EPB 311- Strategies for Dealing with Groundwater Treatment Systems Having High Natural Ammonia

Background

The occurrence of ammonia (NH_3) in the water source is often associated with pollution due to sewage infiltration, use of nitrogen-fertilizers or livestock wastes. Naturally occurring ammonia that is present in most waters, results from biological degradation of nitrogenous organic matter which is very common in Saskatchewan groundwater. The concentration levels of natural ammonia in groundwater and surface water are generally below 0.2 mg/L.

Ammonia, when in contact with chlorine, will react rapidly to form chloramines; therefore, breakpoint chlorination is one of the essential treatment techniques for the removal of ammonia in raw water. Breakpoint chlorination is the addition of chlorine to the water or wastewater source until the chlorine demand has been satisfied. Further dosage of chlorine passing the breakpoint will result in free chlorine residual.

Chloramination process takes place in a number of different stages. Chlorine will first react with NH_3 to form monochloramines (NH_2Cl). This reaction will occur up to the peak of the breakpoint curve as shown in Figure 1. Additional free chlorine then reacts with monochloramines to form dichloramines ($NHCl_2$) and then trichloramines or nitrogen trichloride (NCl_3) and nitrates before the breakpoint is achieved.

Health and Safety Concerns

Ammonia

The major health concern with ammonia in drinking water is the risk of nitrification resulting in formation of nitrites and nitrates. Nitrates are known to cause serious illness such as methaemoglobinaemia, or fatality in infants less than six months of age. According to the Water Security Agency (WSA) and Health Canada (2003), the maximum acceptable concentration (MAC) for nitrate in drinking water is 45 mg/L (equivalent to 10 mg/L as nitrate-N) and 3.2 mg/L for nitrites. According to the United States Environmental Protection Agency the maximum contaminant level (MCL) for nitrates is set at 10 mg/L and 1 mg/L for nitrites. In Saskatchewan, nitrite levels are generally less than 10 mg/L (majority of them are less than 5 mg/L) in the affected communities and nitrite/nitrate levels are not a concern

Chloramines

One type of possible cancer-causing agent from chloramines is monochloramine. The formation of pure monochloramine (NH_2Cl) is dependent upon pH, ratio of chlorine to ammonia-nitrogen, temperature and contact time. Health Canada, Australia, New Zealand and World Health Organization all have established a Maximum Acceptable Level for total chloramine in drinking water at 3 mg/L. At present, Saskatchewan has no guideline for monochloramine, but may adopt Health Canada guideline in the future. Alberta has suggested a combined residual of 3 mg/L (maximum) whereas British Columbia established 3 mg/L (maximum) for monochloramine. Ontario, Manitoba and Quebec have not yet advised the maximum allowable concentrations for combined or monochloramine. Monochloramine will likely not result in complaints about taste and odour at concentrations of 3 mg/L or even 5 mg/L in drinking water supplies; however, dichloramines may cause complaints at concentrations of 0.5 mg/L or higher. It is also important to remove chloramines from water used for blood dialysis. Minimum treatment standards for the provision of safe drinking water rely on a free chlorine residual to provide proper disinfection prior to distribution. Required disinfection will most likely not be achieved in raw waters containing ammonia unless breakpoint chlorination is reached prior to distribution. This is due to ammonia's rapid reaction with available chlorine thus interfering with the achievement of adequate CT (minimum treatment) for the inactivation of contaminants such as viruses.

Chloramines are not recommended as a primary disinfectant due to its high Contact Time (CT) value required for pathogen inactivation. However, they can be used for secondary disinfection protection against microbial growth in distribution systems. American Water and Wastewater Association (AWWA) recommends a goal of 2 mg/L combined chlorine for water leaving the plant and 1 mg/L throughout the distribution system when chloramines are used as a secondary disinfectant in the presence of another primary disinfectant such as free chlorine.

Interferences with the N, N-diethyl-p-phenylenediamine test (known as the DPD test) free chlorine test will occur if combined chlorine present has high concentrations, because it can break through into the free chlorine fraction. This interference can be avoided or reduced by:

- Adding sodium arsenate or thioacetamide immediately after mixing DPD reagent which can stop this interference;
- Using syringaldazine as indicator (FACTS method); or
- Using DPD method but completing the test as quickly as possible. However, if breakpoint is not achieved/and or ammonia is present, the values are not representative of free chlorine levels.

