TECHNICAL MEMO

Prepared For: Paula Dawe, P.Eng.
Prepared By: Jessica Strickland
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Re: Analysis of Manganese Speciation Data

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1. Background

The Guidelines for Canadian Drinking Water Quality (GCDWQ) will be revised in 2019 to include a new guideline for manganese. The existing guideline, last updated in 1987, was an aesthetic objective (AO) of 0.05 mg/L based on taste and staining of laundry and plumbing fixtures. However, new scientific studies are showing health effects related to exposure to high manganese levels in drinking water (Health Canada, 2018). The new guideline has both a maximum acceptable concentration (MAC) of 0.12 mg/L and an AO of 0.02 mg/L.

Health Effects

Manganese is an essential nutrient at low doses, but ingesting high amounts of manganese in drinking water can lead to health effects, primarily on the nervous system. Some studies in humans suggest an association between manganese in drinking water and neurological effects in children. When exposed to high levels, infants may develop learning and behavioural problems, while older children and adults may acquire problems with memory, attention, and motor skills (Health Canada, 2018). The proposed MAC of 0.12 mg/L is based on health effects in infants, primarily formula-fed, but is intended to protect all Canadians.

Aesthetic Considerations

Concerns regarding the presence of manganese in drinking water are often related to consumer complaints regarding discoloured water. The proposed AO of 0.02 mg/L (20 µg/L) is intended to minimize the occurrence of discoloured water complaints and to improve consumer confidence in drinking water quality.

2. Assessment of Proposed Guideline for NL

Manganese is one of the most abundant metals on the earth's surface, making up approximately 0.1% of the earth's crust. Manganese is not found naturally in its pure (elemental) form, but is a component of over 100 minerals and is widely distributed in air, water and soil (WHO, 2017).

Manganese may be present in surface and ground water sources in the environment from natural sources (rock and soil weathering) or as a result of human activities (such as mining, industrial discharges and landfill leachate). Higher levels in aerobic waters are usually associated with industrial pollution. Manganese is detected in nearly 97% of surface water sites (WHO, 2017).

There are currently six (6) manganese removal systems in Newfoundland and Labrador. They are all in operation and installed in the following communities as indicated in Table 1: Bunyan's Cove, Harbour Grace, Holyrood, Marysvale, Port Hope Simpson and West St. Modeste. The province does have additional drinking water supplies that exceed the MAC of 0.12 mg/L for manganese. These exceedances are all attributed to natural sources due to rock and soil weathering.

Table 1: Fe & Mn Removal Systems in NL

Community Name	Supply Name	Type of Process/System
Bunyan's Cove	#1 Wellfield	Chlorine (sodium hypochlorite) oxidation, two (2) media filters (Turbidex™), and three (3) greensand media filters
Harbour Grace	New Southside Well (Well #3)	Air injection oxidant and two (2) manganese dioxide media filters (Filox™)
Holyrood	Main Line	Chlorine (sodium hypochlorite) oxidation, and three (3) greensand and anthracite media filters
Marysvale	Drilled	pH adjustment (soda ash), Chlorine (sodium hypochlorite) oxidation, two (2) media filters (NextSand™), and two (2) manganese dioxide media filters (Filox™)
Port Hope Simpson	Arnold's Brook and Pond	pH adjustment (soda ash), chlorine (sodium hypochlorite) oxidation, four (4) greensand filters, potassium permanganate for backwash regeneration
West St. Modeste	Well Field	Two (2) depth media filters in parallel (Cullsan® G50 and Cullcite), two (2) ion exchange units in parallel (CH-2 Cation Exchange Resin)

Contaminant Exceedances

An assessment of all public water supplies in Newfoundland and Labrador was conducted to determine the extent of the proposed MAC and to provide a priority list for manganese corrective measures. The following categories were assigned:

- Tier 1 – regular exceedances with averages above the proposed MAC; and
- Tier 2 – semi-regular exceedances with averages close to the proposed MAC.

Tier 1:
There are 14 water supplies in the Tier 1 category. The majority of water supplies in Tier 1 are groundwater which service very small populations.

Tier 2:
There are 11 water supplies in the Tier 2 category. The water supplies in Tier 2 consist of both surface water and groundwater and service a range of populations.

Aesthetic Exceedances

The proposed AO guideline is 0.02mg/L. There were 138 water systems with exceedances detected for manganese during the 2017-2018 fiscal year, based on the proposed AO.

