AMMONIA - WATER TREATMENT CHALLENGES

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ABSTRACT (500 WORDS MAXIMUM)

Ammonia can be present in groundwater due to natural conditions or as a result of agriculture and/or industry in the area. Ammonia does not present any direct risks to health when present in water. However, it does cause taste and odour issues and depending on conditions can have indirect health effects. There are two primary effects of concern; the first being oxidation of ammonia to nitrite, which is dangerous to health even in small quantities, and the second is ammonia reacting with chlorine, reducing the effectiveness of chlorine disinfection, which can lead to bacterial outbreaks. These problems lead to ammonia removal being desirable in water treatment. Ammonia is difficult to remove due to its high solubility and limited reactiveness.

This paper discusses treatment options for water high in ammonia with specific reference to controlling issues associated with taste and odour, nitrification and disinfection by-product formation. Options discussed include breakpoint chlorination, chloramine disinfection, chlorine dioxide disinfection, ion exchange and reverse osmosis. The relative advantages and disadvantages of these methods will be discussed including additional treatment considerations of these processes. Additionally, a new treatment technology biological ammonia removal will be discussed. This technology incorporates biologically active filters seeded with ammonia oxidising (AOB) and nitrogen oxidising bacteria (NOB) and has been successfully trialled in pilot and full-scale plants in the US, Europe and Asia. The potential implementation in the New Zealand setting and risks of this process will be discussed in detail.

The paper includes New Zealand examples from South Taranaki's Patea and Waverley WTPs. These plants have challenging groundwater sources, high in ammonia, manganese and iron. The process solution selected for these two plants varied based on raw water conditions including ammonia levels and operational challenges caused by these conditions. The technologies considered and the decision making behind the final process selection are discussed. This includes the decision to employ chlorine dioxide disinfection at the Patea WTP, which is the first know municipal water supply to employ such a treatment technology.

KEYWORDS

Ammonia, chlorination

PRESENTER PROFILE

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1   INTRODUCTION

Ammonia can be present in raw water sources due to natural conditions or as a result of agriculture and/or industry in the area. Ammonia is a common pollutant in raw or treated domestic, agricultural and industrial wastewater. Natural levels in groundwaters are usually below 0.2 mg of ammonia per litre (The Water Security Agency 2019). However, in some areas higher levels of ammonia may be present as a result of the degradation of naturally occurring organic matter (Taranaki Regional Council 2015).

The protection of freshwater rivers, streams and groundwater sources from effects of domestic agricultural and industrial contamination is an important issue. Ammonia is a key indicator of freshwater quality and is found to be toxic to aquatic life. The National Policy Statement for Freshwater Management 2014 is aiming to improve freshwater quality nationally and reduce the effects of ammonia in New Zealand's freshwater environment.

Ammonia at concentrations expected in drinking water does not present any direct risks to health and as a result a health-based guideline for ammonia in drinking water has not been derived by the World Health Organization (WHO 2003). However, the Drinking-water Standards for New Zealand (DWSNZ) 2005 (revised 2018) have adopted the aesthetic guideline value of 1.5 mg/L corresponding to the WHO reported odour threshold (WHO 2003).

The main concerns of elevated ammonia levels in drinking water sources are the following:

- Taste and odour

  Ammonia has an objectionable odour and above the odour threshold of 1.5mg/L significant taste and odour complaints may be experienced (WHO 2003, DWSNZ 2005 (revised 2018)).

- Decreased disinfection efficiency

  If drinking-water containing more than 0.2 mg of ammonia per litre is chlorinated, as much as 68% of the chlorine may react with the ammonia and become unavailable for disinfection (WHO 2003). This can lead to bacterial outbreaks due to inadequate chlorination. Dosing high levels of chlorine to adjust for this leads to additional issues. These include increased operating cost, disinfection by-products and taste and odour issues.

- Oxidation of ammonia to nitrite

  Catalytic oxidation of ammonia to nitrite or by ammonia oxidising bacteria can lead to high levels of nitrite. Nitrite is known to cause methaemoglobinaemia (sometimes referred to as blue baby syndrome) in bottle fed infants at low levels. The DWSNZ 2005 (revised 2018) includes maximum acceptable values (MAV) for short term and long term nitrite exposure in drinking water of 3 and 0.2mg/L respectively to protect against this.

These issues provide significant treatment challenges for raw water high in ammonia.
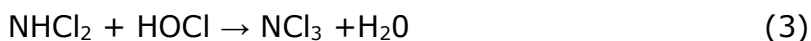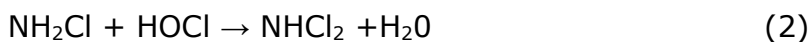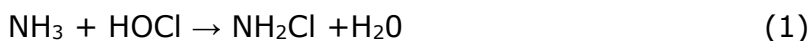
2 TREATMENT OPTIONS

As a result of the issues identified, removal of ammonia from raw water high in ammonia is desirable to achieve quality potable drinking water and avoid issues with disinfection. However, ammonia is found to be difficult to remove due to its high solubility and limited reactiveness. Several common treatment options have been identified and used globally for the treatment of water high in ammonia. These are described below including relative advantages and disadvantages of each.

