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Water Quality

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What's Your Ammonia IQ?

Although ammonia is unregulated, its presence in drinking water causes a variety of problems. The most effective way to mitigate these problems is to minimize ammonia's presence. **BY PHILIP J. BRANDHUBER, PHD**

***Editor's Note**: This is the first of three articles to help water system operators understand ammonia and how to monitor and control its effects at the plant and in the distribution system. This article provides background information about ammonia, its chemistry, origin, and the problems it can cause. Next month's article will discuss ammonia treatment options. The final article will provide case studies explaining how utilities have dealt with ammonia.*

AMMONIA (NH_3) often presents unexpected challenges for drinking water utilities. Other regulated inorganic contaminants, such as arsenic, receive a lot of publicity. But ammonia and the problems it causes are discussed less frequently. Although ammonia is unregulated, its presence in water has various implications for utilities.

The presence of ammonia can be intentional or unintentional. When used with chlorine to form chloramine at water plants, ammonia's presence is intentional. However, in this instance, unreacted ammonia can enter the distribution system, degrade treated water quality, and feed nitrification. When ammonia is present in chlorine-disinfected water, it causes the unintended formation of combined chlorine, which has a lower disinfection capacity than free chlorine.

When ammonia naturally occurs in raw water or is present in a distribution system, its presence is unintentional. In such cases, ammonia exerts a demand on oxidants, such as chlorine or permanganate, consumes the oxidant, and increases the amount of oxidant needed.

Whether present intentionally or unintentionally, ammonia should be closely monitored and controlled in the treatment plant and distribution system. Failure to do so can result in higher chemical consumption, lower-quality water, loss of disinfectant residual, taste-and-odor events, and customer complaints.

AMMONIA CHEMISTRY

Ammonia is a colorless gas that dissolves easily in water. Gaseous ammonia consists of a nitrogen atom bonded to three hydrogen atoms (NH_3). When dissolved in neutral-pH water, a fourth hydrogen atom is added to its structure, forming the positively charged ammonium ion (NH_4^+). This process, at 25°C, is summarized by the following equilibrium reaction:

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

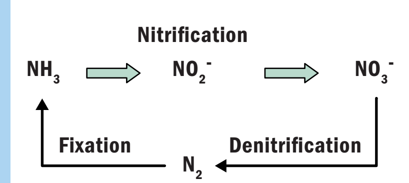
In water, the NH_4^+ form predominates at pH levels of less than 9.3, and the NH_3 form predominates at pH levels greater than 9.3. Therefore, in most cases, ammonia in drinking water is present as the ammonium ion.

Ammonia and the Nitrogen Cycle. Ammonia plays an important role in a complex natural process called the nitrogen cycle (see figure below). In this process, nitrogen is converted to various forms that are related to its oxidation state. Nitrogen contained in ammonia is in its most reduced (lowest) oxidation state. Starting from this point, nitrogen in ammonia can be oxidized to higher oxidation states, converting ammonia first to nitrite (NO_2^-) and then to nitrate (NO_3^-). The process, which is performed by microorganisms, is called nitrification. The same process is used in wastewater treatment plants to treat ammonia.

After nitrate is formed, the denitrification process reduces nitrogen in nitrate to gaseous nitrogen (N_2) and back to ammonia via fixation. Because nitrification of ammonia by microorganisms is fairly easy

Ammonia and the Nitrogen Cycle

Nitrogen's transformation to various chemical forms can be carried out by both biological and nonbiological processes.



Ammonia in surface and tap water supplies often is a result of runoff in agricultural areas where fertilizer is applied to the ground. High ammonia levels aren't usually found in well water supplies, because bacteria in the soil convert the ammonia to nitrates.

to accomplish, ammonia isn't stable when microorganisms are present. The fact that ammonia can serve as food for nitrifying microorganisms—which, in turn, produce regulated compounds, such as nitrite and nitrate as by-products—has important consequences for drinking water systems.

Ammonia–Chlorine Reactions. Ammonia and chlorine can be mixed to form a weak disinfectant called chloramine. Depending on the ratio at which chlorine and ammonia are mixed and the pH at which mixing occurs, three types of chloramines can be formed. Chemically the reactions are

- Monochloramine
  $NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O$
- Dichloramine
  $NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O$
- Trichloramine
  $NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$

When all three chloramine compounds are present, they're called chloramines. However, monochloramine is more commonly referred to as chloramine (without the "s").

Because the presence of dichloramine and trichloramine can cause taste-and-odor problems and are less-effective disinfectants, drinking water systems adjust water chemistry to ensure chloramine is predominantly formed.

Generally, all three chloramine compounds can be formed intentionally or unintentionally. Chloramine is intentionally formed by carefully mixing controlled ratios of chlorine to ammonia at a set pH. As a residual disinfectant, the primary advantage of chloramine is that it doesn't form regulated disinfection by-products.

Ammonia can be present in raw water and is most commonly found in groundwater. If ammonia isn't detected or monitored, chloramines can be formed unintentionally when the raw water is chlorinated. The unintended presence of chloramines is often indicated by an unexplained difference between total and free chlorine residual measurements.

AMMONIA'S ORIGINS

There are numerous sources of ammonia and ways in which ammonia can get into treatment plants or distribution systems. As mentioned previously, nitrogen in ammonia is readily converted into other forms of nitrogen via the nitrogen cycle, so natural levels of ammonia are usually low. Yet in some parts of the United States, natural ammonia is present in groundwater drawn from clay aquifers that have a high capacity to hold ammonium ions.

