A FRAMEWORK FOR BETTER UNDERSTANDING DRINKING WATER QUALITY IN HAPPY VALLEY-GOOSE BAY LABRADOR: INDICATIONS FOR OPTIMIZATION

AND PROTECTION OF MUNICIPALLY SUPPLIED WATER

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A framework for better understanding drinking-water quality in Happy Valley-Goose Bay, Labrador: Implications for optimization and protection of municipally supplied water

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Disclaimer:

The information in this report is provided for informational purposes only. Although, I provide interpretation of the quality of water sources (i.e. groundwater and surface water), drinking water, and possible causes of its seasonal and spatial variations based on the data we have collected during the research period, this subject involves complex hydrochemical and physical processes, and a detailed discussion is not attempted here. Therefore, readers should not rely solely upon the research results herein for either general or specific purposes.

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MEET THE RESEARCH TEAM



Dr. Merline Fonkwe (P.Geo.) is a geoscientist – applied geochemistry and mineralogy at the Labrador Institute of Memorial University of Newfoundland. One of her main lines of research is devoted to water chemistry, stable isotopes and drinking water treatment and supply, particularly in small and rural communities. She is particularly interested in the protection of groundwater source and identification of potential physical and chemical hazards and their impact on tap water quality. The purpose of her research is to assist municipalities to develop a better

water quality management tailored to their unique water supply conditions, and thus to protect the health and well-being of local residents and foster customers' satisfaction and trust in the quality of their tap water. Dr. Fonkwe works in close partnership with community residents, municipal and private drinking water supplies, and governments.



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rocks across Labrador, in order to determine their oxide mineral compositions and textural relationships for an increased understanding of oxide formation processes.

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EXECUTIVE SUMMARY

Background:

This research project was driven by the recurring complaints and concerns voiced in the media by residents living in the Valley area of the community of Happy Valley-Goose Bay, Labrador. Drinking water in this town is supplied by two water treatment plants (a municipality treatment plant and a DND treatment plant), which use raw water from two different sources (groundwater from multiple wells versus surface water from Spring Gulch brook) and use two different processes of drinking-water treatment. In fact, the drinking water supplied in the Valley area has a unique distribution arrangement. To meet demand, the Valley area is served by a blend of treated waters from a storage reservoir (Sandhill reservoir), which is fed by both water treatment plants. Most of the time, treated water from the municipal treatment plant dominates in the mixture. As water travels through the distribution system and household plumbing, specific reactions can occur either in the water itself and/or at the solid–liquid interface at the pipe walls; this is strongly influenced by the physical and chemical characteristics of the water. These reactions can introduce undesirable chemical compounds and/or favor the growth of bacteria in the drinking water, causing the deterioration of the quality of water reaching the consumer taps. In the distribution system in general, these chemical constituents and bacteria may pose potential threats to health or the water's aesthetic qualities (smell, taste or appearance). Drinking water should be not only safe, but also palatable.

Objectives:

The focus of this research is on the Valley area of Town. The main objectives were to: (*i*) evaluate the physical parameters and the concentrations of chemical constituents of groundwater and surface water (Spring Gulch) sources and municipally supplied water in the distributions systems; and (*ii*) investigate the effects of treatment conditions, distribution arrangements, and seasonal and spatial variations on the quality of drinking water. The ultimate purpose is to assist the municipality in providing safe and aesthetically pleasing water at consumers' taps. In addition, stable isotope geochemistry was used to assess the importance of precipitation (rain or snow) for groundwater recharge and to investigate the relationships between the groundwater, Spring Gulch and the Churchill River.

Design, methodology and approach:

Water samples were collected in March, June, July and October 2015 at five key locations: (*i*) municipality treatment plant; (*ii*) DND treatment plant; (*iii*) Sandhill reservoir; (*iv*) five private households and one government building in the Valley area; and (*v*) one private household in the

northern sector of the town, which is solely served by DND treatment plant, for comparison. Moreover, an extra sampling session was done during a period over the winter, when drinking water in the town was exclusively supplied by the DND treatment plant, due to the shutdown of the municipality treatment plant for repair. This provided an additional opportunity to compare the treated water distributed by each plant, while controlling the downstream effects of the residence time to water quality in the distribution system, especially in the Valley area. Sampling locations were chosen at various distances from the Sandhill reservoir, and a variety of sampling periods (winter, spring, summer and fall) and types of tap water sample ("first draw" and "flushed") ensured that seasonal and spatial changes could be adequately described. The concentrations of 38 major and trace elements were measured together with inorganic anions, alkalinity and THMs. pH, temperature, EC, TDS and ORP were measured directly at the sampling sites. Hydrogen and oxygen stable isotope compositions were measured for water samples from raw water sources (groundwater and Spring Gulch), treated waters, rainfall, and the Churchill River.

