NITRATE MONITORING AND MANAGEMENT STRATEGIES FOR THE VILLAGE OF PORT WILLIAMS

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1. PROJECT OBJECTIVES

Port Williams is located in the Annapolis Valley, an area of intense agricultural activity in Nova Scotia. Drinking water supply for the community is supplied by water from 5 groundwater wells, located within the village, and is treated by chlorination. Elevated nitrate levels in Well #2 have prompted concerns from plant operators that this water source may exceed the Maximum Acceptable Concentration (MAC) of 10 mg/L for nitrate. The current strategy for nitrate management in the water supply for Port Williams is to blend groundwater from the high-nitrate well (Well 2) with groundwater from the lowest-nitrate well (Well 6) by drawing water from the two sources simultaneously. The objectives of this research study are to (1) assess current nitrate concentrations and management strategy as well as distribution system quality in Port Williams over a period of 16 months, and (2) evaluate alternative nitrate management options to remove nitrate from contaminated well water.

2. BACKGROUND

2.1. Nitrate migration into groundwater

Agricultural activities tend to have a significant impact on the levels of nitrate in groundwater, due to application of nitrogen-containing fertilizers, such as urea, ammonia, ammonium nitrate and manure (Böhlke, 2002). Migration of nitrate into groundwater is a multi-step process which typically involves (1) conversion of fertilizer ammonia to nitrate by bacterial oxidation (i.e., nitrification) (Glaser et al, 2010), (2) transport of nitrate into the subsurface by infiltration of surface water (i.e., percolation) (Seiler and Gat, 2007), and (3) transport of nitrate from the unsaturated zone into the groundwater (i.e., infiltration) (Seiler and Gat, 2007).

The total nitrate load available for transport into the groundwater from the surface is impacted by agricultural practices, such as the extent of fertilizer application, as well as activities such as tillage, which increases the rate of nitrification due to increased oxygen exposure (Reddy, 2011). Nitrate leaching is typically highest from land used for vegetable production, ploughed pasture, and grain production, while cut grasslands and forest produce low levels of nitrate leaching (Di and Cameron, 2002). Nitrate concentrations in groundwater in Kings County, NS, were found to be higher near agricultural areas than near forested lands (Blair, 2001). A study performed in 2013 on the Thomas Brook watershed area of the Annapolis Valley found that the most significant factors for nitrate leaching into the groundwater were nitrate application rate and crop rotation system (Amon-Armah et al, 2013).

Rates of infiltration of surface water into the unsaturated zone, and percolation into groundwater depend on a range of hydrological and geological factors. The rate of infiltration of water into the subsurface is higher in soils with intermediate moisture content, through coarse grained soils, and in flat topographies (Seiler and Gat, 2007). The vast majority of the water in the subsurface unsaturated zone is recycled back to the surface through evaporation, however a small amount (~ 2%) contributes to groundwater recharge (Seiler and Gat, 2007). Percolation of water into the groundwater mostly occurs at a slow rate of 0.5 to 3 meters per year, although rapid transport on

the order of meters per day may occur after precipitation events through large pores and fissures in the rock or soil material (Seiler and Gat, 2007). Recharge of groundwater through the unsaturated zone mostly happens during the winter when evaporation rates are lower (Seiler and Gat, 2007).

A widely-used model (DRASTIC) developed by the United States Environmental Protection Agency (USEPA) uses seven parameters to evaluate the vulnerability of groundwater to pollution. Risk factors for groundwater vulnerability include (1) shallow water depth (< 30 feet), (2) high groundwater recharge rates (3) porous aquifer media (i.e., sand and gravel, basalt, karst), (4) poor or porous soil cover (i.e., gravel, sand, peat), (5) flat topography (i.e., < 6 % slope), (6) fast transport through unsaturated zone, and (7) high hydraulic conductivity in the aquifer (USEPA, 1987).

Impacts on groundwater concentration as a result of land use changes typically occur over long time horizons. In a 30-year investigation of the fate of land-applied nitrogen fertilizer, it was found that between 8-12% of the nitrogen (N) had leached into the water (groundwater or surface water), and 12-15% remained in the soil, and may continue to leach into the water over subsequent decades (Sebilo et al, 2013). A monthly sampling program over a 16-month period in 1999-2000 determined that nitrate levels in groundwater samples did not vary seasonally (Blair, 2001). Other studies have shown that agricultural activities do not have an immediate impact on groundwater quality. A field study in the Thomas Brook watershed found that *E coli* levels in shallow groundwater monitoring wells were not directly related to the timing of manure application, with higher *E coli* loadings found before manure application than after in some cases (VanderZaag et al, 2010).

2.2. Prior work

Extensive groundwater nitrate monitoring studies have been conducted in Kings County, Nova Scotia in 1989, from 1999 to 2000, and from 2002 to 2011 at over 100 well sites. From 1989 to 2011, between 19 and 34 of 130-142 wells (i.e., 15 to 25% of the study sample) exceeded the MAC (Maximum Acceptable Concentration) for nitrate of 10 mg/L (NSE, 2012). A trend of increasing nitrate concentrations was observed in 10 % of the wells studied, while 30 % of the wells had a trend of decreasing nitrate, and 60 % had no significant trend (NSE, 2012). The Centreville-Canning-Port Williams area had highest levels of groundwater nitrate in Kings County, and had the highest increase in nitrate concentrations in 1999-2000 compared to the 1989 study.

3. NITRATE MANAGEMENT

3.1 Reduce nitrate leaching from fields

One strategy to reduce nitrogen leaching from fields is for farmers to apply less N fertilizer, or to time fertilizer application to periods of high plant growth (Di and Cameron, 2002). It was found that farmers in the Thomas Brook watershed area tended to over-apply N fertilizer, particularly on high value crops (Amon-Armah et al, 2015). In general, farmers may over-apply N fertilizer

for a variety of reasons, including seasonal variation in fertilizer costs, cost to transport and apply fertilizer, and uncertainty about weather and soil conditions (Sheriff, 2005).

Nitrate leaching tends to be highly seasonal with higher nitrate leaching occurring in late autumn, winter and early spring, when there is no uptake of nitrogen from plants, and water largely drains from the fields, rather than evaporating (Di and Cameron, 2002). After a corn crop, up to 95% of N leaching loss can occur from November to May when there is no plant growth to uptake nutrients (Di and Cameron, 2002). Some strategies to reduce leaching of nitrate during these times include growing a cover crop after harvest to uptake some of the soil nitrogen, or delay ploughing until late autumn or spring to prevent extensive mineralization of nitrogen sources to nitrate prior to high leaching season (Di and Cameron, 2002).

3.2 Prevent nitrate migration to groundwater

Another approach to nitrate management is to prevent migration of leached nitrate into the groundwater by establishing buffer zones or installing denitrification walls. Buffer zones, or strips of natural vegetation surrounding surface water sources, have been shown to mitigate groundwater pollution by nitrate. Since fertilizer is not applied to buffer zone vegetation, these areas dilute nitrogen concentrations from runoff (Spruill, 2000). Additionally, these areas provide organic matter to the water table to facilitate biological denitrification processes (Spruill, 2000). Denitrification walls are built by excavating soil in a trench extending below the water table, and mixing the soil with a solid waste carbon source (typically sawdust, although other materials can be used) before replacing it (Long et al, 2011). The carbon source supports biological denitrification of nitrate, and can be effective for nitrate removal for decades before needing to be replenished (Long et al, 2011; Robertson et al, 2000).

3.3 Nitrate removal from water source

If land management strategies are not effective for nitrate reduction in the well water, options for removing nitrate from the well water can also be investigated. Nitrate removal technologies typically focus on either (1) degradation of nitrate into N_2, or (2) separation of nitrate into a concentrated waste stream. Degradation of nitrate is a reduction reaction which can be accomplished through biological or chemical means. Separation process are physical treatment processes, which may require secondary treatment of the concentrated waste stream before it can be discharged to a receiving body. A summary of available treatment processes for nitrate removal is provided below.

3.3.1. Biological treatment

Biological denitrification uses denitrifying bacteria to perform this reaction, as the bacteria will use nitrate as a source of oxygen in anaerobic conditions. Biological denitrification requires an external energy source, which can be supplied by organic carbon, in the form of simple alcohols or organic acids (Lorrain et al, 2004), synthetic polymers (Luo et al, 2014), or waste materials (Wang et al, 2013), or by inorganic energy sources, such as hydrogen (Haugen et al, 2002) or sulfur (Sierra-Alvarez et al, 2007).

3.3.2. Catalytic reduction

Chemical reduction of nitrate can be performed using catalysts, such as palladium and indium in the presence of hydrogen gas as an electron donor (Choe et al, 2015), or using photocatalytic materials such as titanium dioxide in the presence of light (Yang et al, 2013).

3.3.3. Ion exchange

Ion exchange processes pass nitrate-containing water through a bed of resin. The resin beads contain exchangeable anions, such as chloride and bicarbonate, which can be replaced with nitrate. The resin can then be regenerated in a strong brine solution, which produces a highly concentrated nitrate brine, which requires denitrification treatment before discharge or reuse (Kapoor and Viraraghavan, 1997).