The treatment processes can be categorized as either alternative disinfection methods or ammonia removal processes. Alternative disinfection methods include breakpoint chlorination, chloramine disinfection and chlorine dioxide disinfection. These processes seek to provide effective disinfection residual and limit harmful disinfection by-products while avoiding challenges faced by ammonia. Ammonia removal processes seek to remove ammonia from raw water prior to traditional disinfection. These include biological ammonia removal, ion exchange and reverse osmosis.

2.1 BREAKPOINT CHLORINIATION

Breakpoint chlorination also known as shock chlorination involves the dosing of chlorine to water beyond its breakpoint to achieve a free chlorine residual. Breakpoint chlorination can be achieved by dosing in sufficient quantities any chlorine-based disinfectants, such as chlorine gas and sodium hypochlorite.

Chlorine reacts with ammonia in successive reactions forming monochloramine, dichloramine and trichloramine respectively via the following reactions:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \qquad\qquad (1)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \qquad\qquad (2)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \qquad\qquad (3)$$

At any point in time the total chlorine residual is made of free chlorine ($HOCl$, OCl^-) and combined chlorine (NH_2Cl, $NHCl_2$, NCl_3). Both dichloramine and trichloramines are known to cause unpleasant tastes and odours in drinking water (Krasner & Barrett 1984). As a result, breakpoint chlorination can lead to significant taste and odour issues.

At higher Cl-NH3 ratios these reactions compete with other complex oxidative reactions forming products such as nitrogen gas and nitrate in addition to trichloramine (Valentine & Jafvert 1992, Pressley 1972, Crittenden et al, 2013).

The schematic below shows how the total chlorine residual changes with chlorine dose (see figure 1). Initially the total chlorine residual increases as the chlorine dose is increased. Most of the chlorine residual is comprised of combined chlorine (primarily monochloramine) at this point (Crittenden et al, 2013).

In zone B the total chlorine residual decreases as the chlorine oxidizes chloramine compounds. At the breakpoint the oxidization of the all chloramine compounds is complete and further additional chlorine added is seen as free chlorine residual. The actual location of the breakpoint residual and maximum residual are influenced by pH

temperature and other constituents of the raw water including organic matter, organic nitrogen and reduced substances (Crittenden et al, 2013).

Figure 1:   Typical breakpoint chlorination curve
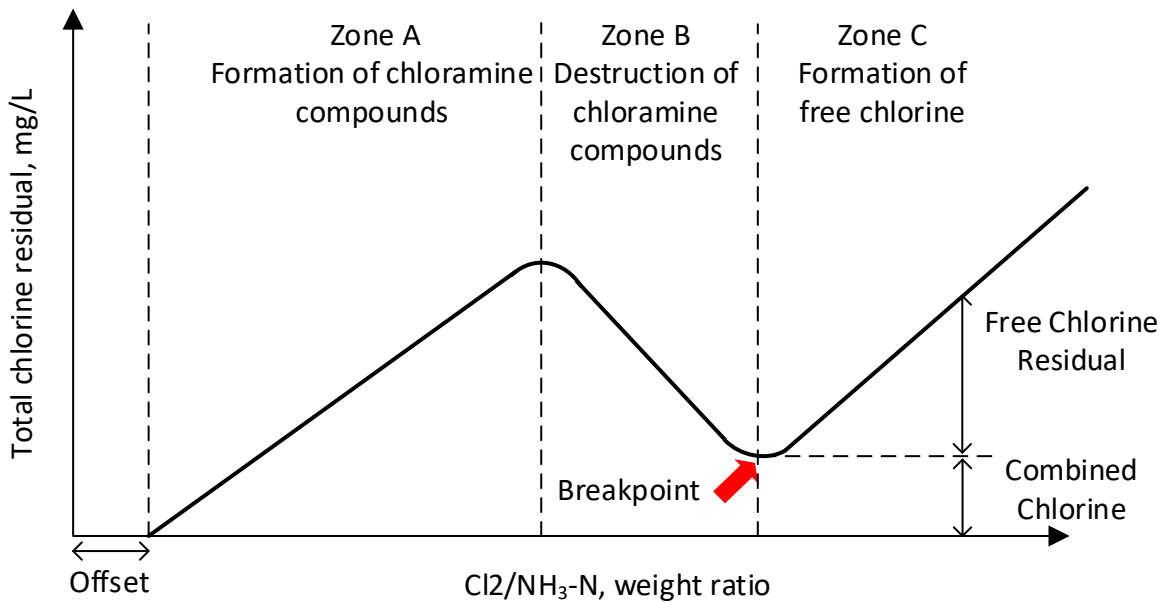
Breakpoint chlorination is considered a cost-effective strategy for raw waters with low ammonia levels. However, for raw water with high ammonia content achieving breakpoint chlorination often involves impractically high dose rates of chlorination. Typically, a dose around 8mg/L of chlorine is required for every 1mg/L of ammonia (The Water Security Agency 2019).