Findings:

The physical parameters and chemical compositions of raw groundwater differed significantly amongst the supply wells and varied between the seasons. As expected, groundwater quality was considerably different to that of the surface water (Spring Gulch). Groundwater was fresh or brackish, soft or very hard with a nearly neutral pH range. Moreover, groundwater showed a change between mildly reducing (negative ORP) and oxidizing (positive ORP) conditions, indicating differences in organic material loading. Spring Gulch was fresh, soft and moderately alkaline, and showed consistent oxidizing conditions, suggesting very little accumulation of organic material. The up-gradient former landfill does not appear to have affected the quality of the water wells over the time frame of this study. Given their similar stable isotopic signatures, the groundwater, Spring Gulch and the Churchill River are likely interconnected. During the study timeframe, they were most likely recharged by snowmelt runoff in spring 2015, with lesser rainfall events during the following summer.

Groundwater was characterized by higher concentrations of Cl⁻, SO₄^{2–}, Ba, Mg, K, Na, S, Ca, Sr, Si, Fe, Mn, and Br[–] compared to Spring Gulch water; the levels of F[–] in both water sources were very low, and the other analyzed elements were not detected. Similar trends were observed in their treated (or finished) waters; yet treated water from the municipal treatment plant was consistently hard (i.e. contained high concentration of mineral substances) and showed significantly lower levels of Cl[–], SO₄^{2–}, Ba, Mg, K, Na, S, Ca, Sr, Si, Fe, Mn, and Br– than the "parent" groundwater. Removal efficiencies for Fe and Mn were higher than 90%; however, THMs formed during the

treatment process. The difference between raw and treated Spring Gulch water was negligible, except that the concentrations of F- were higher in treated water as the result of fluoridation (addition of fluoride) done at the DND treatment plant to promote dental health, and THMs also formed during the treatment process. The concentrations of total THMs and of each THM species, varied among the two treatment plants: THMs in treated water at the municipal treatment plant consisted mainly of CHCl₃, CHCl₂Br and CHBr₃ with lesser amount of CHClBr₂, whereas CHClBr₂ was the sole THM component in treated water at the DND treatment plant. Levels of total THMs in treated water at the DND treatment plant were consistently below the Canadian health-risk guideline and considerably lower than the total THMs in treated water at the municipality treatment plant; the latter exceeded the health risk guidelines at one particular time.

The physical and chemical properties of the blend of treated waters at the Sandhill reservoir, as well as those of the tap water at the distribution line in the Valley area, typically reflected the compositions of the treated waters, which dominated in the mixture. Nonetheless, the constituents in the mixture of treated waters were slightly diluted, when treated water from the municipality treatment plant dominated in the mixture; the opposite trend was observed when the majority of treated water in the mixture was from the DND treatment plant. In tap water, irrespective of the physical and chemical characteristics of the dominant treated water in the blend, the elements with the lowest variation (both seasonal and spatial) were Cl⁻, SO₄^{2–}, Ba, Mg, K, Na, S, Ca, Sr, Si, Br[–] and F^- , and those which displayed significant changes (mostly spatial, i.e. intra- and inter- household/ government building) were THMs, Fe, Mn, Cu, Pb and Zn. The first group of elements typically included naturally-occurring elements from the raw water sources, with the exception of F⁻ added to water during the treatment process at the DND treatment plant. The concentrations of F⁻ were still too low to promote dental health, although they meet the Canadian aesthetic-based standard. On the other hand, the second group of elements were either formed by the reactions between the organic matter and chlorine in water (i.e. THMs) or released by corrosion reactions with the materials of the distribution systems and plumbing inside the private households and government building (i.e. Fe, Mn, Cu, Pb and Zn). Both treated waters were corrosive, but treated water from DND treatment plant seemed to be less corrosive than the treated water from the municipality.

Although Cl– levels met the Canada aesthetic-based guideline, high hardness and levels of Fe, Mn, Cu, and Zn locally exceeding aesthetic-based guidelines would have likely justified the aesthetic problems detected by the consumers. Moreover, concentrations of total THMs increased gradually in the distribution line and locally exceeded health-risk guideline, as did Pb. These chemical constituents were found to be of the greatest concern as they (and also Cu) have been linked to health problems in both children and adults. As a mitigation strategy to lower the metal exposure,

flushing effectively reduced the levels of Cu and Zn, but did not always lower levels of Fe, Mn, THMs and Pb below the aesthetic- or health-based guidelines.

Practical implications and recommended actions:

This research provides crucial information not only on the quality of drinking water sources, but also on the variability of water quality at consumer's taps. It is intended help the municipality administrators and plant operators to develop and implement strategies for managing water quality across the distribution systems and ultimately, providing safe, aesthetically pleasant tap water. Moreover, this study provides sound baseline information on groundwater geochemical evolution to foster the sustainable management of fresh groundwater resources in coastal aquifers.