3.3.4. High-pressure membrane filtration

High pressure membrane filtration membranes, such as nanofiltration (NF) and reverse osmosis (RO) can also separate nitrate from water. Nanofiltration operates by either a size-exclusion mechanism (for the removal of dissolved organics), or a result of charge interactions between the contaminant and the membrane surface (for the removal of ionic species). NF is typically used to remove multivalent ions, such as hardness species (i.e, Mg^{2+} and Ca^{2+}), rather than monovalent ions, such as nitrate (NO_3^-). However, some removal of nitrate can be achieved with NF, or NF can be used as a pre-treatment step for RO, in order to reduce the scaling effects of hardness cations (Van der Bruggen and Vandecasteele, 2003). RO forces water across a semipermeable membrane, with nitrate, salts and other contaminants left behind in a concentrated waste stream, and can achieve high removals of nitrate from the treated water (Darbi et al, 2003).

3.3.5. Electrodialysis

Electrodialysis separates nitrate into a concentrated stream by attracting the nitrate through a membrane towards a positively charged electrode under an applied voltage (Kapoor and Viraraghavan, 1997).

4. RESEARCH OBJECTIVES

4.1. Nitrate monitoring program

The primary focus of the sampling program was to determine the extent of nitrate contamination of groundwater, including the variation in nitrate levels seasonally, as well as year-to-year. The secondary focus of the sampling program will be to establish baseline conditions in the distribution system, including physical parameters, such as temperature and pH, as well as indicators for corrosion potential, such as chloride to sulfate mass ratio (CSMR) and iron and lead levels. This data will be used to inform decisions about which treatment options for nitrate removal should be further explored.

4.2. Treatment options

The objective of bench-scale experimentation was to evaluate biological denitrification and anion exchange as treatment options for nitrate removal from contaminated groundwater.

The objective of biological denitrification experiments was to evaluate an agricultural waste product, corn stalk, as a carbon feedstock for denitrification and compare it to a traditional soluble carbon feedstock, acetate, in batch and column configurations.

Anion exchange tests were conducted to evaluate the effectiveness of a commercial nitrate selective anion exchange resin for nitrate removal from Port Williams well water. Secondary experiments were also conducted to characterize spent brine from regenerating the resin and evaluate biological denitrification as an option for managing this waste stream.

5. MATERIALS and METHODS

5.1. Sampling Program

Figure 1 below displays the locations of the nine sampling sites within the Village of Port Williams. The five groundwater wells which comprise the water supple for the Village are indicated with yellow markers. The treatment plant inlet and outlet are marked with a blue circle, the distribution system point “Shop” is marked with a red circle, and the private well “Farm” is marked with a purple circle. Water samples were taken from all nine sampling sites on a bi-weekly basis between May 2016 and August 2017.

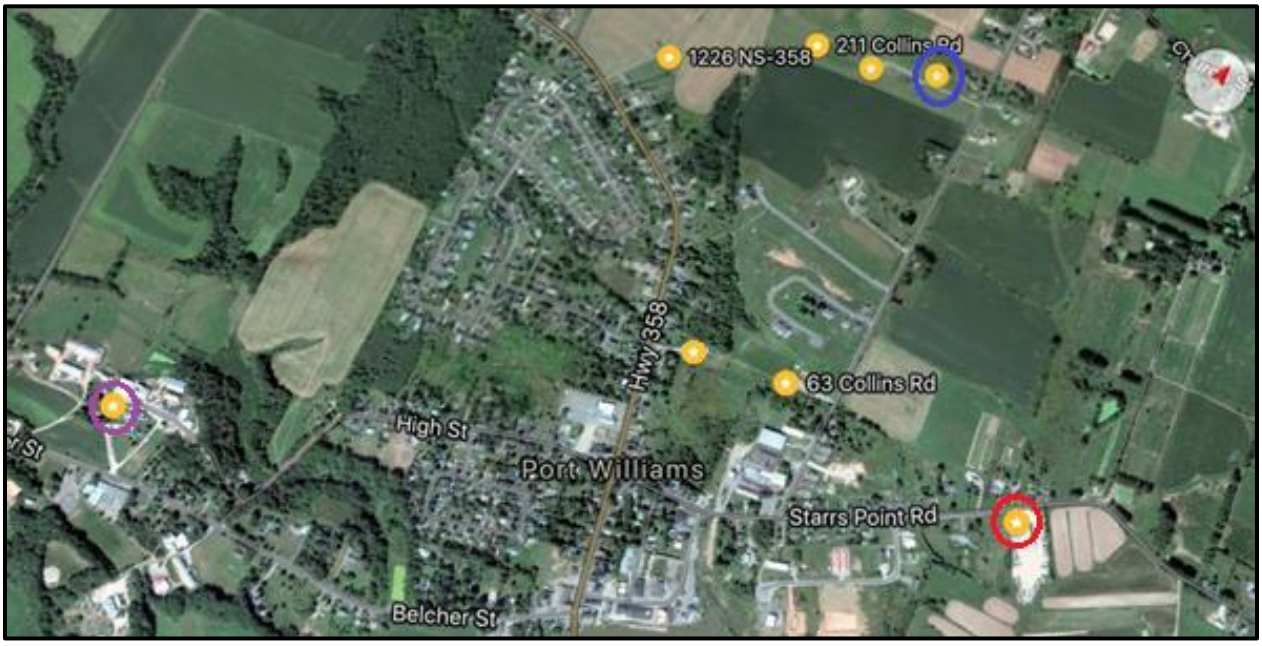

Figure 1. Sampling points for groundwater wells, treatment plant inlet and outlet, distribution system and private well

Water samples were taken from flushed pipes and taps. Groundwater wells were pumped for 1-2 minutes, and all well and distribution system taps were flushed for at least 30 seconds prior to sampling. Inlet and outlet sampling taps were continuously running, so no additional flushing was required before sampling.

Dissolved oxygen (DO), oxidation-reduction potential (ORP), temperature and pH were measured on-site with a Thermo-Scientific Orion STAR A326 probe. Microbiological testing was performed on water sampled directly into sterile 50-mL centrifuge tubes dosed with 0.1 mL sodium thiosulfate solution in order to quench any residual chlorine. Samples were stored at 2°C and 0.1-mL samples were plated on R2A agar within 24 hours, and counted one week later for heterotrophic plate count (HPC), following Standard Method 9215.

Anions (chloride, nitrite, nitrate, sulfate and phosphate) were measured within 24 hours of sampling, otherwise samples were frozen. Anion analysis was performed on a Metrohm Ion Chromatograph with carbonate eluent running at 0.2 mL/min. The anion exchange column was maintained at 45°C throughout analysis**.** Samples for iron and lead were acidified to a pH < 2 with concentrated nitric acid, and analyzed using IC-PMS.

Ferric iron, ammonium, and free and total chlorine were measured by colourimetric methods using a Hach UV-VIS spectrometer. Free and total chlorine were measured on treatment plant inlet and outlet samples, as well as distribution system and private well samples. Water for chlorine testing was sampled into chlorine demand-free glassware, which had been soaked in a 2 mg/L chlorine solution for 24 hours, triple-rinsed with Milli-Q water and dried for 24 hours prior to sampling. Free and total chlorine were analyzed within 3 hours of sampling.

5.2. **Biological Denitrification**

Corn stalk was gathered in late November 2016 from a harvested and cut field near Canning, NS. Corn stalk samples were selected from remaining stalk sections standing two to three feet high with roots still connected to the ground. Sections of stalk between six and eighteen inches in length were cut near the roots using a sharp blade. Samples were refrigerated at 2°C while awaiting drying. Corn stalks were dried in an oven at 105°C for at least 48 hours. Stalk samples for batch tests were prepared by removing the woody outer layer, and cutting the spongy stalk interior into 0.5-1 cm length pieces. Figure 2 below shows the corn field during sampling, the whole cross-sectional profile of corn stalk and separated interior corn stalk material. For column tests, whole dried corn stalks, trimmed to the column length and an approximate mass of 12 grams were inserted into the glass column casings.

Figure 2. Counterclockwise from top left: harvesting corn stalk, cross section of corn stalk, spongy corn stalk interiors

Batch biological denitrification tests were performed in sealed 250-mL glass flasks. Flasks were stoppered and sealed with parafilm to prevent gas exchange and allow anoxic conditions to develop during tests. Test flasks were covered with opaque tape and capped with aluminum foil to maintain dark conditions within the flasks and prevent the growth of photosynthetic algae.

Batch tests were performed on synthetic groundwater consisting of distilled water buffered with 45 mg/L $NaHPO_4$, 45 g/L KH_2PO_4, 120 mg/L NaCl, and spiked with 0.1445 g/L KNO_3 to provide NO_3-N levels of 20 mg/L. Carbon sources were provided by adding appropriate volumes of a 11.7 g/L sodium acetate solution, or 12.3 g/L cellulose suspension, or by directly adding weighed masses of dried corn stalk interior.

Each test flask was dosed with 5 mg/L of bacterial culture added from stock bacterial solutions acclimated to either acetate or cellulose feedstock for at least three months. Initial culture samples were acquired from activated sludge from a municipal wastewater treatment plant, and were mixed on a shaker table at 100 RPM with synthetic groundwater containing 20 mg/L of NO_3-N and 290 mg/L of sodium acetate or 310 mg/L of cellulose to maintain C:N ratios of 3 and 10, respectively. Culture media was replenished every 2 weeks to maintain a viable bacterial population by (1) turning off shaker table to allow bacterial flocs to settle to the bottom of the flasks, (2) gently decanting 200 mL of spent culture media, (3) re-filling the flasks with fresh

culture media containing carbon source and nitrate, and (4) re-capping the stock flasks and returning them to the shaker table.

Test flasks were set on a shaker table (shown in Figure 3) and mixed at 100 rpm for one week prior to sampling and analysis. Samples were analyzed for anions (Cl, NO_2, NO_3, SO_4, PO_4), DO, ORP and pH.