Additionally, design of breakpoint chlorination systems for the purpose of ammonia removal must consider the time required for the oxidation reactions to occur (Crittenden et al, 2013). When instantaneous free chlorine residuals are required chlorine doses may be 20 times or more the ammonia content to accommodate for these reaction times (Suez 2019a).

Breakpoint chlorination requiring high level dosing of chlorine can lead to high treatment cost and operator requirements. Elevated levels of dichloramine and trichloramine caused by oxidation of ammonia often lead to taste and odour issues. Additionally, high chlorine doses can lead to the formation of disinfection by-products potentially compromising treated water quality. These include the following compounds; trihalomethanes (THMs), haloacetic acids (HAAs), bromates, chlorates and nitrites (The Water Security Agency 2019, Hua & Reckhow, 2007). The formation of disinfection by-products and taste and odour causing compounds due to high levels of chlorination required is the main factor that precludes the use of breakpoint chlorination of water high in ammonia.

2.2   CHLORAMINE DISINFECTION

Chloramine disinfection or chloramination is the process of adding chloramine to drinking water to disinfect it. Specifically, monochloramine is added to raw water to provide disinfection.

Chloramine has been used as a drinking water disinfectant in the US since the 1930's. The US EPA estimates that more than 1 in 5 Americans consume drinking water treated with chloramines (USEPA 2019a). Many water suppliers in the US have employed chloramine disinfection to limit disinfection by-product formation and meet regulatory requirements (Shull 1981, USEPA 2019a). Chloramines form only trace amounts of THMs and trihalogenated HAAs (THAAs) and significantly lower levels of dihalogenated HAAs (DHAA) and unknown total organic halogen (UTOX) (Diehl et al. 2000). UTOX are organic halogen compounds that cannot be attributed to a known specific disinfection by-product however may contain compounds of health concern.

It is found that chloramines are less effective than chlorine as bactericides and viricides. Chloramines require significantly longer than chlorine at low doses to provide effective inactivation of protozoa and viruses (Kawamura 2000, National Research Council 1980).

For these reasons, chloramine is most commonly used as a method of secondary disinfection. The primary disinfectant first kills or inactivates bacteria, viruses, and other potentially harmful organisms in drinking water. The secondary disinfectant provides longer lasting treatment and barrier to recontamination in the water network. Using chloramination as a secondary disinfectant is used as an alternative to maintaining a free available chlorine residual in the network.

Chloramination is preferable in this regard as it is slower to decay and easier to maintain a residual in the network. Additionally, it limits the formation of disinfection by-products through ongoing reactions in the network (Kawamura 2000, Crittenden et al. 2013).

In the 1970's the USEPA proposed restricting the use of chloramine as a primary disinfectant. This restriction was not applied, and discretion was instead given to the state or primary authority. Currently several supplies in the US including Denver and Philadelphia use chloramination effectively as a form of primary disinfection (Shull 1981, Crittenden et al. 2013, Kawamura 2000). Many more supplies use chloramination as a secondary disinfectant across the US, Canada, Great Britain, Finland, Spain and Sweden (Lenntech 2019a). Chloramination can also be used in combination with other disinfectants to reduce THM's and maintain a longer lasting residual.

The current New Zealand drinking water standards do not allow for compliance with bacteriological requirements through chloramination and combined chlorine residual. This includes compliance criteria for both water leaving the treatment plant and water in the distribution network (DWSNZ 2005 (revised 2018)). It is recommended that future revisions of the drinking water standards consider allowance for chloramination as a secondary disinfectant based on current scientific knowledge and international application. This would provide drinking water suppliers additional options to limit / control disinfection by-product formation.

2.3   CHLORINE DIOXIDE DISINFECTION

Chlorine dioxide is a good alternative to chlorine gas for disinfection of drinking water. Chlorine dioxide is a very selective oxidizer and has a theoretical oxidizing capacity of over 2.5 times that of chlorine. Chlorine dioxide has an oxidation state of +4 and is highly electrophilic, accepting up to five electrons. It reacts by accepting electrons and forming chlorites (ClO_2^-) and chloride. Unlike chlorine it does not react through addition subtraction reactions producing limited halogenated organic by-products (Lenntech 2019b, National Research Council 1980, Aieta and Berg 1986). Chlorine dioxide is able to

penetrate cell walls and disrupt protein synthesis (National Research Council 1980, Aieta and Berg 1986).