In order to meet or achieve appropriate disinfection requirements, the community has to maintain free chlorine residual as specified in 27 (6) of *The Waterworks and Sewage Works Regulations*.

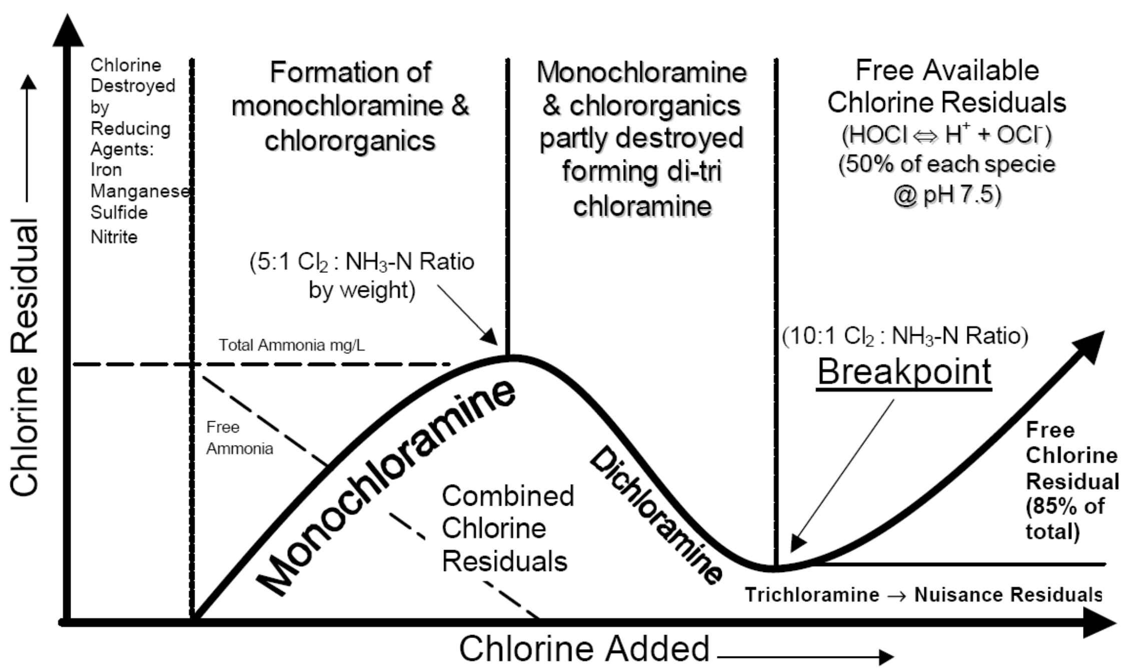
To test for chloramines:

- Hach indophenol method can be used. Portable devices are available; or
- ChemScan method utilizing light absorbance, measures monochloramines directly.

To test for free ammonia:

- Indophenol method also can be used to test free ammonia (range 0.5 mg/L max), usually needs dilution for higher concentrations; or
- Hach SensIon ammonia electrode (range 0.05~14000 mg/L) can be used.

Figure 1: Breakpoint Chlorination Curve



Possible Strategies to Deal with Ammonia

A number of different strategies have been presented to deal with the occurrence of ammonia in groundwater. It is suggested that breakpoint chlorination is an appropriate strategy to deal with ammonia when levels are low. Breakpoint chlorination will ensure "true" free chlorine residual in the distribution, but keeping in mind that a chlorine dose of about eight to 10 times the ammonia concentration may be required for achieving breakpoint disinfection. On the other hand, if ammonia levels are high in the groundwater source, appropriate measures such as treatment of raw water to minimize or remove ammonia levels may be considered. A nitrification-monitoring program should be considered to monitor nitrite and nitrate levels. Some of the factors indicating nitrification and strategies to minimize nitrification are listed below:

Factors indicating nitrification (AWWA, 2006)

- Decrease in total chlorine residual. Research has shown that a chlorine demand of 5 mg/L is exerted by 1 mg/L of nitrite;
- Increase in Heterotrophic Plate Count (HPC) bacteria and potentially increase in total coliforms;
- Decrease in free ammonia;
- Increase in nitrite (up to and above 0.05 mg/L as N);
- Decrease in Dissolved Oxygen (DO) (moldy and earthy-tasting water); and
- Decrease in alkalinity and pH.