As demonstrated by our statistical analysis of consumer perceptions of tap water quality in October 2014, the results presented here also highlights some possible misconceptions of the appropriate authorities as to the extent of the chemical safety and aesthetic problems of water reaching consumer taps (which are site- specific and differ from house to house), and possible ways they can be addressed. Mitigations strategies should be evaluated and implemented at the municipal treatment plant to reduce the formation of THMs (and other chlorination disinfection by-products), as well as to combat water corrosiveness and hardness. Furthermore, the municipality's decision to add fluoride to drinking water might warrant a re-examination and systematic review, giving the low levels of naturally-occurring fluoride in groundwater source. In the meantime, the appropriate authorities should encourage residents to test their tap water for Pb (and other metals) by a certified laboratory, especially in houses built before 1990, but even in newer houses with plastic pipes and brass faucets and other plumbing fixtures. Location-specific testing is necessary because the results of this study indicate that Pb comes from materials in the houses' plumbing, not in the town's water distribution pipes, and the composition of plumbing materials varies from house to house. Moreover, residents should be encouraged to use topical fluoride (e.g. fluoridated toothpaste, varnish, gel or mouth rinse) or other measures to promote dental health, as recommended by the Canadian Dental Association.

Partner organizations and participants:

- The municipality of Happy Valley-Goose Bay
- The Canadian Forces Base 5 Wing Goose Bay
- The NunatuKavut Community Council
- Water Resource Management Division, Department of Environment and Conservation NL
- Volunteer homeowners (6 from the Valley area and 1 from the northern sector)
- Volunteer government building in the Valley area

KEYWORDS

Small and rural community water supply
Happy Valley-Goose Bay
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Tap water quality
Seasonal and spatial changes
Physical parameters
Hydrochemistry
Disinfection by-products trihalomethanes (THMs)
Total alkalinity and total hardness
Nutrients
Inorganic anions
Major and trace elements
Tap-water lead (Pb)
Stable hydrogen and oxygen isotope ratios
Groundwater recharge
Water quality management
Labrador

1. INTRODUCTION

1.1. Project background

Drinking water is absolutely essential for optimum healthy living and wellbeing, and must be kept free of undesirable chemical constituents and bacteria, which are capable of adversely impacting human health. It must not only be safe, but also aesthetically acceptable for human consumption. The quality of drinking water is determined by the physical, hydrochemical and biological qualities of water sources (i.e. surface water, groundwater or others), combined with the applied treatment process and distribution practices. Both natural processes (e.g. weathering of bedrock minerals, leaching of chemical components from soil and bedrock, surface runoff, saltwater intrusion in coastal areas, etc.) and human activities (e.g. landfill leachate, industrial and municipal wastewater discharge, etc.) can change the quality of the water source or lead to its contamination (e.g. Medema et al., 2003; Appelo and Postma, 2005; Zhu and Schwartz, 2011). In order to enable the provision of safe and pleasant water, thereby protecting human health, drinking water suppliers must adhere to Canadian and provincial guidelines (except for First Nation reserves) health- and aesthetic-based for drinking water quality (e.g. Health Canada, 2014).

While the fitness of drinking water can be determined through effective monitoring of its physical, chemical and biological qualities, standards for the protection of drinking water's aesthetic qualities are much more difficult to establish (Health Canada, 2014; World Health Organization WHO, 2011). Because the aesthetic characteristics of drinking water can be assessed directly by human senses, they provide consumers with their only empirical basis for judging the safety of at their taps (McGuire, 1995; Jardine et al., 1999; WHO, 2011). Therefore, tap water that has an objectionable smell, taste or appearance can erode the confidence of consumers in drinking water supplies, could considerably affect their attitude towards drinking water suppliers, and possibly lead to the use of water from alternative sources, such as water treated with in-home devices, commercial bottled water, and untreated water sources, such as spring, river, lake and/or ice-melt water in rural communities (Fonkwe 2015; Fonkwe and Schiff, 2016; Goldhar et al., 2013; Hanrahan et al., 2014: 2015; Kolodziej, 2004; Sarkar et al., 2015; WHO, 2011). Even though aesthetic aspects may not present as direct a health risk as microbiological contamination or the presence of organic and inorganic components, several studies have shown that these latter parameters may have an effect on or could be associated with aesthetic problems (e.g. Dietrich, 2006).

Many small and rural communities in Newfoundland and Labrador (and elsewhere in Canada) are facing drinking water access and/or quality problems, mainly due to the lack of: (*i*) government

water treatment systems and/or adequate treatment technologies to remove contaminants; (*ii*) fully trained and qualified operators of water treatment facilities; (*iii*) protection of water resources; and (*iv*) management capacity and financial resources (Dunn et al., 2014; Goldhar et al., 2013; Guilherme and Rodriguez, 2014; Lightfoot, 2014; Minnes and Vodden, 2014; Scheili et al., 2015; White et al., 2012). Happy Valley-Goose Bay, the largest community in central Labrador, is not an exception to the at times poor acceptability of small communities' drinking water, as demonstrated by some consumers' complaints voiced in traditional news and social media. Figure 1 gives images from the Happy Valley-Goose Bay in local newspaper, *The Labradorian* and local CBC News for a period between 2008 and 2015. Typical water quality concerns reported by residents are about the aesthetic qualities, safety and healthiness of their tap water, its corrosion of household appliances, and/or the number of boil water advisories.