Natural ammonia can also be released from decomposing organic matter in sediments of lakes or reservoirs during turnover. Generally, when elevated levels of ammonia are found in water, the source of the ammonia is human activity. Human activity releases ammonia into water in various ways, including discharge of wastewater, use of ammonia fertilizers, domestic animal manure, and malfunctioning septic systems, as shown in Table 1 on page 14.

If present in raw water, ammonia can enter a treatment plant or distribution system. Ultimately, it doesn't matter whether the ammonia source is natural

NITRIFICATION BASICS

NITRIFICATION IN THE ENVIRONMENT

Nitrifying bacteria are found in soils, compost piles, wastewater, fresh water, marine habitats, and in most other aerobic environments. The highest concentration of nitrifying bacteria are found in the upper 10-cm layer in soils, at the sediment–water interface in rivers and streams, and attached to the sides of aeration tanks in wastewater treatment plants.

Considerable amounts of nitrifying bacteria, as well as ammonia, nitrate, and other nitrogen-based compounds, are brought into rivers through the discharge of treated and untreated urban wastewater. In the marine environment, nitrifiers are localized in the upper 200 meters of the water column or at the sediment–water interface.

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. Other sources of nitrogen can include agricultural runoff from fertilization or livestock wastes or contamination from sewage.

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.

Source: Manual of Water Supply Practices M56: *Fundamentals and Control of Nitrification in Chloraminated Drinking Water Distribution Systems*.

Table 1. Ammonia Sources

Ammonia can originate from several sources in raw water, treatment plants, and distribution systems.

Natural Sources	Man-Made Sources	In Water Plants and Distribution Systems
■ Some clay aquifers ■ Wildlife	■ Wastewater discharge ■ Fertilizer ■ Domesticated animal manure ■ Septic systems ■ Landfill leachate ■ Industrial release	■ Present in raw water ■ Added to form chloramines (with free chlorine) ■ Decomposition of chloramines in distribution system ■ Added to reduce bromate formation (ozone plants)

or results from human activity; it behaves the same regardless of its source.

When chloramines are formed, they can serve as an ammonia source in a distribution system. Whether intentionally or unintentionally formed, chloramines are inherently unstable and will degrade with time, releasing ammonia. Because decay occurs over many days, degrading chloramines don't create problems in the treatment plant but may release ammonia into the distribution system. The presence of organic matter, nitrite, or metals will accelerate the rate of chloramine decomposition and ammonia release. Maintaining an elevated pH in the distribution system increases chloramine stability and reduces potential ammonia release.

AMMONIA-CAUSED PROBLEMS

Ammonia can cause a range of problems in plants and distribution systems, as shown in Table 2. In a plant, ammonia usually manifests itself in unexpected oxidant behavior, needing more oxidant than expected, obtaining lower residual readings than expected, or measuring larger-than-anticipated differences between total and free chlorine residual.

Ammonia also causes significant problems in distribution systems. Because ammonia is a food source for commonly occurring nitrifying bacteria, ammonia will, under extreme conditions, promote uncontrolled biological growth in a distribution system (nitrification). Nitrification has serious consequences. As noted in the nitrogen cycle described above, nitrification produces nitrite and nitrate, which are regulated contaminants.

Under severe conditions, nitrite and nitrate can exceed regulated maximum contaminant levels (MCLs). Nitrification can also lead to bacterial growth in a distribution system, causing taste-and-odor problems, as well as total coliform. Under such conditions, it's impossible to maintain a disinfectant residual. If not quickly addressed, severe nitrification can present public health concerns. Even slight nitrification conditions can make it difficult to maintain residual and address customer complaints regarding taste and odor or discolored water.

MINIMIZING AMMONIA

A nitrification event can be caused by many factors, but the fundamental problem is the presence of ammonia. The most effective way to prevent nitrification is to minimize ammonia's presence.

Author's Note: *This article was prepared jointly by members of the AWWA Inorganics and Inorganic Contaminants Research committees. Contributors include Jennifer Baldwin, CH2M Hill; Nicole Blute, ARCADIS/Malcolm Pirnie; Amlan Ghosh, Jacobs Engineering; Michelle DeHaan, Park City Water; Tarrah Henie, California Water Company; France Lemieux, Health Canada; and Darren Lytle, US Environmental Protection Agency.*

Table 2. Ammonia-Related Treatment Problems

Ammonia can cause a range of problems in treatment plants and distribution systems.

In a Plant		In a Distribution System	
Problem	**Cause**	**Problem**	**Cause**
Excess oxidant consumption	Ammonia is competing for oxidant	■ Low or no residual ■ Elevated turbidity ■ Elevated heterotrophic plate count ■ Elevated nitrite/nitrate ■ Taste-and-odor complaints	■ Nitrification of ammonia ■ Formation of dichloramine and trichloramine
Low free chlorine residual	Ammonia is forming chloramines	Excess biofilm	Ammonia feeding and promoting biogrowth
Low chlorine-to-ammonia ratio when forming chloramine	Unexpected presence of ammonia in raw water	Detection of ammonia	■ Improper chloramination conditions at plant ■ Decomposition of chloramines