Figure 3. Batch biological denitrification test flasks on shaker table apparatus

Column tests were performed in glass filtration columns. Test water was pumped at a rate of 0.3 to 0.6 mL/min by a Masterflex peristaltic pump from a glass reservoir replenished every 2-3 days. Influent test water was introduced to the bottom of the columns, and was filtered to waste or collected for sampling from tubing at the top of the columns. Test water was groundwater from Well 6 spiked with KNO_3 to an approximate NO_3-N concentration of 20 mg/L. For acetate tests, test water was spiked with 290 mg/L of sodium acetate, for a C:N ratio of approximately 3, and columns were packed with filter media of sand, anthracite or recycled crushed glass. For 3 days prior to commencing the test, synthetic groundwater spiked with acetate-conditioned bacteria solution was recirculated through the columns to seed the columns with bacteria. For corn stalk tests, corn stalk lengths weighing approximately 12 grams were inserted in the column filter tubes and used as both support media and carbon source. For 3 days prior to corn stalk column tests, nitrate-spiked groundwater was recirculated through the corn stalk columns to allow endogenous bacteria to begin growing prior to treatment. No bacterial solution was added to corn stalk column tests. Corn stalk used in column test and column test apparatus are shown in Figure 4.

Figure 4. Left: Dried whole corn stocks, Right: Column denitrification test apparatus with 4 columns in operation (three with corn stalk, one blank)

5.3. **Ion Exchange**

Ion exchange tests were performed using Purolite 521E nitrate-selective anion exchange resin beads at doses of 1.5, 3 and 4.5 g/L in a 1 L ECE Engineering jar tester, shown in Figure 5. Preliminary testing determined that ion exchange beads reached equilibrium with test water within 90 minutes of testing. Test water was mixed with resin at 300 rpm for two hours, after which the mixers were turned off and the resin was allowed to settle. Treated water was decanted for anion analysis. Resin was left in the jars for subsequent testing, in which an additional litre of water was added to the jar for mixing. This process was repeated until a sufficient total volume of water had contacted the resin to completely saturate it with nitrate and no further nitrate removal from test water was observed.

Figure 5. Jar tester used for ion exchange experiments

5.4. **Characterization and Treatment of IEX Regenerant Brine**

Once the ion exchange resin was saturated with nitrate from multiple jar tests, the resin was collected and regenerated with a high NaCl salt solution to drive chloride back onto the resin and release nitrate into the regenerant brine. The resin from all jar tests was combined and split into two batches containing 9 grams of spent resin. One batch of resin was regenerated with a seawater sample collected from the waterfront of Wolfville, NS, and filtered through a 0.45 μm membrane filter. The seawater was characterized by IC analysis and found to have 11.1 g/L of chloride. The other batch of resin was regenerated with a pure NaCl solution modeled after the seawater sample, made with 18.3 g/L of NaCl (to provide 11.1 g/L of chloride). Both batches of resin were regenerated by mixing them in the jar tester in 5 bed volumes of brine for 2 hours, according to the manufacturer's instructions. Spent regenerant brine was then characterized by ion chromatography.

A synthetic IEX regenerant brine was modeled after the spent regenerant brine from the IEX regeneration tests, and treated by batch denitrification tests with acetate or corn stalk as the carbon source, and seeded with low- or high-chloride adapted bacterial cultures. Synthetic brine was made with 16.5 g/L NaCl and 1.53 g/L KNO_3 and was treated in one week batch denitrification tests using corn stalk and acetate as the carbon source. Batch tests were seeded with bacterial culture from previous low-salinity studies, as well as a bacterial culture acclimated to high salinity conditions. The high-salinity culture was produced by culturing a sample of mud from approximately 6 inches below the surface of the intertidal zone near the mouth of the Cornwallis River in Port Williams, NS. The high-salinity culture was cultured over 4 weeks

similar to the cultivation technique described previously in this report, in 158 mL distilled water spiked with 32 mg/L NaCl, 0.1445 g/L, and 0.85 mL of acetate or cellulose solution.

6. RESULTS and DISCUSSION

6.1. Sampling Program

6.1.1 Physical Parameters

Figure 6 below displays average pH and temperature values from groundwater wells and treatment plant inlet and outlet throughout the sampling period. The levels of pH remained relatively constant, with an average value of 7.11 ± 0.53. The minimum pH value was 5.53, observed in Well 2 during December, and the maximum pH value was 8.25, observed in Well 4 during August. The average temperature in groundwater wells and treatment plant was 11.9 ± 2.3 °C, and varied considerably during the year, with the lowest temperatures observed between December and March, and the highest temperatures observed in August.

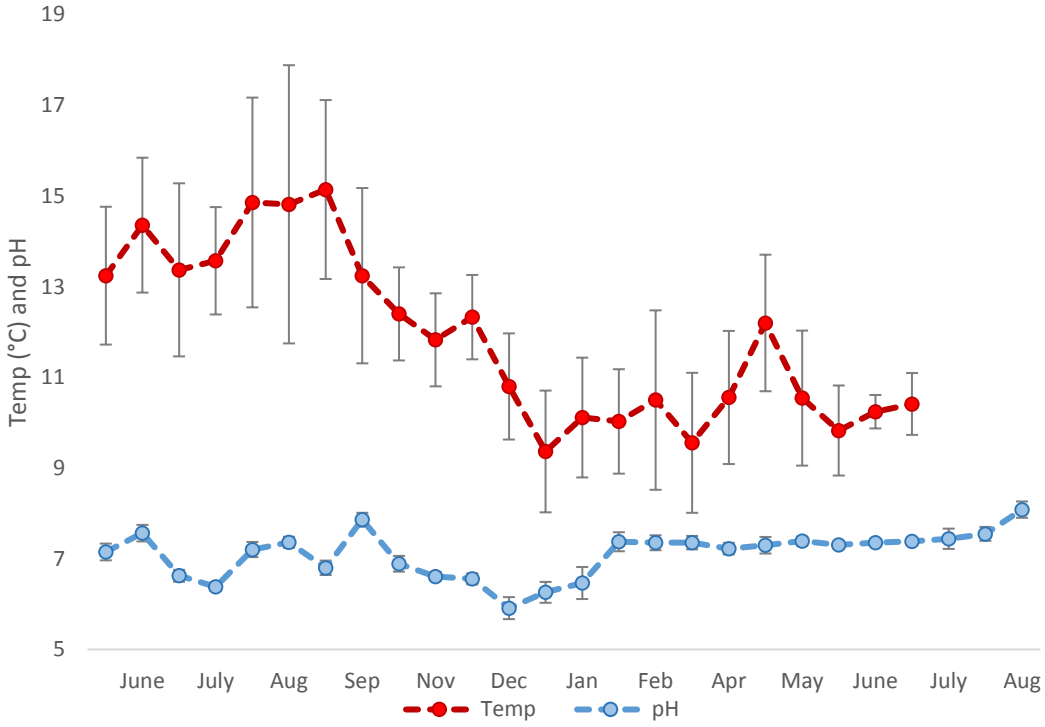

Figure 6. Average temperature in groundwater wells and treatment plant inlet and outlet over sampling period

Figure 7 displays the minimum and maximum temperatures observed at each sampling point. The minimum temperatures ranged from 7.4 °C in Well 6 to 10.4°C in Well 5a. Low influent well water temperatures would be expected to negatively impact any biological treatment. Several researchers have observed dramatic decreases in denitrification rates at low temperatures. Delanghe et al (1994) found that the maximum denitrification rate in an ethanol

fed bioreactor occurred at 40 °C, with denitrification activity decreasing linearly by a factor of 1.9 for each 10 °C drop in temperature. Assuming a similar response to temperature, denitrification rates at the coldest well water temperatures observed in this study could be expected to be only 49% of rates observed in room temperature experiments, and 62% of rates in the highest well water temperatures in the summer.

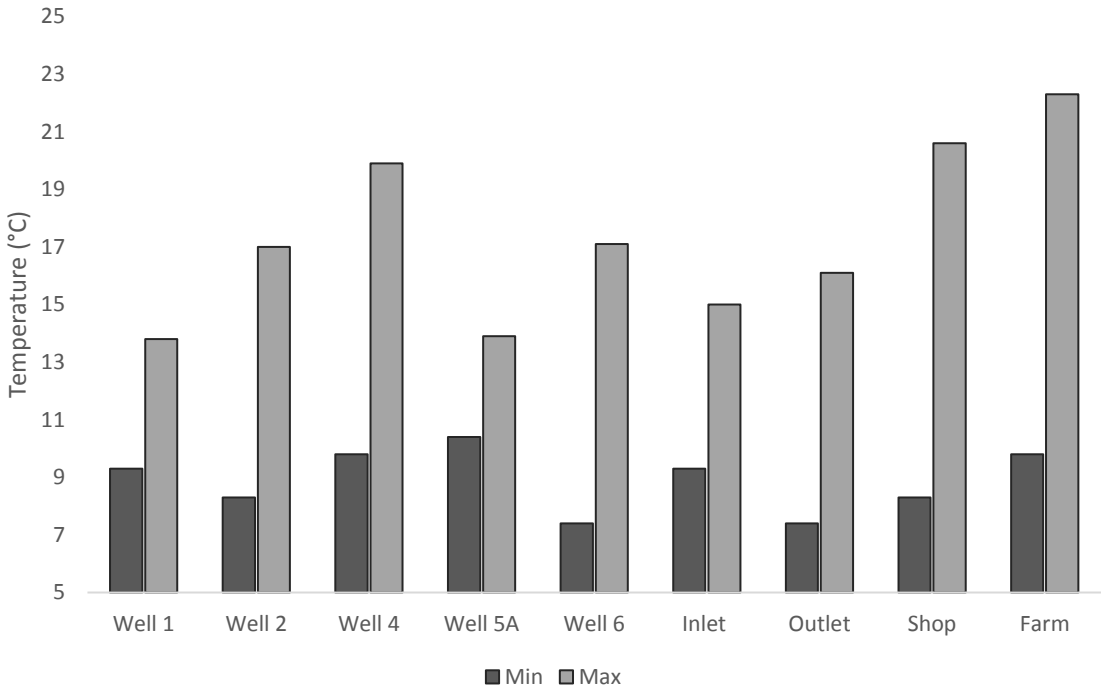

Figure 7. Minimum and maximum recorded temperatures in groundwater wells, treatment plant inlet and outlet, distribution system and private well