3. Manganese Speciation

In water, manganese occurs in both dissolved and suspended forms, depending on such factors as pH, anions present and oxidation-reduction potential. The most common oxidation states are Mn (II) and Mn (IV). The species of manganese that is present in drinking water is determined by oxidation/reduction, precipitation/dissolution, and sorption/desorption reactions. In alkaline (pH > 8-9) and oxidizing conditions, conversion of Mn (II) to Mn (IV) will occur (Health Canada, 2016). Hence, Mn (IV) is insoluble and can be found in the particulate state in water. The treatment options are dependant on the type of manganese present in the drinking water - dissolved Mn is an approximation for Mn (II) (Health Canada, 2016), and total manganese includes both the dissolved Mn (II) and particulate Mn (IV). Particulate Mn (IV) is determined by subtracting dissolved Mn (II) from total Mn.

A special sampling program was conducted to determine the type of manganese most common in NL. Total and dissolved manganese was sampled at the tap analyzed for 23 water supplies taken from the Tier 1 and 2 categories. Table 2 displays the water supplies used in the study and the results of the analysis. Samples were collected mostly in the summer for groundwater sources, and mostly in the fall for surface water sources.

Table 2: Manganese Analysis

Community Name	Supply Name	Date Sampled	Source Type	Total Mn	Dissolved Mn (II)	Particulate Mn (IV)
Bauline	#1 Brook Path Well	2018-09-26	GW	0.17	0.17	0.00
Bay St. George South	#1 Well Heatherton (Home Hardware)	2018-09-26	GW	0.28	0.22	0.06
Brent's Cove	Paddy's Pond	2018-12-05	SW	0.10	0.10	0.00
Brigus South	#1 Well Forge Hill	2018-09-26	GW	0.21	0.21	0.00

Brigus South	#2 Well Dunphey's Hill	2018-09-26	GW	0.02*	0.03*	0.00
Bunyan's Cove	#1 Wellfield	2018-11-21	GW	0.12	0.12	0.00
Cavendish	#2 Well – Tom Critch	2018-12-06	GW	0.11	0.01	0.10
Chanceport	Bridger's Cove Pond	2018-12-06	SW	0.01	0.01	0.00
Fogo Island	Sandy Cove Pond	2018-12-14	SW	0.06	0.06	0.00
Great Brehat	Little Steady Pond	2018-11-06	SW	0.01	0.01	0.00
Lawn	Brazil Pond	2018-12-11	SW	0.04	0.04	0.00
Marysvale	Drilled	2018-09-21	GW	0.13	0.13	0.00
Millertown	Water Pond	2018-11-06	SW	0.01	0.01	0.00
Sheshatshui	Wells 1, 2 & 3	2018-10-24	GW	0.10	0.02	0.08
Ship Cove-Lower Cover-Jerry's Nose	#1 Well – PJ's Variety Shop	2018-11-06	GW	0.07	0.03	0.04
St. Andrews	#2 Well	2018-09-26	GW	0.27	0.27	0.00
St. Andrews	#4 Well Strip Road Well	2018-09-26	GW	0.25	0.22	0.03
St. Lunaire-Griquet	Lookout Brook	2018-11-06	SW	0.04	0.03	0.01
Swift Current	Drilled	2018-12-14	GW	0.01	0.01	0.00
Wabana	Normore Crescent East #1	2018-09-25	GW	0.14	0.14	0.00
Wabana	Scotia #1	2018-09-25	GW	0.10	0.10	0.00
Wabana	#3 Yard West Mines South	2018-09-25	GW	0.23	0.23	0.00
Wabana	#4 West Mines Road	2018-09-25	GW	0.17	0.16	0.01

* Results confirmed by accredited laboratory

According to the data in Table 2, dissolved Mn (II) is present more frequently and abundantly in NL than particulate Mn (IV). This information is critical in choosing the correct treatment option for the removal of manganese. This test was relatively inexpensive and should be conducted prior to the selection of manganese treatment systems.

Effects of Seasonality

Levels of the speciation of Mn in drinking water, particularly in surface water sources, is dependent on seasonal effects including water temperature and pond/lake turnover which tends to occur in the spring and fall in waterbodies in the province. In 2017, drinking water sampling conducted in

April in the Central region resulted in unexpectedly high Mn results from several systems with surface water sources. It was theorized that these samples may have captured the effects of pond/lake turnover, when colder, denser water at the surface sinks to the bottom and warmer, less dense water rises to the surface. It has also been noticed that Mn levels tend to increase with warmer water temperatures, as was observed in August 2018 when a Mn event occurred on the Petty Harbour-Long Pond system used by the City of St. John's.

