in the controlled conditions at a water treatment plant. Rittmann and Snoeyink (1984) reported that nitrification of ammonia-containing groundwater resulted in "biologically stable" water that did not permit bacterial growth in the distribution system. Kurtz-Crooks et al. (1986) showed that the chlorine demand of ammonia-laden groundwater was

reduced after nitrification. Nitrification was found to lower treatment costs and reduce formation of trihalomethanes.

Bibliography

- Barrett, S.E., M.K. Davis, and M.J. McGuire. 1985. Blending Chloraminated and Chlorinated Waters. *Jour. AWWA* (1): 50-61.
- Bone C.C., Harrington G.W., Oldenburg P.S., Noguera D.R. "Ammonia Release from Chloramine Decay: Implications for the Prevention of Nitrification Episodes", *Proceedings of AWWA Annual Conference*, Chicago, IL, 1999.
- Grady, C.P.L, Jr., and H.C. Lim, 1980. *Biological Wastewater Treatment*. Marcel Dekker, NY
- Gujer W., and D. Jenkins, 1974. A Nitrification Model for Contact Stabilization Activated Sludge Process. *Water Res.*, 9(5):5.
- Hack, D.J. 1984. State Regulation of Chloramine. *Jour. AWWA*, 77(1):4
- Holt, David, Rory D. Todd, Anaick Delanoue, and Jennifer S. Colbourne. 1995. A Study of Nitrite Formation and Control in Chloraminated Distribution Systems. *In Proc. 1995 AWWA Water Quality Technology Conference; Part II*. Denver, Colo.: AWWA.
- Kirmeyer, G.J., M. Friedman, J. Clement, A. Sandvig, P.F. Noran, K.D. Martel, D. Smith, M. LeChevallier, C. Volk, E. Antoun, D. Hildebrand, J. Dyksen, and R. Cushing. 2000. *Guidance Manual for Maintaining Distribution System Water Quality*, Denver, Colo.: AwwaRF and AWWA.
- Kirmeyer, Gregory J., Lee H. Odell, Joe Jacangelo, Andrzej Wilczak and Roy Wolfe. 1995. *Nitrification Occurrence and Control in Chloraminated Water Systems*. Denver, Colo.: AwwaRF and AWWA.
- Kirmeyer, G.J., G.W. Foust, G. L. Pierson, J.J. Simmler, M.W. LeChevallier. 1993. Optimizing Chloramine Treatment. Denver Colo.: AwwaRF and AWWA
- Kurtz-Crooks, J., V.L. Snoeyink, M.D. Curry, and M.L. Reynolds. 1986. Technical Note: Biological Removal of Ammonia at Roxana, Illinois. *Jour. AWWA*, 78(5):94-95
- M/DBP Stage 2 Federal Advisory Committee (FACA2). June 27-28, 2000
Washington, DC
- Mahmood, F., J. Pimblett, N. Grace and B. Utne. 1999. Combining Multiple Water Sources and Disinfectants: Options for Water Quality Compatibility in Distribution Systems. *In Proc. 1999 AWWA Water Quality Technology Conference*, Tampa, Fla.: AWWA.

- Muylwyk, Q., A.L. Smith and J.A. MacDonald. 1999. Implications on Disinfection Regime when Joining Water Systems: A Case Study of Blending Chlorinated and Chloraminated Water. *In Proc. 1999 AWWA Water Quality Technology Conference*, Tampa Fla.: AWWA.
- Murphy, Bart, J. T. O'Connor, T. L. O'Connor. 1997. Willmar Minnesota Battles Copper Corrosion Part 1. *In Public Works*, October 1997.
- Odell, Lee H., Gregory J. Kirmeyer, Andrzej Wilczak, Joseph G. Jacangelo, Joseph P. Marcinko, and Roy L. Wolfe. 1996. Controlling Nitrification in Chloraminated Systems. *Jour. AWWA*, 88(7):86-98.
- Potts, D.E., W.G. Williams, C.G. Hitz. 2001. A Satellite Chloramine Booster Station: Design and Water Chemistry. *In Proc. 2001 AWWA. Distribution System Symposium*, San Diego, California: AWWA.
- Rittmann, B.E., and V.L. Snoeyink. 1984. Achieving Biologically Stable Drinking Water. *Jour. AWWA*, 76(10): 106-114.
- Sawyer, C.N., and P.L. McCarty. 1978. *Chemistry for Environmental Engineering*, 3rd edition, McGraw-Hill, NY.
- *Stage I DBP Rule FACA Meeting, 2000.
- Schrempp, Tom, Ron Goold, Bennet Kwan and Darshan Sarai. 1994. Effect of Mechanical Cleaning and Free Residual Chlorine on the Chlorine Demand and Nitrification Process in a Chloraminated System. *In Proc. 1994 AWWA Water Quality Technology Conference; Part II*. San Francisco, Ca.: AWWA
- Skadsen, J. and Larry Sanford. 1996. The Effectiveness of High pH for Control of Nitrification and the Impact of Ozone on Nitrification Control. *In Proc. 1996 AWWA Water Quality Technology Conference*. Boston, Mass.: AWWA.
- Snoeyink, V.L., and D. Jenkins. 1980. *Water Chemistry*. John Wiley and Sons., NY
- Song, Daniel J., Ali Sheikholeslami, Linnea L. Hoover, Kathrin A. Turner, H. Hubert Lai, and Andrzej Wilczak. 1999. Improvement of Chloramine Stability Through pH Control, TOC Reduction and Blending at EBMUD, California. *In 1999 AWWA Annual Conference Proceedings*. Chicago, Ill.: AWWA.
- Stewart, M.H., and I. Nancy. 1997. Nitrification in Chloraminated Drinking Water and Its Association with Biofilms. *In 1997 AWWA Water Quality Technology Conference*. Dever, Colo.: AWWA.