6.1.2. Nitrate

Figure 8 below displays nitrate-nitrogen (NO_3-N) values for the five groundwater wells, and includes the 10 mg/L MAC value for comparison. Nitrate levels in Well 2 were consistently near or above the MAC throughout the study period, with an average nitrate concentration of 8.357 ± 4.264 mg/L NO_3-N and 61% of observed NO_3-N values greater than 9.9 mg/L. However, the other four groundwater wells remained consistently below the 10 mg/L MAC, with average NO_3-N values in Well 1 of 6.716 ± 2.303 mg/L, in Well 4 of 5.250 ± 3.286 mg/L, in Well 5a of 4.524 ± 2.855 mg/L, and in Well 6 of 2.897 ± 1.327 mg/L.

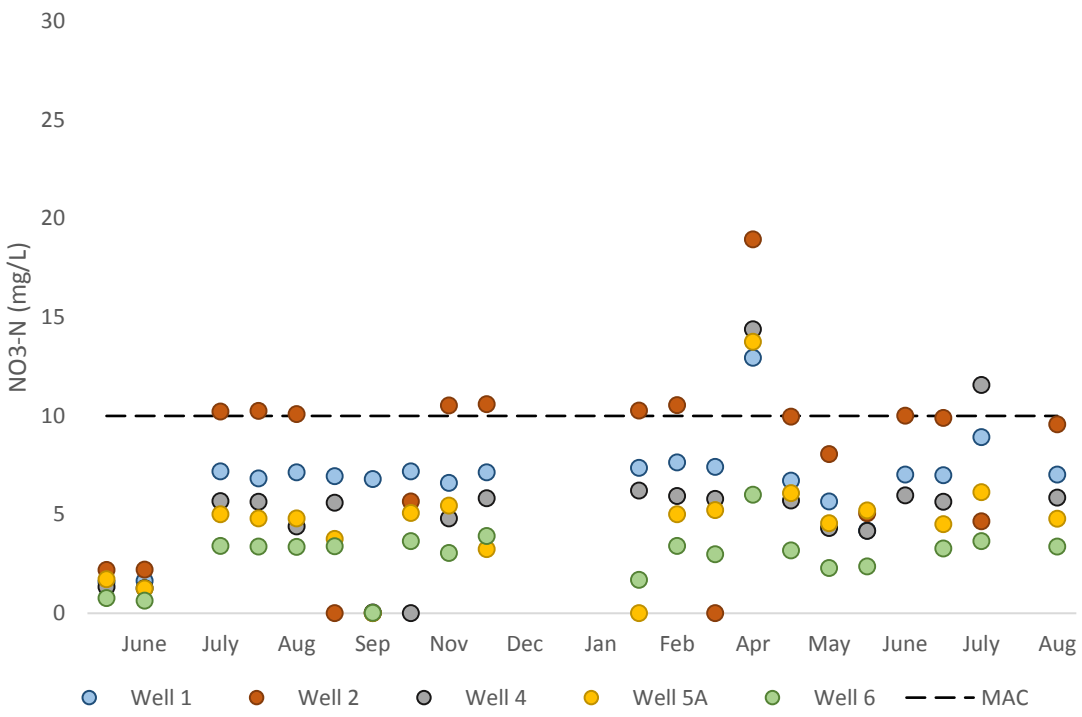

Figure 8. Nitrate concentrations in groundwater wells over sampling period

Figure 9 displays NO_3-N values for the treatment plant inlet and outlet, distribution system point, and private well. Nitrate levels in the treatment plant inlet, outlet and distribution system point remained consistently below the MAC. Average outlet values were 4.567 ± 2.482 mg/L. The current management strategy of blending high-nitrate groundwater from Well 2 with low-nitrate groundwater from Well 6 appears to be highly effective in maintaining nitrate levels in distributed water below the MAC.

In contrast, groundwater sampled from the private well was regularly observed to have nitrate levels above the MAC, with multiple readings over 20 mg/L, and average nitrate concentrations of 13.937 ± 9.713 mg/L. Nova Scotia Environment conducts a regular nitrate monitoring program in the King's County area, which primarily samples water from private wells. In 2011, of the 120 wells sampled, 28 wells, or 23% of wells sampled, exceeded the drinking water guideline. Of these wells, 18 had nitrate values between 10 and 20 mg/L, and 10 wells had nitrate values exceeding 20 mg/L.

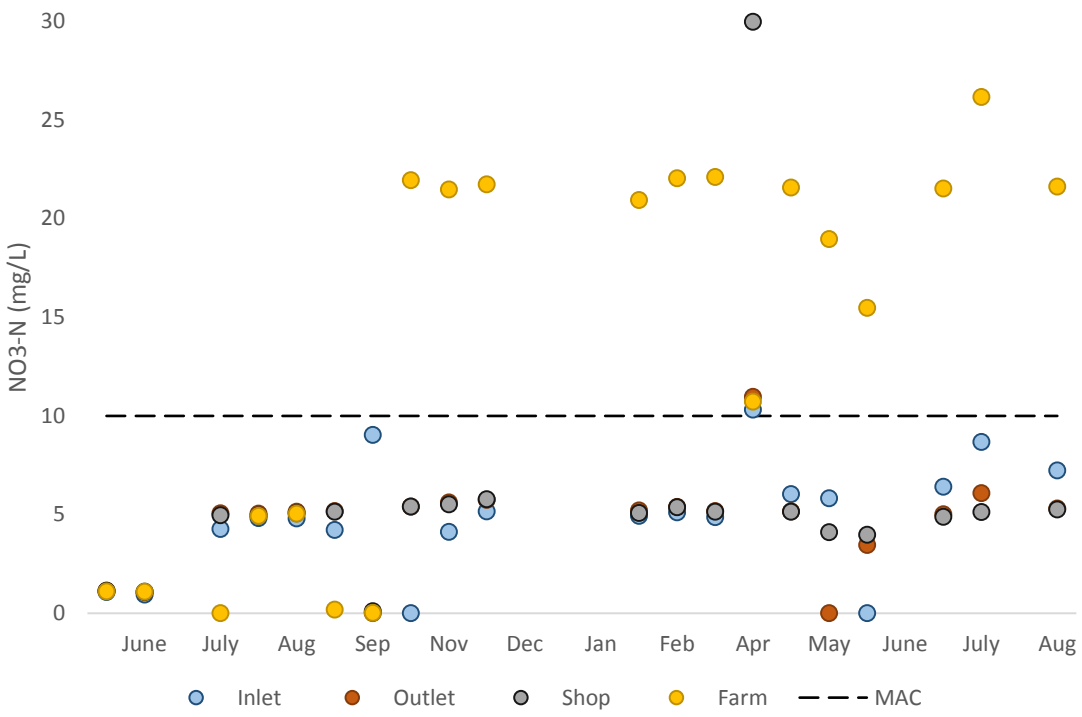

Figure 9. Nitrate concentrations in treatment plant inlet, outlet, distribution system and private well over sampling period

6.1.3. Chloride, Sulfate and CSMR

Average chloride, sulfate, and chloride-to-sulfate mass ratios (CSMR) for each sampling site is displayed in Figure 10. Average groundwater chloride concentrations ranged from 16.149 ± 8.198 mg/L in Well 4 to 100.951 ± 45.594 mg/L in Well 1. The average CSMR from the treatment plant outlet was 3.134 ± 0.351 mg/L, and at the distribution system sampling point was 3.591 ± 1.414 mg/L.

CSMR levels greater than a threshold value of 0.5-0.77 may indicate potential for galvanic corrosion of lead where lead is connected to copper (for example, lead solder on copper piping) in the distribution system or premise plumbing (Edwards and Triantafyllidou, 2007; Nguyen et al, 2011). The CSMR levels observed at all sampling points in this study were well above this threshold. However, actual lead corrosion depends the type and condition of pipe material, and may depend on other water quality factors, such as pH and alkalinity (Nguyen et al, 2011).