Chlorine dioxide does not react with ammonia nitrogen (NH^3) or bromide and has limited reactivity with elementary amines. Chlorine dioxide will react most readily with tertiary amines and least readily with primary amines (Lenntech 2019b, National Research Council 1980). Like chloramines, chlorine dioxide forms only trace amounts of THMs and THAAs and significantly lower levels of DHAAs and UTOX compared to chlorine (Diehl et al. 2000).

The main by-products of concern with chlorine dioxide dosing are chlorites and chlorates. These are found to be carcinogenic and also cause oxidative stress and damage to red blood cells. The World Health Organization has provided a provisional guideline value of 0.7 mg/L for both chlorites and chlorates (WHO 2016). The USEPA has set maximum contaminant level of 0.8 mg/L and 1 mg/L respectively for chlorites and chlorates (USEPA 2019b). The current New Zealand Drinking Water Standards have provisional maximum acceptable values (PMAV's) of 0.8mg/L for both chlorites and chlorates (DWSNZ 2005 (revised 2018)). As a result, consideration must be given to chlorite and chlorate formation during generation of chlorine dioxide and in the distribution network due to breakdown of chlorine dioxide.

Chlorine dioxide is found to be at least as effective or more effective as a bactericide compared with chlorine gas (National Research Council 1980, Kawamura 2000, Aieta and Berg 1986). It is also found to be more effective than chlorine at inactivating many viruses such as cryptosporidium (Chauret et al., 2001, Junli et al., 1997, National Research Council 1980). At higher pH, chlorine dioxide is found to be significantly more effective than chlorine (National Research Council 1980).

Chlorine dioxide gas is very unstable and is explosive when stored under pressure. As a result, chlorine dioxide gas is most commonly generated onsite at low concentrations using sodium chlorite as a precursor. Sodium chlorate can also be used but is generally only used for industrial applications where large volumes of high concentrate chlorine dioxide are required, such as in the pulp and paper industry. Several different package systems exist for generating chlorine dioxide from sodium chlorite. These include aqueous chlorine – sodium chlorite systems, gaseous chlorine – sodium chlorite systems and electrochemical chlorine dioxide generators.
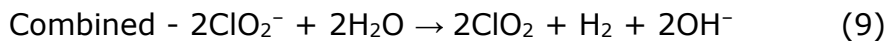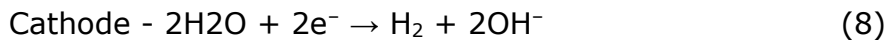
Aqueous chlorine – sodium chlorite systems produce chlorine dioxide through the reaction of an aqueous chlorine solution such as sodium hypochlorite or hydrochloric acid (see equations 4 and 5 below). Chlorine dioxide solutions of 6-10g/L are typically produced and these are diluted and stored at about 0.5-1g/L and dosed to raw water as required.

$$2NaClO_2 + HOCl \rightarrow 2ClO_2 + 2Na^+ + Cl^- + OH^- \qquad (4)$$

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5Na + 5Cl^- + H_2O \qquad (5)$$

Gaseous chlorine – sodium chlorite systems react sodium chlorite with chlorine gas under vacuum to produce chlorine dioxide (see reaction 6 below). This produces high yields of chlorine dioxide solution.

$$2NaClO_2 + Cl_{2\,(g)} \rightarrow 2ClO_2 + 2NaCl \qquad (6)$$

Electrochemical chlorine dioxide generators produce high conversions of chlorine-free chlorine dioxide from sodium chlorite and water through electrolysis. The reactions occurring are described below:

Anode - $ClO_2^- \rightarrow ClO_2 + e^-$ (7)

Cathode - $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (8)

Combined - $2ClO_2^- + 2H_2O \rightarrow 2ClO_2 + H_2 + 2OH^-$ (9)

Chlorine dioxide is widely used in many European countries including Italy, Germany, France and Switzerland (Lenntech 2019a, Crittenden et al. 2013). It is primarily used to maintain a disinfection residual in the distribution network. In the US it is mostly used for taste and odour control with some usage for algal control, iron and manganese removal and disinfection (Aieta and Berg 1986). Chlorine dioxide use in New Zealand is primarily limited to the dairy and food and beverage industry. However the New Zealand drinking water standards do allow for compliance with the bacteriological requirements through the use of chlorine dioxide. In addition, up to 3 log credits of protozoal removal are available (DWSNZ 2005 (revised 2018)). However, due to high C.t values required (536 min.mg/L at 15°C for 3 log credits) this is usually impractical to achieve.

2.4   ION EXCHANGE AND REVERSE OSMOSIS

Ammonia can also be removed from raw water through physical separation process that exclude ammonium ions such as ion exchange and reverse osmosis. These methods are typically quite costly and rarely used in water treatment for ammonia removal alone. These processes also produce significant waste streams which is also a consideration. Ion exchange and reverse osmosis processes are well known in the industry and as such will not be discussed in detail in this paper.