- Thomas P.M. "Formation and Decay of Monochloramine in South Australian Water Supply Systems", *12th Federal Convention, Australian Water and Wastewater Association*, Adelaide, Australia, p.268-276, 1987.
- U.S. Environmental Protection Agency. 2002a. Chemical Health Effects Tables. <http://www.epa.gov/safewater/tcrdsr.html>. May 7, 2002.
- U.S. Environmental Protection Agency. 2002b. Microbial Health Effects Tables. <http://www.epa.gov/safewater/tcrdsr.html>. May 7, 2002.
- U.S. Environmental Protection Agency. 2001. *National Primary Drinking Water Regulations*. Federal Register, 19(141).
- U.S. Environmental Protection Agency. 1991, *National Primary Drinking Water Regulations: Lead and Copper Rule (Final)*, Federal Register.
- U.S. Environmental Protection Agency. 1989a. *National Primary Drinking Water Regulations: Analytical Techniques; Coliform Bacteria; Final Rule*. Federal Register, 54(135): 29998-30002.
- U.S. Environmental Protection Agency. 1989b. *Drinking Water; National Primary Drinking Water Regulations; Filtration, Disinfection; Turbidity, Giardia lamblia, Viruses, Legionella, and Heterotrophic Bacteria; Final Rule*. Federal Register, 54(124):27486-27541.)
- Valentine R.L., Ozekin K., Vikesland P.J. "Chloramine Decomposition in Distribution System and Model Waters", AWWA Research Foundation, Denver, CO, 1998.
- Verstraete, W., and M. Alexander. 1973. Heterotrophic Nitrification in Samples of Natural Ecosystems. *Envir. Sci. Technol.*, 7(39).
- Watson, S.W., F.W. Valos, and J.B. Waterbury, 1981. The Family Nitrobacteraceae. In *The Prokaryotes*. Edited by M.P. Starr et al. Berlin: Springer-Verlag.
- Wilczak, Andrzej, Joseph G. Jacangelo, Joseph P. Marcinko, Lee H. Odell, Gregory J. Kirmeyer, and Roy L. Wolfe. 1996. Occurrence of nitrification in chloraminated distribution systems. *Jour. AWWA*, 88(7):74-85.
- Wilczak, Andrzej, 2001. Chloramine Decay Rate: Factors and Research Needs. In *2001 AWWA Annual Conference Proceedings*. Washington, D.C.: AWWA.
- Wolfe, R.L., E.G. Means, M.K. Davis, and S.E. Barrett. 1988. Biological Nitrification in Covered Reservoirs Containing Chloraminated Water. *Jour. AWWA*, 80(9):109-114.

Wolfe, Roy L., Nancy I. Lieu, George Izaguirre and Edward G. Means. 1990. Ammonia-Oxidizing Bacteria in a Chloraminated Distribution System: Seasonal Occurrence, Distribution, and Disinfection Resistance. *Appl. Environ. Microbiol.*, 56(2): 451-462.

Wolfe, R.L., and N.I. Lieu. 2001. Nitrifying Bacteria in Drinking Water. In *Encyclopedia of Environmental Microbiology*, edited by G. Bitton. New York: John Wiley and Sons.

Woolschlager, J.E., B.E. Rittmann, P. Piriou and B. Schwartz. 2001. Developing an Effective Strategy to Control Nitrifier Growth Using the Comprehensive Disinfection and water Quality Model. In *Proc. World Water and Environmental Resources Congress*. Renton, Vir.: ASCE.