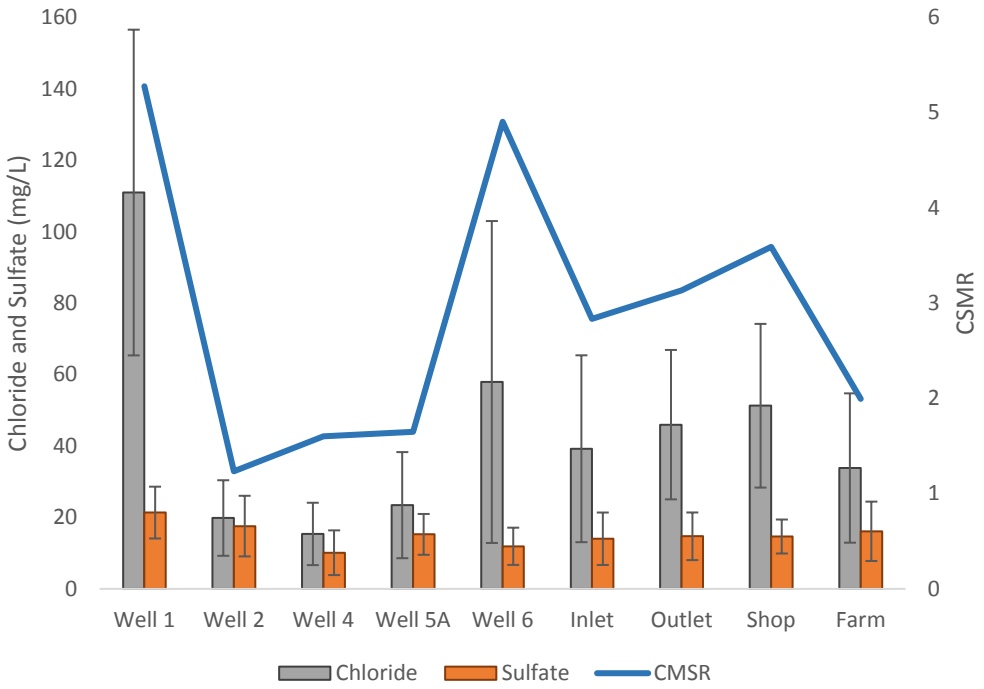

Figure 10. Average chloride and sulfate concentrations (primary axis) and CSMR (secondary axis) in groundwater wells, treatment plant inlet and outlet, distribution system and private well

6.1.4. Metals

Figure 11 and 12 display total and ferric iron and lead concentrations, respectively, as compared to their respective MACs of 300 ppb and 10 ppb. With the exception of Well 4, which exceeded on average the MAC for iron, none of the sampling points were observed to have excessive iron or lead corrosion. The two wells (Well 1 and Well 6) with the highest average CSMR values (5.11 ± 2.13 mg/L and 4.78 ± 2.70 mg/L, respectively) did not have high metals levels relative to the lower CSMR wells, suggesting that metal release at the well heads was influenced more by pipe material than CSMR. The distribution system in the Village of Port Williams is primarily composed of PVC piping, which may account for the low metals levels in the distribution sampling point.

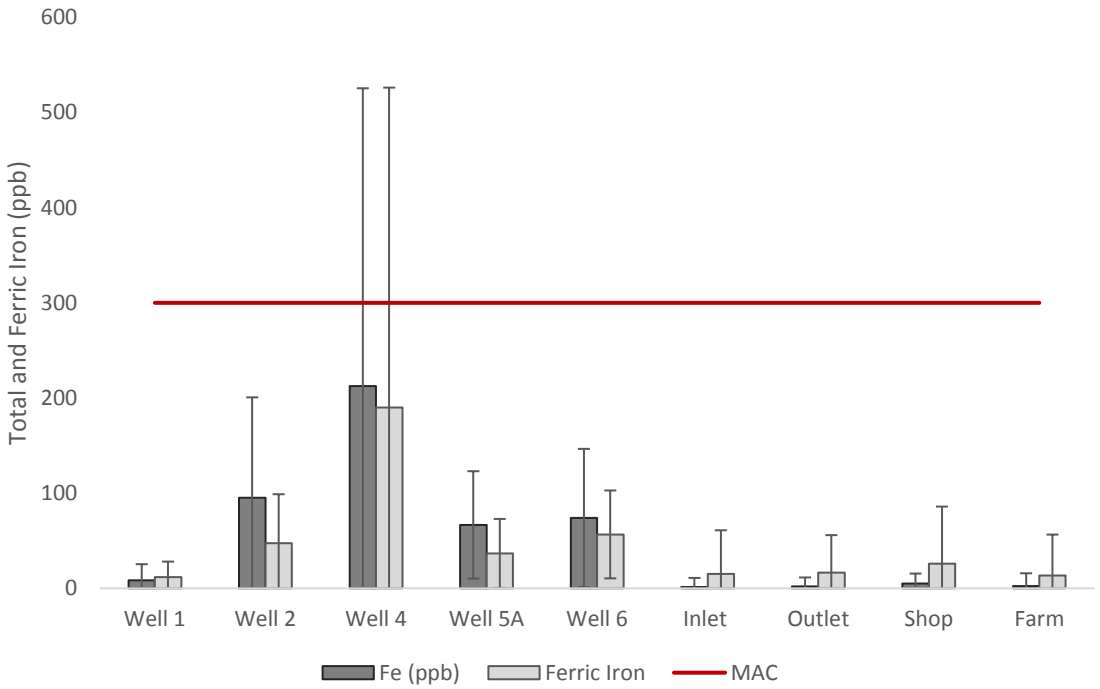

Figure 11. Average total and ferric iron concentrations in groundwater wells, treatment plant inlet and outlet, distribution system and private well, with comparison to MAC of 300 ppb

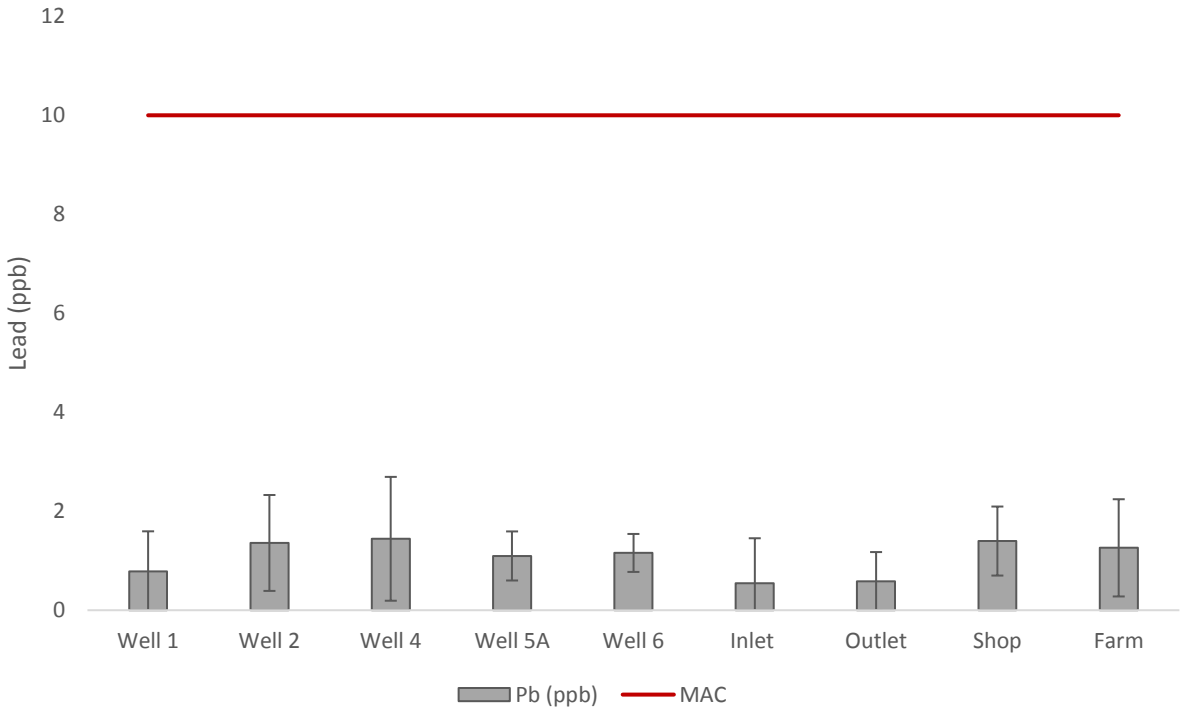

Figure 12. Average lead concentrations in groundwater wells, treatment plant inlet and outlet, distribution system and private well, with comparison to MAC of 10 ppb

6.1.5. Chlorine and HPC

Average heterotrophic plate counts (HPC) from all sampling points, reported in CFU per mL, are displayed in Figure 13 below. HPC counts were highest at the treatment plant inlet, with an average of 1794 ± 3808 CFU/mL, and lowest at the treatment plant outlet, with an average of 61 ± 190 CFU/mL.