The residents' complaints and concerns triggered the development and implementation of this research project and the ultimate goal of Part 2 (the subject of this report) is to shed some light on the question "Is it safe to drink?" As for Part 1 of this research, the focus was an online survey questionnaire conducted in October 2014 to measure (quantitatively and qualitatively) residents' satisfaction and acceptance of drinking water in Happy Valley-Goose Bay. The survey research showed that most of respondents resided in the Valley area of town and in general, have indicated dissatisfaction with the quality of their tap water, corroborating the complaints in the media (Fonkwe, 2015; Fonkwe and Schiff, 2016). This represented a convincing indication of the need for an evaluation of the quality of drinking water supplied by the municipality, specifically in the Valley area, to assess whether or not consumer perceptions of tap water quality are correlated with measured physical and chemical water quality.

Drinking water in the Valley area is a blend of treated waters from two water treatment plants, the municipal treatment plant and the Department of National Defence (DND) treatment plant, which draw their raw water from two different types of sources (groundwater from multiple wells versus surface water) and therefore use two different treatment processes. The municipality has found it difficult to maintain water quality across the distribution line throughout the Valley area. Although this blending arrangement has been practiced since the municipal water treatment plant began operation in 2002, systematic investigations have yet to be undertaken concerning the seasonal and spatial changes of the physical and hydrochemical qualities of the water sources, drinking water in the distribution lines in the Valley area. The present research fills in these data gaps and provides critical information for municipality administrators and plant operators to tailor their actions in order to improve the safety and pleasantness of water at consumer taps.

"Residents upset at water quality" - *The Labradorian, December 15, 2008.*



In-house water filter system completely covered in an orange residue after only two months usage -Courtesy Jenny McCarthy.

"Happy Valley-Goose Bay residents concerned over tap water quality" - The Labradorian, January 06, 2014.



Tap left running overnight to prevent her water lines from freezing turned brown a white face cloth put in the sink - Courtesy Derek Montague.





(A) Difference between new filters (white) for a reverse osmosis water filtration system and the old filters covered with a brownish "slimy" substance). (B) Corroded part of a two-year-old water heater - Courtesy Derek Montague.

"Labrador business owner wants refund for disgusting water" - CBC news on July 3, 2015.



A full bathtub showing water quality in Happy Valley-Goose Bay after an annual flushing of water service lines (Photo from CBC New July 03, 2015).

Figure 1: Selected photographs reported in local newspapers and radio between 2008 and 2015, referring to the complaints and concerns about the quality of their tap water from residents living in the Valley area.

1.2. Research rationale and motivation

Before treated water reaches consumer taps, it must pass through a distribution system. One challenge facing suppliers is that water quality (microbiological, physicochemical and aesthetic parameters) tends to worsen along the way. Given that the municipality has found it difficult to maintain water quality during distribution throughout the Valley area of the town, despite the care taken to provide residents with safe and aesthetically pleasant tap water, it is critical to address resident concerns about the quality and safety of their tap water. Giving that protection measures taken at water treatment plants can be very expensive, it is advantageous to investigate the physical and hydrochemical qualities of water from the point-of-collection (water treatment plants and reservoir) to the point-of-use (i.e. at the household faucets), in order to provide decision-making personnel with the necessary information to implement strategies for managing water quality across the distribution systems.

This research will contribute critical information for a better understanding of local water treatment and distribution arrangements, because it integrates a holistic sampling approach to provide new information regarding the current situation of drinking-water quality in Happy Valley-Goose Bay. Moreover, given the fact that a former landfill site is located up-gradient from the groundwater supply wells and that hydroelectric power generating facilities under construction on the Churchill River may affect the groundwater quality of the public supply-wells, it is necessary to understand the processes controlling groundwater geochemical evolution in order to assess the degree of vulnerability to pollution for long-term management strategies.

1.3. Research objectives

The main aim of this project was to investigate the seasonal and spatial variations of the physical and hydrochemical qualities of water sources and municipally supplied drinking water in the distributions systems. The ultimate purpose is to examine the effects of treatment conditions and blending of treated waters on the quality of tap water Valley and to assist the municipality to provide safe and aesthetically pleasing water at the consumer' taps. In addition, stable isotope geochemistry was used to investigate the origin of groundwater source and its relationship with Spring Gulch and the Churchill River. The research involves the following tasks:

1. Consulting with community residents and local organizations at various stages of the research project.

- 2. Identifying and selecting sampling locations, and recruiting volunteer homeowners in targeted areas of the distribution network (i.e. tap water in private households and a government building).
- 3. Performing test analyses of water samples for the disinfection by-products trihalomethanes (THMs) by gas chromatography-mass spectrometry (GC-MS) at the Stable Isotope Laboratory of Memorial University of Newfoundland; and selecting reference laboratories for the analysis of inorganic anions, alkalinity, major and trace elements and stable isotopes.
- 4. Collecting water samples in winter, spring, summer and fall, and analysing water samples for THMs, 39 major and trace elements, 7 inorganic anions, alkalinity and stable isotopes of hydrogen and oxygen; and also measuring physical parameters (pH, temperature, electrical conductivity, total dissolved solids and oxidation-reduction potential).
- 5. Investigating the quality of drinking water sources (5 groundwater wells and surface water), and the changes in physical parameters, THMs, inorganic anions, and major and trace elements of treated drinking water, as functions of treatment and distribution parameters, both seasonal and spatial (within and between private households and the government building along the distribution system toward the system's extremity).
- 6. Determining the stable isotope ratios for hydrogen and oxygen in groundwater and Spring Gulch water sources, as well as in rainwater and the Churchill River (which borders the groundwater wells).