4. Treatment Options

Several treatment methods are available to lower the concentration of manganese in drinking water. The treatment typically involves multiple unit processes and mainly consists of converting dissolved Mn (II) to particulate Mn (IV) that can be clarified and/or filtered. The desired method will depend on the form of manganese that is present in the source water. The main treatment options for manganese removal include:

- Oxidation/Filtration;
- Oxidation/Adsorption;
- Biological Filtration;
- Membrane Filtration; and
- Ion Exchange.

Oxidation/Filtration

Oxidation

Oxidation converts the dissolved forms of manganese to an insoluble form which permits their subsequent removal by physical/mechanical means. The rate at which oxidation occurs can be highly dependant on pH and oftentimes temperature. The most common chemical oxidants used in water treatment for manganese removal are potassium permanganate, ozone and chlorine as shown in Table 3.

Table 3: Chemical, dosage, optimum pH and minimum reaction time required to oxidize 1 mg of Manganese (Civardi & Tompeck, 2015)

Oxidant	Chemical Formula	Dosage	pH	Reaction Time
Potassium Permanganate	$KMnO_4$	1.92 mg	> 5.5	< 20 sec
Ozone	$O_{3\,(aq)}$	0.88 mg		10-30 sec
Chlorine (Hypochlorous Acid)	HOCL	1.30 mg	> 8.0	2-3 hr
Oxygen	O_2	0.29mg	>9.0	> 1 hr

Potassium permanganate (KMnO4)

$KMnO_4$ is effective in oxidizing many organic compounds and can be used at higher dosages for treatment of manganese, iron and sulfide compounds. However, the dose must be exact to prevent water from turning pink if overdosed. The use of $KMnO_4$ will form a Mn precipitate that will require sedimentation and/or filtration. In order for quick detention time, a water temperature of 20℃ is required, otherwise dissolution can take up to a half hour (Civardi & Tompeck, 2015). Permanganate is typically suitable for the following conditions:

- Water quality issue is primarily manganese;
- Detention time is limited; or
- Pre-treatment of surface waters where pre-chlorination would produce elevated levels of disinfection by-products.

Ozone (O_3)

O_3 is considered to be very effective for oxidizing iron and manganese. The main disadvantage of using ozone for oxidation is it must be generated on-site, requiring specialized equipment. Also, the cost of producing ozone is typically expensive. Ozone is applicable for the following conditions:

- Raw-water organic concentrations prevent the use of chlorine due to the formation of disinfection by-products;
- Insufficient detention time for use of permanganate;
- Iron and manganese causing taste and odor problems;
- Raw water bromide levels are low; or
- Complex forms of iron and manganese.

Chlorine

Chlorine can be dosed either as chlorine gas or as a solution (sodium hypochlorite or calcium hypochlorite). Chlorine is an effective oxidant for high pH conditions (>8.0), but is known to potentially form by-products (Civardi & Tompeck, 2015). Chlorine in any of its forms is generally suitable for:

- Most groundwater where water is low in organic matter and addition of chlorine will not cause disinfection by-products to exceed established limits; or
- Surface water plants that employ clarification and dual-media filtration, where the addition of chlorine after clarification can be useful in oxidizing the manganese and continuously regenerating the manganese dioxide coating that forms on the sand particles.

Oxygen (O_2)

Aeration is mainly used to remove gas from water containing hydrogen sulfide and release it into the atmosphere. Aeration also helps to oxidize iron, and at a higher dose, pH and reaction time, it can also be used to oxidize manganese. A pH adjustment system is often necessary to obtain the appropriate value for the reaction. Aeration is generally suitable for the following conditions:

- Only iron is present and there is greater than 15 minutes of detention time;
- Iron and manganese present at levels higher that 5 mg/L used with other oxidants such as chlorine or potassium permanganate; or
- Raw-water organic concentrations prevent the use of chlorine due to the formation of disinfection by-products.

Filtration

Once Mn(II) has been oxidized to form Mn(IV), filtration is required to remove the manganese precipitate from the water. The selection of the optimum filtration system is dependent on several factors such as source water (groundwater or surface water), levels of manganese, turbidity level, total organic carbon concentration and additional contaminants. Typical filtration processes that are used following oxidation include conventional treatment with media filtration (sand and anthracite), or low pressure membranes (ultrafiltration or nanofiltration).

Adsorption/Oxidation

The removal of dissolved manganese via adsorption and oxidation processes is achieved through the use of an oxidant chemical and manganese oxide coated filter media. Oxidant chemicals discussed previously (potassium permanganate or chlorine) are typically used to oxidize Mn (II). The manganese oxide coated filter media is capable of adsorbing additional Mn (II) and retaining it in the filter bed. Suitable media for manganese adsorption includes: manganese greensand, manganese dioxide-coated sand and manganese dioxide ore. Typical Media used for filtration are displayed in Table 4.