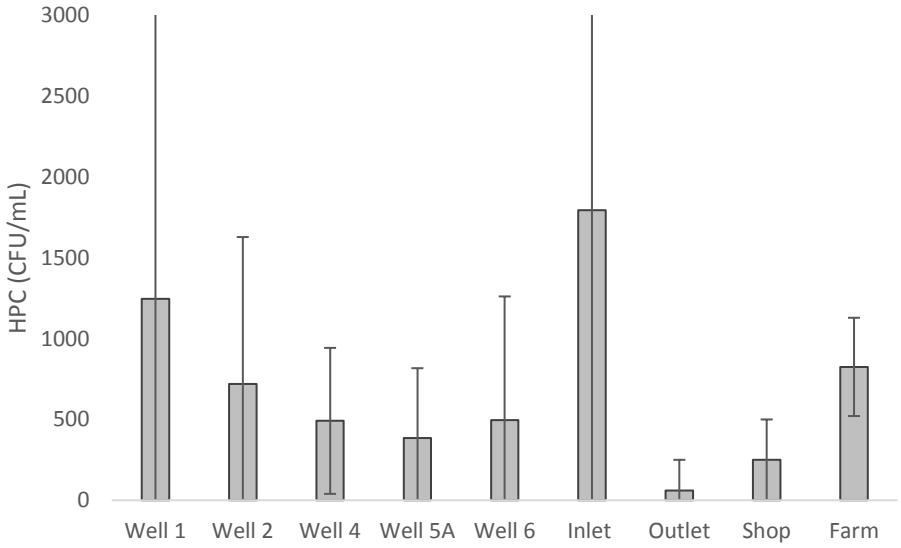

Figure 13. Average heterotrophic plate count (HPC) results for all sampling points, reported in colony forming units (CFU) per mL

Free and total chlorine levels for the treatment plant inlet and outlet and distribution system sampling point are displayed in Figure 14 below. Free and total chlorine concentrations were 1.04 ± 0.37 mg/L and 1.20 ± 0.36 mg/L, respectively, at the treatment plant outlet, and 0.84 ± 0.44 mg/L and 0.90 ± 0.34 mg/L, respectively, at the distribution system sampling point.

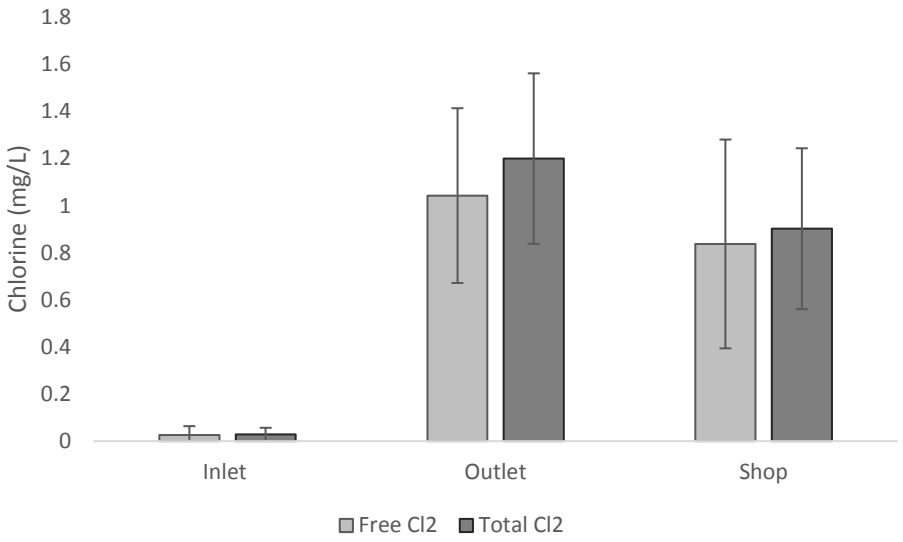

Figure 14. Average free and total chlorine concentrations in treatment plant inlet and outlet and distribution system sampling site

6.2. **Biological Denitrification**

6.2.1. **Batch Tests**

Figure 15 below displays the percent removal of nitrate from batch tests with 20 mg/L initial nitrate over a 1-week denitrification period. Acetate, corn stalk and pure powdered cellulose were tested as carbon sources at various carbon-to-nitrogen (C:N) ratios ranging from 3 to 89, depending on carbon source. Tests using acetate as the carbon source were able to achieve substantial denitrification at much lower carbon source doses than corn stalk tests, while corn stalk tests achieved denitrification with lower carbon source doses than powdered cellulose tests. Denitrification tests with acetate as the carbon source were able to remove 87% of nitrate from test flasks with a C:N ratio as low as 3. At a C:N ratio of 44, corn stalk test flasks achieved nearly complete removal of nitrate. However, flasks with powdered cellulose as the carbon source were only able to achieve 80% removal of nitrate with a C:N ratio of 89.

In general, simpler organic molecules, such as acetate and methanol, tend to be more easily digested by bacteria than more complex molecules, such as sucrose and cellulose-based materials. Higher denitrification rates have been observed using acetate and methanol as a substrate as compared to sucrose (Lorrain et al, 2004). Furthermore, certain cellulosic waste products may contain some simple, easily digestible organic which wash out near the beginning of testing, allowing for more rapid bacterial uptake and denitrification than on a more uniformly complex carbohydrate material (Fan et al, 2012). This may explain why high removals of nitrate in this study were observed with lower doses of acetate than corn stalk, and with lower doses of corn stalk than pure cellulose.

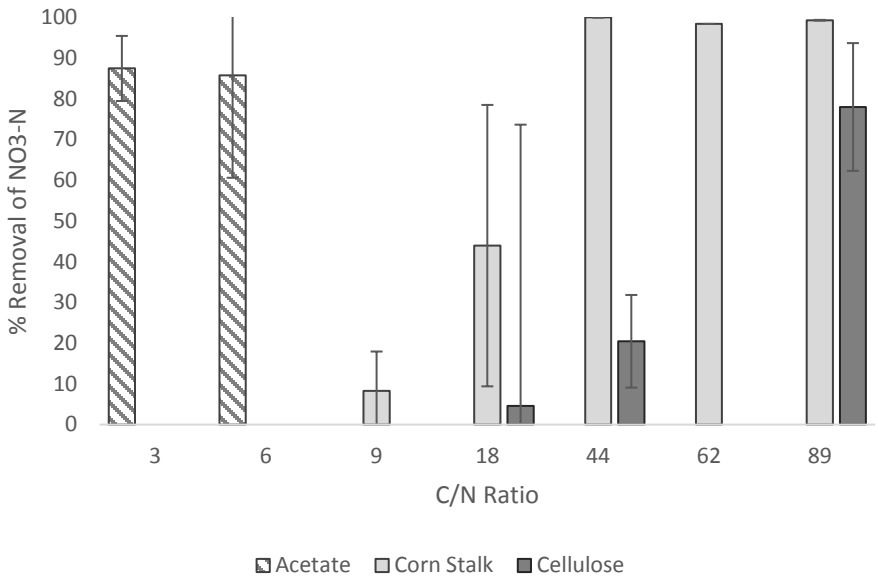

Figure 15. Percent removal of nitrate in one-week batch tests with acetate, corn stalk and cellulose at various C:N

6.2.2. **Column Tests**

Figures 16 displays nitrate concentrations in raw water and water treated by acetate denitrification columns as an average of the three columns throughout the test period. Results are from two column test runs, from December 2 to 5, 2016 and January 19 to 22, 2017. Acetate columns removed 95% of nitrate, on average, treating raw water with an average value of 16.85 ± 1.07 mg/L nitrate to 0.13 ± 0.06 mg/L in Column 1, 2.08 ± 3.72 mg/L in Column 2, and 0.35 ± 0.61 mg/L in Column 3.

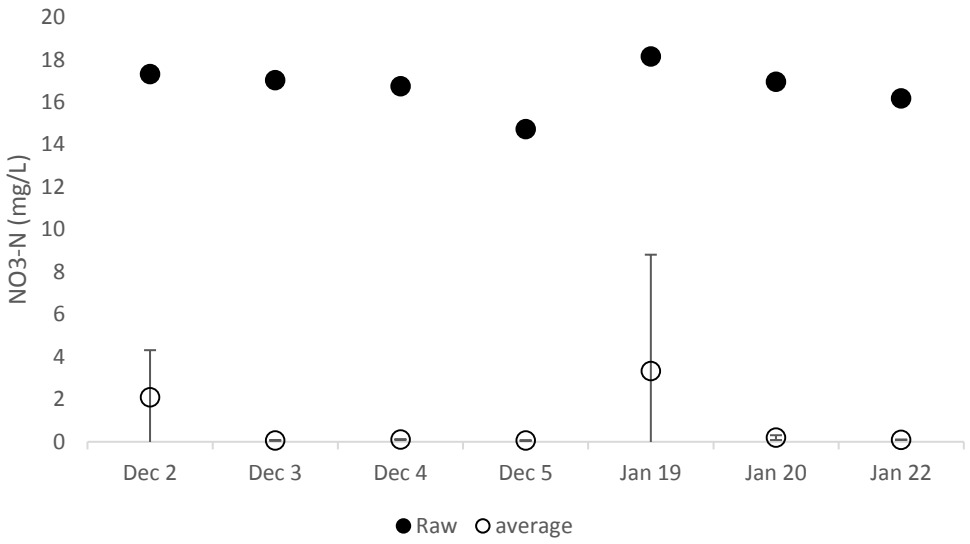

Figure 16. Nitrate concentrations in raw water and water treated with acetate columns

Figure 17 displays nitrate concentrations in raw water and water treated by corn stalk denitrification columns throughout the test period. Results are from a five-week test period in June and July 2017. The first half of the test period, until July 19, consisted of one blank column (no corn stalk) and three corn stalk columns, run separately, and displayed as an average value on the graph. The second half of the test period consisted of two single columns, displayed as an average value, and one set of two corn stalk columns in series. The average nitrate concentrations in raw water and the blank column were 27.39 ± 6.57 mg/L and 29.02 ± 6.97 mg/L, respectively. The average nitrate concentration in water treated by single corn stalk columns was 17.90 ± 4.93 mg/L, and by two columns in series was 12.13 ± 2.92 mg/L, representing an average removal rate of 35% and 49% by single columns and two columns in series, respectively.