The outcomes of this research are intended contribute to: (*i*) improving water quality management and providing a reliable supply of safe and aesthetically acceptable drinking-water to consumers; (*ii*) building and maintaining consumer confidence; (*iii*) promoting and protecting the health and well-being of residents; (*iv*) planning for a sustainable drinking groundwater resource; and (*v*) training highly qualified personnel.

1.4. Knowledge mobilization and deliverables

The development and implementation of this research project involved several consultations with volunteer homeowners and meetings with local government organizations. Research findings have been presented to audiences in the local community at Labrador Institute of Memorial University in Happy Valley-Goose Bay and at the Municipality of Happy Valley-Goose Bay. One abstract submitted in February 2016, has been accepted for oral presentation at the upcoming National Water and Wastewater conference 2016 organized by the Canadian Water and Wastewater Association (CWWA) in Toronto (ON), November 13–16, 2016. Moreover, three additional

manuscripts are in advanced stages of development and preparation. Copies of all papers will be given to the Harris Centre upon their publications.

Specific deliverables provided to date include:

- Kyla Penney and Merline Fonkwe (2016): Summer Research Program: Evaluation of the groundwater source of drinking water and Iron ore mineralogy. The Labrador Institute of Memorial University, Happy Valley-Goose Bay, NL (*August 11, 2016*).
- Merline Fonkwe and Rebecca Schiff (2016): Is it safe to drink? Residents' perceptions and hydrochemical characteristics of municipally-supplied tap water in the Valley area of the community of Happy Valley-Goose Bay, Labrador. 2016 National Water and Wastewater Conference, Toronto (ON), November 13–16, 2016 in Toronto (*submitted on February 2016; accepted on June 2016 for presentation on November 15, 2016*).
- Danielle Spearing and Merline Fonkwe (2015): Assessment of drinking water quality in Happy Valley-Goose Bay. The Labrador Institute of Memorial University, Happy Valley-Goose Bay, NL (*August 13, 2015*).
- Merline Fonkwe (2015b): Assessment of municipally-supplied drinking water in the community of Happy Valley-Goose Bay, Labrador: Preliminary results. Meeting with the councillors of the municipality of Happy Valley-Goose Bay, NL (*July 15, 2015*).
- Merline Fonkwe (2015a): A framework for better understanding drinking-water quality in Happy Valley-Goose Bay, Labrador: Implications for optimization and protection of municipally supplied water. Midterm Project Report to the Harris Centre of Memorial University (*March 27, 2015*).

In addition, the project has also gained attention from local media, including a newspaper article published on August 1, 2014 and February 29, 2016 in *The Labradorian* Happy Valley-Goose Bay (NL), and an interview of the project leader and principal investigator Dr. Merline Fonkwe by the local CBC radio on August 25, 2014. The project was featured in news releases by the Municipality of Happy Valley-Goose Bay in July 3, 2015 and February 23, 2016.

2. STUDY AREA: THE COMMUNITY OF HAPPY VALLEY-GOOSE BAY

2.1. Physiography and climate

Happy Valley-Goose Bay is a small, remote community in the province of Newfoundland and Labrador (53°30' N and 60°41' W; Fig. 2). It covers an area of 306 km² and has a population of about

8000. The Town is divided into two parts: the northern sector (which is broken down into five neighbourhoods including the Canadian Forces Base (CFB) 5 Wing Goose Bay, the North Side, Dock/Terrington Basin, Spruce Park, and MOT/Hamilton Heights, and the down slope Valley area (subdivided into Upper Valley and Lower Valley) (Fig. 3). The climate is subarctic, marked by heavy snowfall from November to March with snow covering the ground from November to May and high rainfall from June to September (average annual precipitation of 762 mm). The average daily temperatures remain below freezing from November to April and vary between –17.6°C and 15.5°C.

The community of Happy Valley-Goose Bay is home to CFB 5 Wing Goose Bay (Fig. 3). This military air force base was constructed in 1941 on a flat-lying terrace, which has an elevation between 40 to 50 m above sea level and is bordered by the Terrington Basin to the north and the Churchill River to the south. CFB 5 Wing Goose Bay operates its own water treatment system and landfill, among others and provides supplies part of its potable water to the municipality. Before 1990, a variety of residential and industrial wastes generated at CFB 5 Wing Goose Bay were disposed of on-site at several dumping areas making up a poorly-regulated and unlined landfill along the escarpment at the south-southeast boundary of the military property (AMEC, 2009; JWEL, 1992; see Fig. 3). This former landfill site is known to be contaminated by organic and inorganic chemicals leaching from wastes (see Figs. 3 and 4; Fonkwe, 2016; Fonkwe and Trapp, 2016). Groundwater from the landfill site is unconfined and flows south to southeast towards the Churchill River, following low topography (AMEC, 2009; Figs. 3 and 4).