Favorable conditions for nitrification (AWWA, 2006)

- pH 7.5 – 8.5;
- Temperature 25 to 30 ºC;
- Darkness;
- Extended detention time i.e. poor reservoir turnover and dead-end mains (50 per cent daily turnover recommended); and
- Sediments and biofilms development.

Strategies to minimize nitrification (AWWA, 2006)

- Decreasing the detention time;
- Adjusting the pH (increasing);
- Decreasing the Total Organic Carbon (TOC);
- Increasing Cl_2/NH_3-N ratio and chloramine residual;
- Decreasing excess ammonia; and
- Performing occasional breakpoint chlorination.

It is not recommended to use chloramination as primary disinfection due to the limitations in monitoring programs and facility operations in small communities because improper operation can result in taste and odour problems from nitrification or di- and tri-chloramine formation. If groundwater is under the influence of surface water, the particular water source should be treated as a surface water source.

Multiple disinfectants are used when source water is not a true groundwater or is surface water. Ultraviolet (UV) radiation, ozone and chlorine dioxide are possible options for primary disinfection. Site-specific cost analysis will help determine the choice of the strategy to be adopted. Raw water ammonia can be removed using the following removal techniques:

Air Stripping

Separation of unionized-ammonia (NH_3) from water can be achieved with air stripping in a packed tower by raising the pH of water above 10 and increasing the temperature. Since ammonia is soluble in water, a high air/water ratio is required; pH is required to be lowered again (about 8). The operating costs may include electricity, alkali/acid costs and stripper maintenance costs.

Aeration Tower
The purpose of aeration tower is to make oxygen react with reducing species in water for example iron and manganese. Ammonia does not react with oxygen in normal conditions. However, some unionized-ammonia, if present, may also escape in aeration tower due to mass transfer with air.

Ion Exchange
Zeolites are an excellent example for ion exchange materials that can remove ammonia. Clinoptilolite is a most popular and natural zeolite material used for ion exchange. They can be regenerated using brine. Since only the ionized ammonium form can be removed by the ion exchange process, the pH of water needs to be maintained at 7.2-7.6. Water that is high in hardness will have decreased capacity due to the simultaneous affinity and removal of calcium, magnesium and the ammonium ion. There are selective zeolites that will preferentially remove ammonia in high hardness water, however, there may be high levels of sodium in the treated water. Ion exchange seems to be an attractive method especially when low cost minerals can be used as an exchanger and water has low hardness.

Biological
Biological nitrification is one method of removing ammonia but it may increase the levels of undesirable nitrates in water. Use of biological treatment in cold environments does not yield good results. It is a slow process and specific environmental conditions are required for microorganisms. Also, the treatment is very sensitive to pH, temperature and light etc.

Reverse Osmosis (RO)
RO membranes have been shown to remove ammonia effectively. Some small systems in Saskatchewan have installed RO to remove ammonia.

Activated Carbon
Ammonium ions are poorly removed by activated carbon because it only removes large organic molecules. Granular Activated Carbon (GAC) is an effective technology for removing chlorine and chloramines. In case of chloramines, only chlorine is removed. Ammonia, the other component in chloramines, still remains.

Field Test Study

A field study was conducted to determine ammonia levels and other parameters on selected communities. Communities were selected based on location, community size and raw water ammonia levels. The results of analyses of samples showed that:

a) All of the raw water samples are found to be bacteriologically safe;
b) The level of monochloramine in treated water of nine out of 11 communities tested was less than 3 mg/L; and
c) The levels of nitrites and nitrates in treated water and distribution system are low and indicated that nitrification is not a major concern in these communities.

Recommendations

The Water Security Agency will explore the possibility of adopting Health Canada's Maximum Acceptable Concentration (MAC) for total chloramine of 3 mg/L as a provincial guideline. In systems operating before breakpoint, WSA will consider that any free chlorine will shortly become combined. In systems operating after breakpoint, chloramine is largely absent (trichloramines may be present at nuisance levels) and will not interfere significantly with free chlorine readings.

One of the cost effective options when ammonia levels are low is through breakpoint chlorination, but when ammonia levels are high, the community has to conduct a site-specific study to determine an appropriate cost-effective strategy including providing treatment to reduce ammonia levels in raw water.

There are many other ammonia removal technologies available and may be suitable for small communities. Treatment systems, such as ion-exchange, RO and air stripping (via air bubbling) seem to be effective in removing ammonia.