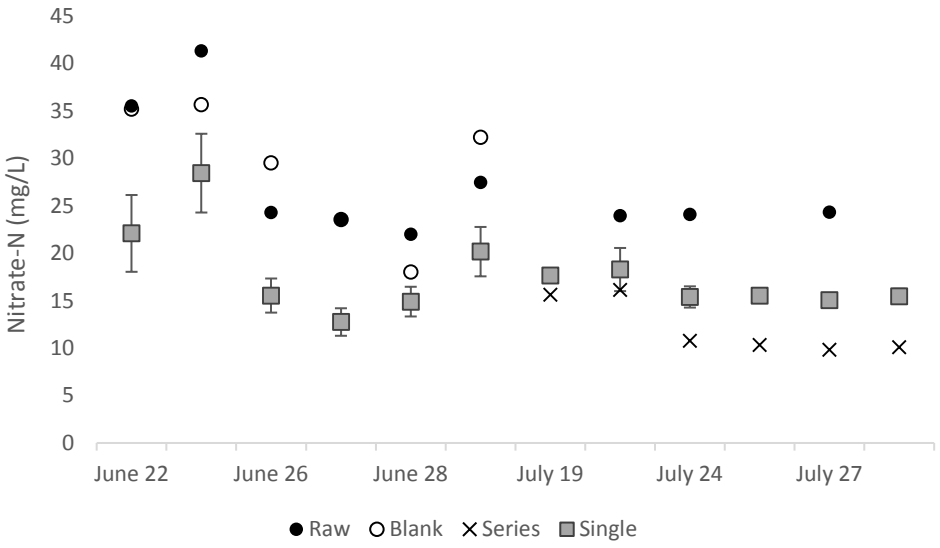

Figure 17. Nitrate concentrations in raw water and water treated with corn stalk columns

Corn stalk was dried and weighed both before and after use in the columns to determine the change in mass of the corn stalk throughout column operation. Figure 18 displays the average initial and final masses and loss of mass of corn stalk used in column tests for 3 weeks (n = 5) or 9 weeks (n = 2). Average mass loss over 3 weeks of operation was 2.0 ± 0.1 grams, while average mass loss over 9 weeks of operation was 1.8 ± 1.0 grams. As there were no significant differences in mass loss between 3 and 9 weeks of operation, these results may suggest that there was an initial rapid release of organic matter from the columns in the first few weeks of operation, followed by slower release in subsequent weeks. Several researchers working with waste products, such as rice stalk and corncobs, as carbon sources observed an initial spike in dissolved organics concentrations in the treated water at the beginning of the testing period, due to washing out of the water-soluble organics from the carbon source (Wang and Wang, 2013; Yang et al, 2015; Xu et al, 2009; Zhang et al, 2012). However, there was a large variation between the two 9-week corn stalk samples, so further work would be required to support this finding.

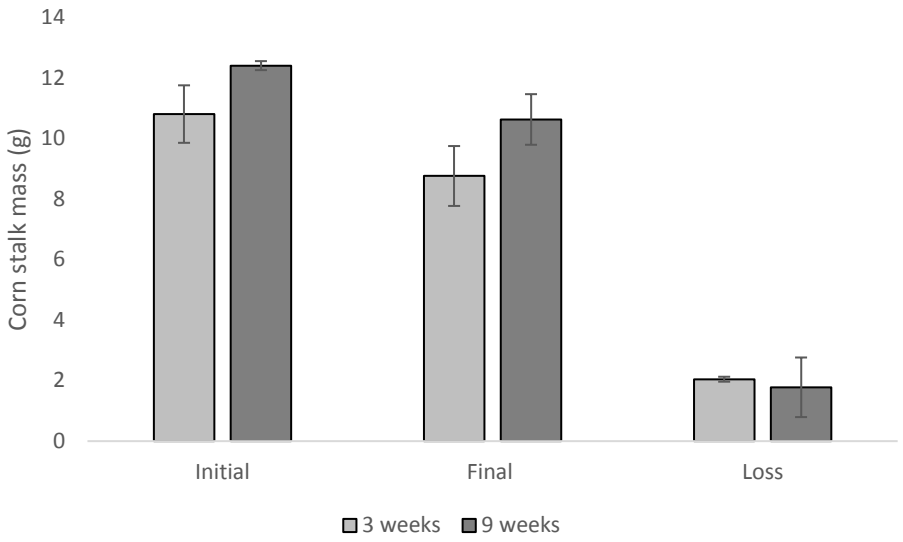

Figure 18. Initial and final masses and loss of mass of corn stalk used in column tests for 3 weeks (n = 5) or 9 weeks (n = 2) of operation

6.3. **Ion Exchange**

6.3.1. **Jar Tests**

Port Williams well water was spiked to a NO_3-N concentration of 20 mg/L and treated with a commercial nitrate selective anion exchange resin in a 1-L jar tester. Figure 19 displays nitrate removal from contaminated groundwater as a function of volume of groundwater treated by the resin. Removal of nitrate decreased in a fairly linear manner up to 600 bed volumes, at which point the resin removed approximately 5 mg/L of nitrate-N. Removals of approximately 10 mg/L of nitrate from an initial concentration of 20 mg/L were achieved near 300-400 bed volumes of groundwater treated.

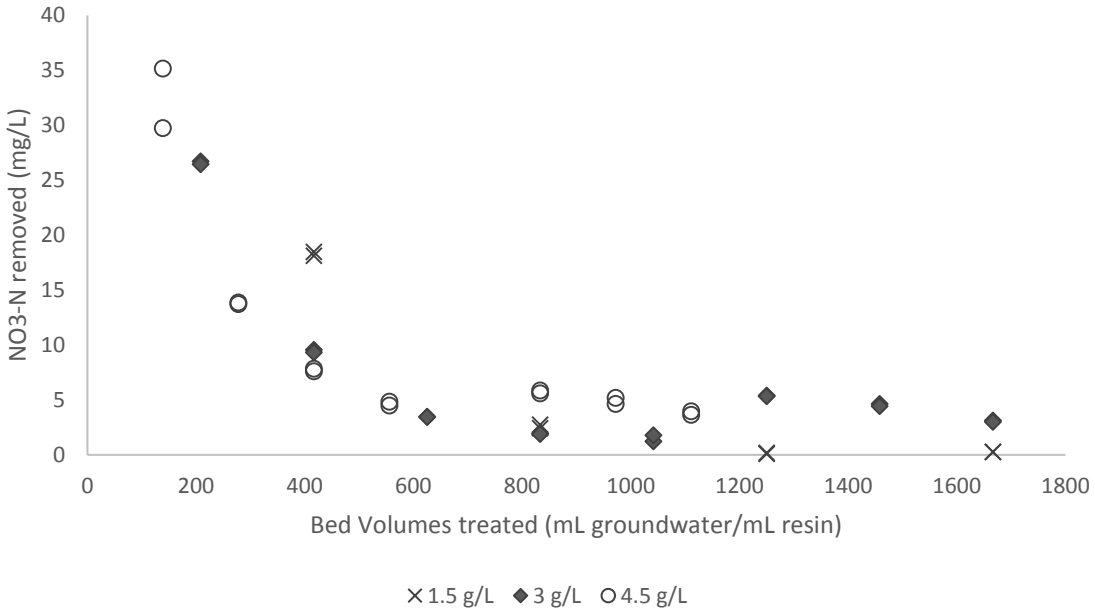

Figure 19. Nitrate removal by IEX resin after treatment of 140-1250 bed volumes of groundwater

Figure 20 displays concentration of chloride added to treated groundwater as a function of nitrate-N removed. Chloride addition and nitrate removal were linearly related, with approximately 2.876 mg of chloride added for every mg of nitrate-N removed. This value is close to the ratio of the mass of chloride (Cl) to the mass of nitrogen (N) (i.e., 2.53), which indicates that the resin was highly selective for nitrate, resulting in a nearly one-to-one ratio of nitrate adsorption and chloride release. Sulfate concentrations did not change from raw to treated water, with initial sulfate concentrations of 14.734 ± 1.757 mg/L and final sulfate concentrations of 14.448 ± 2.619 mg/L. Thus the ion exchange resin used in this study increased the CSMR of the groundwater through chloride addition in a predictable fashion dependent on nitrate removal, but did not cause an additional increase in CSMR through removal of sulfate.

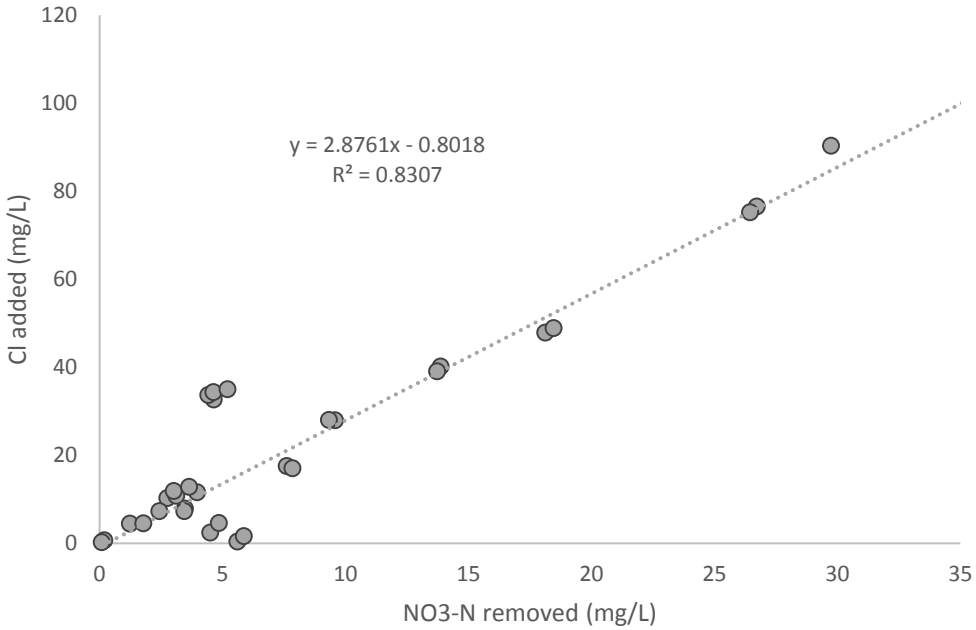

Figure 20. Concentration of chloride added to groundwater as a function of nitrate-N removed

Figure 21 displays the increase in CSMR of groundwater after ion exchange treatment as a function of nitrate-N removed. Based on these results, CSMR would be expected to increase by 0.34 for every mg/L of NO_3-N removed by the anion exchange resin used in this study.