2.5   BIOLOGICAL AMMONIA REMOVAL

Biological ammonia removal involves utilising natural occurring bacteria to oxidize ammonia to nitrite and then nitrate. This typically involves filtration processes seeded with Ammonia Oxidizing Bacteria (AOB) and Nitrite Oxidizing Bacteria (NOB).

Ammonia is converted to nitrite by ammonia oxidising bacteria (AOB), primarily Nitrosomonas (Tako 2010, Lytle et al. 2007, Lytle et al. 2014). These bacteria convert the hydrogen from the ammonia to water and the nitrogen to nitrite as per the equation 10 below.

$2NH_3 + 3O_2 + (AOB) \rightarrow 2NO_2^- + H_2O + 2H^+$ (10)
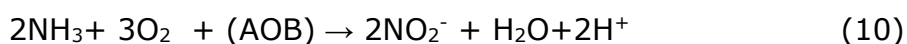
The nitrite is then converted to nitrate by nitrite oxidising bacteria (NOB), primarily Nitrobacter, according to equation 11 below (Tako 2010, Lytle et al. 2007, Lytle et al. 2014).

$2NO_2^- + O_2 + (NOB) \rightarrow 2NO_3^-$ (11)
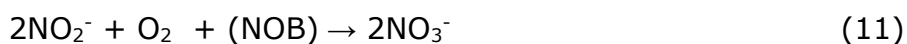
As shown by the equations a supply of oxygen is required for the reaction to take place. In addition to oxygen, alkalinity and phosphate are required to sustain the bacterial growth. In order to oxidise 1g of ammoniacal-nitrogen, 4.6g of oxygen, 7.14g of alkalinity and ~0.01-0.02g of phosphate are theoretically required (Lytle et al. 2007, Heard et al. 2002, Tako 2010). The bacteria also requires an optimal pH of between 7

and 9. Temperature is also a key factor with temperatures between 14 and 27°C required for the process to proceed uninhibited (Tako 2010).

There are several other factors that can affect the bacteria and/or reaction. Iron and manganese can affect the process as they can be oxidised and will consume the oxygen in the water. High organic content can cause growth of rival bacteria, preventing the AOB and NOB from flourishing. High flows or turbulence will prevent the bacteria from being able to bond effectively onto a surface. Additionally, any biological inhibitors/sterilizers (chlorine, iodine etc.) will prevent bacterial growth (Tako 2010).

2.5.1 BIOLOGICAL FILTERS

In order to utilise the AOB and NOB a solid medium is required for the bacteria to live upon. Several solutions exist to achieve this. The simplest is a sand/multimedia filter, which are commonly used in water treatment (Lytle et al. 2007). The filter media provides the surface required for the bacteria to live on and sufficient contact time for the ammonia oxidation to occur. Alternatively, coarser media (such as gravel) can also be used, however these do not provide significant filtration. Other specifically designed media that trap and support bacteria growth also exists.

Sand/multimedia filters are simple and well understood in the water treatment industry. The difference between a normal sand filter and a biological filter is minimal in terms of normal operation (Stembal et al. 2005). The main difference is the requirement for an aeration column upstream of the filter to oxygenate the water. The simplicity of the system allows for ease of operation and low capital and operating costs.

The media depth should be between 1.2m and 2m deep to achieve sufficient contact time for the ammonia reaction (Stembal et al. 2005). A backwash system needs to be employed to remove the solids that build up on the filter. This can be combined with an air scour system to provide a more robust backwash process. Actual filter rates need to be determined by pilot testing, however lower rates will provide greater contact time and reduce the depth required for the ammonia to be fully oxidised.

The aeration and biological components can be combined by using a coarser media (Heard et al. 2002). As the coarser media will decrease the retention time, this will increase the size of the aeration tank required to ensure the water is sufficiently aerated. A filter is required directly after the aerator in order to remove any colloidal material produced in the aerator. Specifically selected pre-seeded media can also be used to reduce the time to establish bacterial growth (Tekerlekopoulou & Vayenas 2008).

2.5.2 EXAMPLES OF BIOLOGICAL FILTER INSTALLATIONS

Pilot and full scale plants have been successfully trialled in the US, Europe and Asia. The bacteria and conditions required for the filters can be achieved regardless of location and the results produced from all the locations show the technology is very promising.

In Hong Kong a trial of biological filters was carried out to determine if the system was viable to replace breakpoint chlorination (Heard et al. 2002). The pilot plant consisted of three filter columns; the first was an aerated coarse media filter (2m media depth) for ammonia removal, the second was an aerated sand filter (1m media depth) for ammonia removal and the third column was catalytic media for manganese removal (1m media depth). Filter rates varied between 5 and 10m/h, with higher rates used once the bacteria was fully established. During periods of stable operation columns one and two removed >80% of ammonia from the raw water. Sodium carbonate was dosed at this plant to achieve the level of alkalinity required for the biological removal to occur.