2.2. Surface and bedrock geology

Happy Valley-Goose Bay lies at the western extremity of Lake Melville, an inlet of the Labrador Sea that runs over 100 km inland. In this area, Lake Melville is surrounded by lowland, gently sloping down toward the lake with very low relief (see Liverman, 1997, and references therein). This contrasts with the bedrock-dominated highland plateaux that rise abruptly from this coastal plain. These plateaux are heavily vegetated and reach elevations of greater than 300 m above mean sea level. Lake Melville is fed by the Churchill River, Goose River and Grand Lake and many other rivers. Landforms in the north and southwest are high and those in the southeast are low. Surficial geology consists of about 100 m thick Quaternary marine and fluvial sediments (Liverman, 1997). These sediments are inferred to overlie the terrestrial red-bed sequence of the Double Mer Formation composed of mostly conglomerate and sandstone, and in places interbedded with thin layers of siltstone and shale (Wardle, 1994; Nunn and van Nosttrand, 1996). Bedrock outcrops are rare at lower elevations (Liverman, 1997). Bedrock is composed of a Paleoproterozoic anorthosite-

mangerite-charnockite-granite suite and the massif anorthosite of the Cape Caribou River Allochthon (Valvasori et al., 2015; Wardle and Ash, 1986).



Figure 2: Map of Canada showing the location the community of Happy Valley-Goose Bay.

2.3. Drinking water supply in the community of Happy Valley-Goose Bay

The community of Happy Valley-Goose Bay is supplied the municipal treatment plant, (locally called *Well Field*) and the treatment plant (locally called *Spring Gulch*) of CFB 5 Wing Goose Bay, maintained by DND (Figs. 3 and 4). The water distribution system's piping material throughout the town consists of cast iron and ductile iron for the water main lines that connects the treatment plant or the reservoirs to the looped pipe network in the streets, and copper pipes for service lines that connect the water main lines to the customers' property lines (F. Brown, pers. comm. June 09, 2014).

DND treatment plant primarily supplies water to CFB 5 Wing Goose Bay and the northern sector of the town (Fig. 3). The rest of the town, the Valley area, is served solely by a blend of treated water from a storage reservoir fed by the two water treatment plants; the municipal treatment plant serves only this storage reservoir (Fig. 3). This unique mixture of treated groundwater and surface water sources varies in blending ratios depending on water consumption demand (peak water use typically during the summer months) or in occasional periods solely by either the municipal treatment plant during low water consumption periods or the DND treatment plant during

shutdown of the municipality water treatment plant for maintenance and repair (as it was the case in February 2015 during the course of this study). In general, the municipal treatment plant meets in average 65% of the town's total water needs, while DND treatment plant supplies the remaining 35% of the water at Sandhill reservoir.



Figure 3: Map (from Google Earth) showing the main parts of town in Happy Valley-Goose Bay and locations of the drinking water treatment and storage facilities of this research interest. Note the former landfill site highlighted in red.

2.3.1. Municipal water treatment plant

The municipal water treatment plant is located 6.5 km west of the town, between the Trans Labrador Highway and the Churchill River, downstream of a former landfill site (Figs. 3, 4 and 5). It has been operated since 2002, using blended water from five groundwater supply wells for its water supply. The groundwater wells are located close to one another in the vicinity of the treatment plant, bordered by the Churchill River, on which a hydroelectric dam complex is currently under construction (Fig. 3 and 4). These wells, named Well #1, Well #2, Well #3, Well #4 and Well #5, reach down between 130–170 feet (ft) through the thick Quaternary marine and fluvial sediments composed of silty clay layers underlain dominantly by fine-grained sand layers (Liverman, 1997; Wardle, 1994; Nunn and van Nosttrand, 1996). The water recharge area is likely extensive and primarily includes areas north of the Churchill River (e.g. NL Water Resources Management Division, 2011).



Figure 4: Map (from Google Earth) showing the location of the groundwater wells and the Spring Gulch brook impoundment. Note the proximity of the groundwater wells to the Churchill River and their locations downstream of a former landfill site.

As is typical in most coastal areas, the groundwater aquifer is composed of freshwater (or terrestrial water) underlain by more dense saltwater, as the result of seawater intrusion (see Fig. 6 modified after Gale et al., 2004). For this reason, water is pumped from Well #1 (168 ft), Well #2 (depth unknown), Well #3 (136 ft) and Well #4 (143 ft) using a dual-pump configuration system: an upper pump extracts water from the freshwater layer at the top of the water column and transfers it into the plant, while a lower pump removes the denser and saltier water from the bottom of the well and discharges it as waste in the Churchill River (Figs. 5 and 6; Gale et al., 2004; M. Clarke, pers. comm., March 2015). In contrast, pumping at Well #5 (155 ft) is accomplished with one pump, which withdraws water, which is transferred into the plant (M. Clarke, pers. comm., March 2015). Well #1 is the oldest among the supply wells and supplies most of the raw water to the plant (M. Clarke, pers. comm., March 2015). The groundwater is classified as sodium-chloride type water (NL Water Resources Management Division, 2011). This indicates that a mixture of freshwater and saltwater is transferred into the plant.