Nguyen et al (2011) observed increased lead leaching from lead solder-copper coupons in controlled bench-scale tests due to a change in CSMR resulting from a range of process changes, including implementation of anion exchange treatment. As a result, these researchers recommend that utilities conduct corrosion tests if they are considering treatment changes that will increase the CSMR if (1) lead-copper connections are present in the distribution system or premise plumbing, (2) the water has alkalinity < 50 mg/L as $CaCO_3$, and (3) the CSMR after treatment will be greater than 0.2. As an alternative, anion exchange resins with carbonate, rather than chloride, as the counter-ion could also be investigated for nitrate removal.

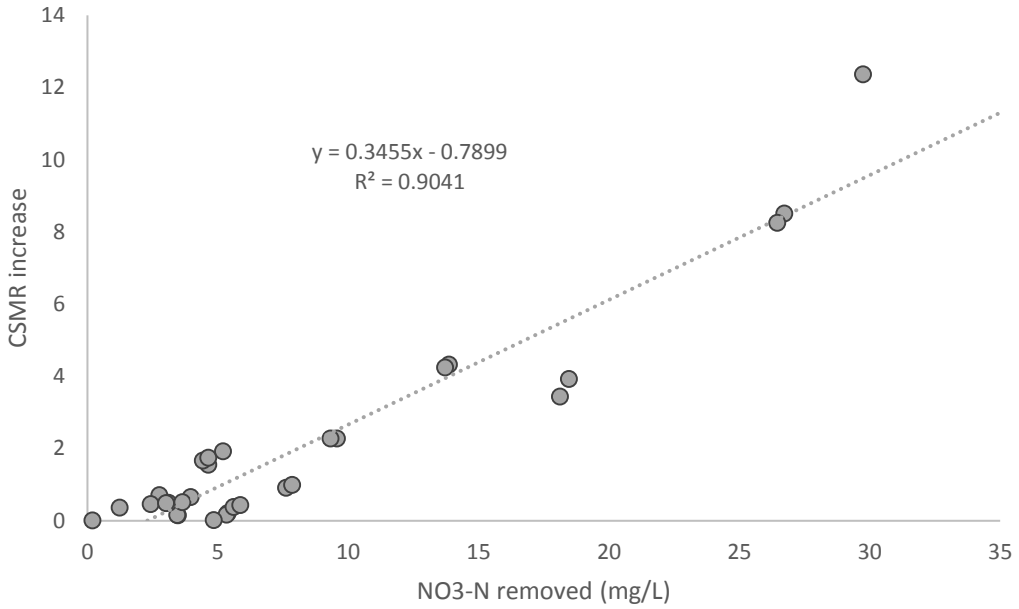

Figure 21. Concentration of chloride added to groundwater as a function of nitrate-N removed

6.3.2. **IEX Regenerant Brine**

Saturated IEX resin was regenerated with (1) a filtered seawater sample from the waterfront of Wolfville, NS, or (2) a solution of NaCl in distilled water, both with a choride concentration of 11.1 g/L (equivalent to 18.4 g/L NaCl). After the regeneration process, spent brine from regenerating saturated IEX resin was characterized by ion chromatography. Table 1 displays chloride and nitrate-N concentrations in spent seawater and NaCl solution regenerant brines. Chloride concentrations in seawater and NaCl solution regenerant brines were 10,659 and 9,638 mg/L, respectively. Nitrate-N concentrations in seawater and NaCl solution regenerant brines were 88.1 and 93.4 mg/L, respectively.

Table 1. Chloride and nitrate concentrations in spent seawater or NaCl solution regenerant brines

	Chloride (mg/L)	NO_3-N (mg/L)
Seawater	10, 659	88.1
NaCl Solution	9.638	93.4

A synthetic spent regenerant brine was modeled after the spent brines from the resin regeneration experiment, and was made with distilled water containing 16.5 g/L NaCl and 1.53 g/L KNO_3. Synthetic spent regenerant brine was treated in one week batch denitrification tests using acetate and corn stalk with C:N ratios of 10 and 90, respectively, inoculated with bacteria cultured in low salinity (LS) or high salinity (HS) solutions. Corn stalk trials removed an average of 47.1%

(±10.2%) of nitrate, as compared to the control flask, with final nitrate values of 98.9 ± 11.6 mg/L. Acetate trials had similar removals, with an average reduction of 42.7% (±5.6%) below the control nitrate concentrations, and final nitrate concentrations of 107.1 ± 7.6 mg/L. There were no significant differences between the low and high salinity cultures in terms of nitrate removal.

Some nitrate accumulation was observed in these experiments, with final nitrate-N levels as high as 21.0 ± 11.4 mg/L in the low salinity culture corn stalk trials. Nitrate-N concentrations were significantly lower ($p = 0.037$) in the high salinity culture tests than in the low salinity tests, with average NO_2-N concentrations of 4.6 ± 5.5 mg/L and 18.1 ± 8.1 mg/L, respectively.

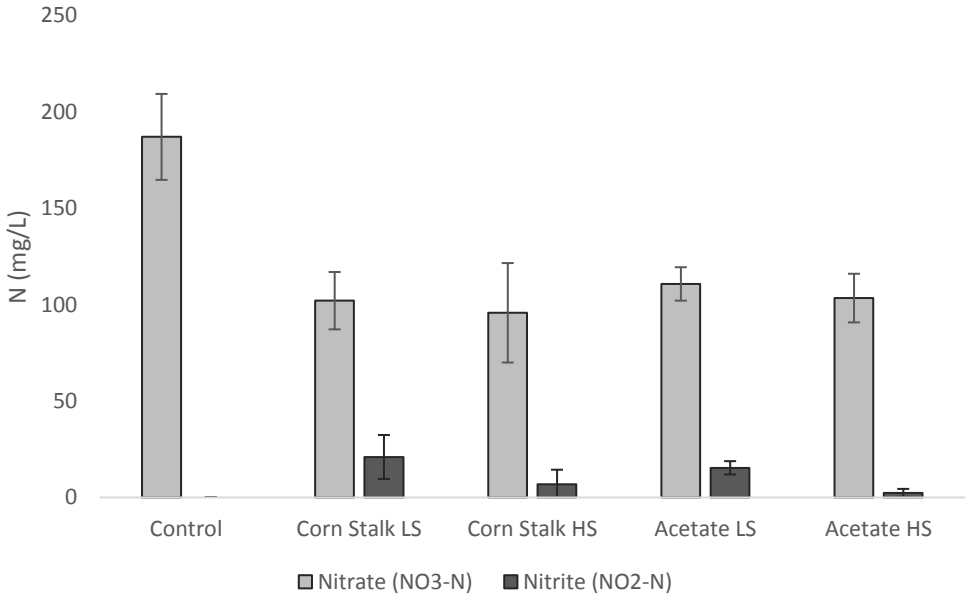

Figure 22. Nitrate-N and nitrite-N in IEX regenerant brine after batch denitrification tests with corn stalk and acetate using high- and low-salinity bacterial cultures

7. CONCLUSIONS and RECOMMENDATIONS

- Nitrate levels in Well 2 were observed to be above the 10 mg/L MAC in over 61% of samples. However, treatment plant outlet values for nitrate were consistently well below the MAC, indicating that current nitrate management strategy of blending high-nitrate groundwater from Well 2 with low-nitrate groundwater from Well 6 is effective.
- It is recommended that Port Williams continue to routinely measure nitrate levels in the wells and distribution system to monitor any changes. Additionally, those with private wells should be notified or possible nitrate contamination and have their wells tested in spring and fall.
- CSMR values for groundwater in Port Williams exceeded the 0.5-0.77 threshold indicating corrosion potential; however, lead and iron levels in water samples were generally well under their respective MACs. If available, service line materials should be

reviewed throughout the system to ensure there is no threat of iron and/or lead corrosion due to the elevated CSMR.

- Corn stalk was effective as a carbon feedstock for biological denitrification tests, although it required substantially higher carbon doses than a traditional soluble feedstock, acetate. It also performed well in column tests, achieving nitrate removals of 35% in single column tests and 49% removal with two corn stalk columns in series.
- Ion exchange tests with a commercial anion exchange resin were effective in removing nitrate from the groundwater, but could be expected to increase CSMR by 0.34 per mg/L of nitrate-N removed.
- Biological denitrification was also effective in reducing nitrate concentrations from ion exchange regenerant brine, with 42% and 47% removals achieved with acetate and corn stalk, respectively in one-week batch trials. Some nitrite accumulation was observed in these trials, but was significantly lower when an appropriate high-salinity adapted bacterial culture was used for testing.

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