Table 4: Filtration Media Types (Civardi & Tompeck, 2015)

Pressure Filter media	Specific Gravity	Surface loading rate	pH	Cost Considerations	Media Life
Manganese Greensand	2.4	Up to 3 gpm/ft^2	>6.2	Inexpensive	Approx. 10 yr.
Manganese Dioxide Coated Sand	2.4-2.6	Up to 12 gpm/ft^2	>6.2	Cost has not increased since introduced in 2005	More than 10 yr.
Manganese Dioxide Ore	4.0*	Up to 15 gpm/ft^2	>6	Greater cost than MnO_2 coated sand	More than 10 yr.

Manganese greensand has been used for decades in North America for manganese removal. The systems are easy to operate, inexpensive and typically last a minimum of 10 years. Potassium permanganate is often used in conjunction with greensand filters for manganese removal. *Manganese dioxide-coated sand* was introduced in 2005 and can replace greensand media as a direct replacement. This media is most similar to greensand as shown in Table 4. Also, *manganese dioxide ore* has been developed as a replacement for greensand but is more expensive than manganese dioxide-coated sand and exhibits a high specific gravity which may cause issues with backwashing.

A combination of oxidant chemicals and filtration processes can be used to increase manganese removal effectiveness.

Biological Filtration

Biofiltration requires the presence of manganese-oxidizing bacteria in the biofilm that forms on the filter media. Aeration is required and a high pH of 7.5 (Civardi & Tompeck, 2015). Installation of a pH adjustment system may be required. If necessary, manganese removal can be enhanced by using a filter medium pre-coated with manganese dioxide. Also, this method is more suitable for groundwater and development of sufficient numbers of bacteria organisms may take 2-8 weeks.

PO Box 8700, St. John’s, NL Tel: 709.729.4048 Fax: 709.729.0320 pauladawe@gov.nl.ca

Membrane Filtration

Hollow-fibre membranes were specifically designed for the removal of pathogens such as Giardia and Cryptosporidium. However, particulate iron and manganese can also be removed using a membrane filter. This method is suitable for removing manganese from groundwater under direct influence of surface water and surface water where membranes are being considered as an alternative to sand/anthracite filtration. The system is also beneficial for manganese levels greater than 5 mg/L as some systems can handle up to 50 mg/L of combined iron and manganese operating in direct filtration mode and achieve a 90 percent recovery (Civardi & Tompeck, 2015). The use of a membrane filter eliminates space and eliminates the need for a clarification system.

Ion Exchange

Ion exchange is typically used as a water softening process to remove calcium and magnesium from water. Ion exchange units can be used for the removal of cations (positively charged ion) or anions (negatively charged ion) depending on the type of resin used in the unit. Manganese is a dissolved cation and this method can remove several milligrams per litre. This method requires backwashing, regeneration with a brine solution and rinsing of the resin. If oxygen or another chemical oxidant is present, oxidation of Mn (II) can occur and the precipitate can accumulate on the resin and reduce the resin's exchange capacity over time.

5. Capital Cost

An estimate for the cost of manganese removal based on community's average system flow in m^3/day is shown in Table 5.

Table 5: Cost of Fe and Mn Removal Systems (CBCL, 2017)

Average System Flow (m^3/day)	Cost
50	$52,715.94
120	$206,109.24
1250	$458,974.74

6. Path Forward

- The province needs to decide on the appropriate reaction to a MAC exceedances of Mn:
  1. Non-consumption order, or
  2. Similar to how THM/HAA exceedances are treated where the communities are not put on a non-consumption order.
- Speciation to determine what type of Mn is of concern should be conducted prior to choosing a treatment type.
- Letters explaining the impact of the change in the Mn guideline should be sent to Tier 1 and Tier 2 communities. Letters can include identified corrective measure options (i.e., Mn removal system, alternative water supply, etc.).
- A public awareness brochure for Mn should be developed.
- The province should develop a special Mn Assistance Program to help communities with capital works funding for Mn treatment systems.
- OETC should develop a special Fe/Mn treatment system curriculum.
- Undertake additional specialized Mn sampling to:

1. Determine which species of Mn is of concern in NL drinking water systems: Mn(II) or Mn(IV)
2. Determine seasonal effects on Mn
3. Determine if chlorination systems have any impact on the Mn speciation from the source to the tap

- Undertake more research into the status and trends of Mn issues in NL.
- WRMD should investigate options for manganese field meters and purchase for use in monitoring drinking water systems with high Mn levels.

7. References

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PO Box 8700, St. John's, NL Tel: 709.729.4048 Fax: 709.729.0320 pauladawe@gov.nl.ca