Figure 5: The municipal water treatment plant, also called "Well Field".



Figure 6: Schematic of the well dual-pump configuration at the municipal water treatment plant (Modified from Gale et al., 2004).

At the municipal treatment plant, water treatment is typically an iron and manganese removal process, also referred to as a direct filtration process (K. Murphy at CBCL Limited, pers. comm., March 2016). Unlike the conventional treatment process, direct filtration doesn't have a sedimentation step, which allows large particles to settle out naturally, prior to the filtration step; therefore, all the particles removal takes place on the filters. Thus, direct filtration process is recommended primarily for the treatment of raw water, which has fairly consistent quality, very low turbidity (5 to 15 NTU) and color (20 to 40 units), and low concentrations of iron and manganese (e.g. Spellman, 2013)

Groundwater is pumped simultaneously from Well #1, Well #2 and Wells #3-4-5 and fed to the base of one reactor vessel, where the chemicals are added (Fig. 5). Then, the water is transferred simultaneously into three filter vessels. Steps for water treatment process are as follow (K. Murphy at CBCL Limited, pers. comm., March 2016):

Step 1 - In the reactor tank:

- *Oxidation* by adding chlorine dioxide (ClO₂) at the beginning of the treatment process to: (*i*) convert dissolved forms of iron and manganese into particulate forms that can be coagulated and filtered; (*ii*) disinfect the water (i.e. kill disease-causing bacteria); and (*iii*) eliminate taste and odor compounds (mainly organic matter) in water.
- *Coagulation-flocculation*: by adding aluminum sulfate [Al₂(SO4)₃] or "alum" to react with small particles in the water and form particles large enough to be filtered out at the next step.

Step 2 - Simultaneously in the three filtration tanks:

• *Removal of iron and manganese* using a greensand filtration system through three filter tanks, which are continuously regenerated by the injection of potassium permanganate (KMnO₄) as the water leaves the reactor vessel, to attract and hold iron and manganese particles.

Step 3 - Treated (or "finished") water on-site storage and distribution:

- *pH adjustment* by injecting calcium hydroxide or lime [Ca(OH)₂] to quickly increase the pH of water that is ready to be distributed;
- *Temporary storage* in the underground reservoir (or clear water well) at the treatment plant site. Depending upon the water demand, the treated water is sent to Sandhill reservoir, a concrete underground reservoir located 7 km from the plant, where water is blended with water from the DND treatment plant. The blended treated water is then sent into the distribution line, which serves the Valley area of the town (Figs. 3 and 8).

Filters are frequently cleaned using a backwash process by which treated water flows upward to flush out accumulated particles; the backwash process stars automatically after a set volume of water is filtered. The slurry sludge released from the filters during backwashing is carried away from the water treatment lines through the backwash line and stored in two underground backwash holding tanks for about a day, during which time the suspended solids settle to the bottom. Then, the supernatant waste-water is drawn off the tanks and discharged into the Churchill River, while the wet residues are gravity drained and stored in two drying beds at the vicinity the plant. Such residues from the water treatment process typically contain minerals and organic matters removed from the raw groundwater, together with the chemicals used during the treatment process. Therefore, consideration should be given to the residue nature and toxicity for appropriate disposal.

The municipal treatment plant is equipped with monitoring equipment for daily sampling and testing of treated water for free chlorine, total chlorine, turbidity and pH to assist with operational decision-making. Free chlorine, which is the concentration of residual chlorine present in treated drinking water as dissolved gas (Cl₂) varied in concentrations between 0.77 and 1.08 milligrams per liter (mg/L) during the sampling period (Table 1). Because chlorine is not stable in water, free chlorine is monitored at representative points in the distribution system by the municipal plant operators. Drinking water is also tested quarterly for trace elements and chlorination disinfection by-products, THMs and haloacetic acids (HAAs) by the Water Resources Management Division of the Department of Environment and Conservation in Happy Valley-Goose Bay (G. De Beer, pers. comm., March 13, 2014). All data are archived at the water treatment plant or through online at the Newfoundland and Labrador Water Resources web portal at <u>http://maps.gov.nl.ca/water/</u>.

2.3.2. Water treatment plant of the Department of National Defence

The DND water treatment plant is located within the CFB 5 Wing Goose Bay property. It was constructed in 1952 and upgraded in 1994 (Figs. 3, 4 and 7). It withdraws raw water from an impoundment of the Spring Gulch brook, which flows from a small, discrete watershed located upgradient to the town. Spring Gulch originates from a combination of rainfall, surface runoff and local groundwater discharge (NL Water Resources Management Division, 2011). Water from Spring Gulch is classified as calcium-bicarbonate type water, suggesting that the water has quick travel times from recharge points and therefore, short contact times with local surficial sediments and other materials (e.g. NL Water Resources Management Division, 2011; AECOM, 2013). The DND treatment plant is located beside the Spring Gulch brook and the water is directly pumped into the plant (as indicated by the arrow in Fig. 7).