In Greene County Ohio, an existing treatment plant that used aeration and multimedia filters for iron removal was analysed to see if it was also providing ammonia removal (Lytle et al. 2007). At the same plant a six-column multimedia filter (1m media depth) pilot plant was also tested. The pilot plant was three sets of two columns in series operating at a filter rate of 5m/h. The full scale plant treated up to 4.5 MLD through three 13.7m^2 filters (filter rate of 5m/h). The full scale plant showed ammonia removal of >90% (1.1mg/l in the raw water to 0.1mg/l in the filtrate). The pilot plant showed similar results to the main plant, once the bacteria had grown sufficiently (after ~70 days). Additionally, it was noted that the presence of iron in the water had no measurable effect on the ammonia removal.

In Guernes-Dennemont France, a pilot plant was initially installed and tested before being scaled up to full scale (Rogalla et al. 1990). The process used was different than others in that ethanol rather than oxygen was used to feed the bacteria. This reduces start up time but significantly increases costs. The plant consisted of an anoxic (non-aerated) column with coarse media (2m depth) before an aerated multimedia filter. Both filters were operated at a filter rate of 5m/h. The anoxic column removes nitrates and nitrites, before the aerated filter removes the ammonia. Optimization of the process gave ammonia removal rates of over 90%. When scaled up the process achieved similar results, effectively reducing nitrates, nitrites and ammonia in the water to safe levels.

In Palo Iowa USA, a pilot scale plant was tested over a year before a full scale plant was installed (Lytle et al. 2014). The pilot plant consisted of a gravel filled aeration column (76cm depth) followed by a multimedia filter column (76cm depth). The pilot plant was operated at a filter rate of 5m/h. It took 150 days for the filters to be fully working, after which they were achieving close to 95% removal of ammonia (3mg/l down to 0.2 mg/l). The full scale plant achieved similar results. This plant also had iron present in the water and it was successfully removed without affecting the ammonia removal.

In Northern Croatia four different pilot plants were trialled to assess the best process for ammonia removal (Stembal et al. 2005). At the first plant, the existing plant aerator was used as the supply source with just a multimedia filter installed for the pilot. The second plant was aerated by percolating through an open column aerator but was otherwise the same as the first plant. The third plant used a closed aerator incorporating compressed air in place of the aeration column. The fourth plant was the same as the third but operated under a higher feed water pressure. The first plant successfully removed iron, manganese and ammonia over its 1.9m depth at a filter rate of 22m/h (high by usual standards). The second plant had low levels of ammonia but high levels of iron and manganese. The maximum reduction of all three components occurred just 0.8m through the filter at a filter rate of 12m/h. The third and fourth plant had high levels of manganese only and the performance was similar to the second plant (near full reduction at 0.8m and 11m/h).

2.5.3 ALTERNATIVE PROCESSES

The main alternative to the aeration column and a multimedia filter is a trickling filter. Trickling filters employ a coarse media with a downward water flow and an upward forced or natural air flow. The primary advantage of these filters is that the bacterial reactions occur in the same vessel as the aeration. The coarse media means that the aeration vessel size is increased to ensure sufficient aeration is achieved. Additionally, some additional filtration is required after the trickling filter to capture any waste organic material and any oxidised metals (such as iron or manganese). The trickling and multimedia filter processes are very similar, as both processes require the same key elements to achieve removal of ammonia. Trickling filters have been successfully trialled a number of times. Ammonia removals of over 90% were achieved using an artificial feed source, with tests to determine the effect of iron and manganese on the filter

performance (Gouzinis et al. 1998). In southern China a filter was setup to determine the removal of ammonia and manganese (Han et al. 2013). The trickling filter had a depth of 1.8m and the ammonia removal varied from 70% to 95% with a manganese removal of 80% to 98%.

Some proprietary processes that utilise optimised versions of the technology exist. Suez produce Nitrazur™ for ammonia and nitrate removal. The product is a specially designed media that allows for high filter flow rates and improved removal rates (Suez 2019b).

2.5.4 APPLICATION IN NEW ZEALAND

Overseas application of biological filters for ammonia removal show promise for adoption in New Zealand. However, our climate may restrict its use in cooler areas. It would be interesting to investigate the potential biological removal that may already be occurring in existing filters in New Zealand such as filters used for iron and manganese removal.

In order to reduce and quantify risks the first step to investigating such a technology for water treatment would be pilot testing. A small pilot scale plant could be developed with filtration and aeration columns to assess the biological removal performance. The other advantage of this approach is that developing the required bacteria growth may take time. If successful, trial media from the pilot could be used to help seed bacterial growth in the full scale plant. This could be critical as seeding from an existing biological filter (such as employed internationally) would likely not be possible for the first few applications in New Zealand (Tekerlekopoulou & Vayenas 2008).

The main concern with biological filters would be the growth of unwanted bacteria that may compromise drinking water quality. Careful control over the filter process and breakthrough of bacteria from the filter would be required. There would be significant expertise in New Zealand from the use of biological filters/ammonia removal in wastewater applications. However different challenges would be faced and additional care would be required to protect public health.

2.6   TREATMENT OPTIONS SUMMARY

The table below summaries the advantages and disadvantages of the treatment process outlined above for treating water high in ammonia. Selection of an appropriate treatment process should consider these in addition to other treatment requirements of the raw water.

Table 1:   Summary of Treatment Options for Treating Water High in Ammonia

Process	Advantages	Disadvantages
Breakpoint Chlorination	- Common water treatment process - Simple well understood process.	- High chlorine dose rates - High ongoing operating cost - Risk of high levels of disinfection by-products - Potential taste and odour issues

Chloramine Disinfection	• Effective for reducing disinfection by-products. • Provides disinfection through combined chlorine residual	• Does not provide compliance with the DWSNZ • Less effective as bactericide and viricide.
Chlorine Dioxide Disinfection	• No THMs. • No reaction with ammonia.	• Risk of high chlorites.
Ion Exchange/ Reverse Osmosis	• Effective removal of ammonia • Proven technology	• High capital cost • Increased waste streams
Biological Ammonia Removal	• Piloted and trialled internationally with effective removal of ammonia	• Unproven technology in New Zealand. • Restricted in cooler climate areas • Risk of unwanted biological growth in filters.

3   CASE STUDY: PATEA AND WAVERLEY WTPS

3.1   BACKGROUND

The Patea and Waverley water treatment plant's supply two small town communities located south-east of Hawera in South Taranaki. Both plants are fed from groundwater by a series of deep bore wells (~150-200m deep).

Raw water from the Patea bores is found to be high in ammonia and iron (see table 2). Raw water from the Waverley bores is found to be high in manganese and iron and have elevated levels of ammonia (although less than drinking water standard guideline values, see table 3). High levels of ammonia are found in groundwater throughout the Taranaki region due to natural occurring hydrological processes (Taranaki District Council 2015). Both plants have typically low turbidity (<1NTU), however turbidity exceeding 1NTU have been measured in the Patea water supply in four samples.

Historically both supplies had been achieving compliance with the drinking water standards through secure bore status. However concerns of bore water security caused by the Havelock North contamination event and sampling showing high plate count and E.coli readings lead to council's decision to provide further treatment.

At Patea, chlorine dosing was investigated, however the chlorine reacted with the ammonia present in the water source and caused taste and odour issues in the supply. This led to many complaints from the community about the water quality. The chlorine demand of the supply was extremely high in order to achieve the breakpoint chlorination and maintain a free chlorine residual. Concerns were raised over the amount of disinfection by-products introduced in this dosing. Sampling indicated that THM and HAA where elevated in the treated water at around 50% of the MAV.

Table 2:   Summary of Patea WTP Bore Water Quality

Constituent	Unit	Min	Mean	Max	GV/MAV [1]
pH [4]	pH	6.66	8.13	8.89	7.0-8.5 GV
Turbidity [4]	NTU	0.04	0.11	8[5]	<1NTU [6] 2.5 NTU GV
Total Ammoniacal-N [2]	mg/L	0.96	2.8	2.06	1.5mg/L GV
Total Iron [2]	mg/L	<0.013	0.148	0.62	0.2mg/L GV
Dissolved Iron [3]	mg/L	<0.02	0.09	0.15	
Total Manganese [2]	mg/L	<0.013	0.009	0.0066	0.4mg/L MAV, 0.04mg/L GV
Dissolved Manganese [3]	mg/L	0.002	0.0036	0.0059	
Dissolved Organic Carbon [3]	mg/L	<0.5	2.42	4.9	0.2mg/L GV

1. Guideline Values (GV) and/or Maximum Acceptable Values (MAV) specified in the DWSNZ 2005 (revised 2018)
2. Based on 11 raw water samples
3. Based on 5 raw water samples
4. Based on over 660 bore water and treatment plant samples collected between Aug 2014 and Aug 2017.
5. 99th percentile of turbidity reading was 0.47NTU
6. Turbidity less than 1 NTU required for at least 95% of the compliance monitoring period for disinfection with chlorine or chlorine dioxide

Table 3:   Summary of Waverley WTP Bore Water Quality

Constituent	Unit	Min	Mean	Max	GV/MAV [1]
pH [4]	pH	7.48	7.96	8.35	7.0-8.5 GV
Turbidity [4]	NTU	0.04	0.09	0.98 [5]	<1NTU[6] 2.5 NTU GV
Total Ammoniacal-N [2]	mg/L	0.18	0.52	0.84	1.5mg/L GV
Total Iron [2]	mg/L	<0.021	0.192	0.537	0.2mg/L GV
Dissolved Iron [3]	mg/L	<0.02	0.09	0.15	
Total Manganese [2]	mg/L	0.002	0.086	0.25	0.4mg/L MAV, 0.04mg/L GV
Dissolved Manganese [3]	mg/L	0.002	0.0036	0.0059	
Dissolved Organic Carbon [3]	mg/L	<0.5	1.1	1.6	0.2mg/L GV

1. Guideline Values (GV) and/or Maximum Acceptable Values (MAV) specified in the DWSNZ 2005 (revised 2018)
2. Based on 13 raw water samples
3. Based on 4 raw water samples
4. Based on over 490 bore water and treatment plant samples collected between Aug 2014 and Aug 2017.
5. 99th percentile of turbidity reading was 0.52 NTU
6. Turbidity less than 1 NTU required for at least 95% of the compliance monitoring period for disinfection with chlorine or chlorine dioxide

3.2   PROCESS SELECTION

Several options where considered for treatment at both sites including breakpoint chlorination, chlorine dioxide disinfection, biological filters, greensand filtration, ion exchange and reverse osmosis. Chloramine disinfection was not considered due to its inability to meet the existing requirements of the drinking water standards.

For Patea the main upgrade aim was to provide effective disinfection and avoid existing taste, odour and disinfection by-product issues. Traditional breakpoint chlorination was found to be uneconomical and was leading to many customer complaints.

A pilot biological ammonia removal plant was proposed to trial biological ammonia removal of the bore water. However, due to cost, the unproven nature of the technology and the need for an immediate upgrade solution, this pilot was never conducted.

Chlorine dioxide disinfection was selected for the Patea WTP. Chlorine dioxide was selected due to its ability to disinfect the bore water without reacting with the high ammonia content. It was assessed that this would limit disinfection by-products and taste and odour complaints.

At Waverley a different treatment process was selected due to the higher iron and manganese levels and lower ammonia levels. Chlorine dioxide was not preferred for this site due to its elevated iron and manganese levels. It was thought that the oxidant demand of these would result in the requirement for high doses of chlorine dioxide and would risk high levels of chlorite in the treated water. The preferred option for Waverley water treatment plant was greensand filtration followed by UV irradiation and chlorine disinfection. A free chlorine residual will be achieved through breakpoint chlorination as the levels of ammonia are much less than those found at Patea.

3.3   INSTALLATION

A chlorine dioxide disinfection plant was specified and installed at the Patea WTP in December 2018. The chlorine dioxide plant is the first known application of chlorine dioxide disinfection in New Zealand for municipal drinking water application.

The plant was installed by Visentia and can produce up to 189g/hr of chlorine dioxide. The chlorine dioxide generator produces chlorine dioxide in a 2000ppm solution from a single sodium chlorite precursor chemical through electrolysis (see photograph 1).

Photograph 1:   Patea Chlorine Dioxide Generator

Chlorine dioxide has been dosed into the raw water prior to the existing plant reservoir at approximately 1.5mg/L. This plant is now successfully commissioned and is producing chlorine dioxide residual in the treated water with no THM and taste and odour issues encountered by the previous plant. The process is undergoing fine tuning to maximise the process outcomes while minimising the required chlorine dioxide dose rates.

The Waverley WTP is currently in detailed design. The contract was awarded to Filtec and construction is expected to begin shortly with completion in early 2020.

4   CONCLUSIONS

Raw water with high levels of ammonia remain a significant challenge to provide effective water treatment. While ammonia does not pose a direct health risk, it provides significant challenges to effective disinfection as well as aesthetic taste and odour issues.

Several options are available for treatment of water high in ammonia. These should be carefully considered alongside other raw water properties and constituents when selecting a treatment processes.

A promising new technology is biological ammonia removal. This process uses biologically active filters seeded with ammonia oxidizing and nitrate oxidizing bacteria to oxidise and remove ammonia from raw water. The process has been demonstrated internationally both in pilot scale and full-scale applications. It would be interesting to see a trial of this technology in New Zealand or investigation into filters potentially already operating in this manner.

This paper provides examples of two plants in the South Taranaki district challenged by high levels of naturally occurring ammonia in its groundwater sources. These plants are currently in the process of being upgraded. The process selection of these two plants varied due to differences in raw water quality. Patea WTP challenged by the highest levels of ammonia has recently had a chlorine dioxide plant installed. The existing chlorination at Patea was found to be uneconomical due to the high doses required and was also leading to customer taste and odour complaints. Chlorine dioxide has the advantage that it does not react with ammonia and produces very little taste and odour issues and disinfection by-products. The plant has been successful at providing disinfection of the water and reducing complaints. However, fine tuning of the plant and process is required to ensure chlorine dioxide dose rates are minimised.

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