The treatment process at the DND treatment plant is typically a purification method. Spring Gulch water is pumped from the Spring Gulch brook and is treated as it flows continuously through the pipes into the underground clear water well (Figs. 3, 4 and 7). The treatment process includes the following steps (DND treatment plant staff pers. comm., October 2015):

- 1. *Filtration* to remove particulate matter from the water;
- 2. *Ultraviolet (UV) disinfection* to kill or prevent the reproduction of disease-causing bacteria, which may be resistant to chlorine;
- 3. *Chlorine disinfection*, using chlorine gas (Cl₂) to ensure the water is free from microbiological contaminants (such as bacteria); and
- 4. *Fluoridation and storage*, addition of a fluoride compound into treated water to help promote dental health, followed by temporary storage in an underground reservoir near the treatment plant site. The water is then distributed to CFB 5 Wing Goose Bay, the northern sector of the town and the Sandhill reservoir, where it is mixed with the treated water from the municipal treatment plant (see Fig. 8).

The authorities of CFB 5 Wing Goose Bay are responsible for routine testing and monitoring of drinking water quality. Free chlorine concentrations in summer and fall were 0.90 and 1.08 mg/L, respectively.



Figure 7: Water treatment plant of the Department of National Defence, also called "Spring Gulch".

3. METHODOLOGY

3.1. Sampling design and approach

A total of 175 samples were collected between March and October 2015 during each of the four seasons, as divided under the Drinking Water Quality Monitoring and Reporting for Public Water Supplies in Labrador by the NL Department of Environment and Conservation: "winter" (January 1st–March 15th), "spring" (May 1st–June 30th), "summer" (July 1st–August 30th), and "fall" (October 1st–November 15th). The main focus of this project was the municipally supplied drinking water in the Valley area of the town. However, sampling was also done at one location in the northern sector of the town (see Fig.3), served by DND treatment plant for comparison. Also for comparison, an extra sampling session took place in winter (March), when the entire town was supplied with drinking water solely from the DND treatment plant, due to the shutdown of the municipal treatment plant for repair. During the timeframe of this study, the percent blends of the treated waters from the municipal and DND treatment plants, varied considerably. Table 1 summarizes the percentages of both treatment plants in the blended water at Sandhill reservoir, together with concentrations of free chlorine residual (Cl₂) provided by each treatment plant.

Table 1: Free chlorine residual (the concentration of residual chlorine, which is present in treated drinking water as dissolved gas, Cl₂) and percent blends of the treated water at Sandhill reservoir recorded during the timeframe of this study. *Free chlorine range for summer and fall only.

		Free	Percent (%) blend at Sandhill reservoir								
			Wi	nter							
			1st sampling	2nd sampling	Spring	Summer	Fall				
Water	MUNICIPAL Source: Mix of groundwater from Wells #1, #2, #3, #4 and #5 <i>Treatment Process</i> : Oxidation, coagulation-flocculation, filtration and pH adjustment	0.77 – 1.08	0	5 (Well #4 not in operation)	60	88	90				
treatment plant	DND Source: Surface water from Spring Gulch brook Treatment process: Filtration, UV and chlorine disinfection, and fluoridation to help promote dental health	0.90 - 1.0*	100	95	40	12	10				

Water samples were collected at: (*i*) both water treatment plants; (*ii*) Sandhill reservoir; (*iii*) five private households and one government building in the Valley area; and (*iv*) one private household in the northern sector (Fig. 8; Table 2). A single pipeline is used to transfer water from Wells #3, #4 and #5 into the plant and therefore the wells cannot be sampled separately. Thus, only their resulting mix samples were analyzed. Permission to access the DND treatment plant was granted only during summer and fall sampling sessions, and therefore water samples were not collected in winter and spring. In the Valley area, the households and government building were selected at increasing distance up to 7 km from the Sandhill reservoir to capture the location changes (temporal changes) in the tap water quality. The selected private households and government building were between 2 and 65 years old at the timeframe of this study (i.e. year 2015). Their plumbing (below the kitchen sink) were made of either copper pipes, plastic pipes or a mix of copper pipes and pipes with other metal alloys.



Figure 8: Sketch map (which is not to scale) showing the locations of the municipal and DND treatment plants, and selected households (H1, H2, H4, H5, H6 and H7) and the government building (H3) in the distribution systems, served by the two treatment plants. (Sketch map prepared by Danielle Spearing).

3.2. Sample collection, preservation and analytical methods

Spring and summer sample collections were conducted by the research assistants, Daniel Frawley and Danielle Spearing, under the supervision of Dr. Merline Fonkwe; the sampling in winter 1, winter 2 and fall was done by Dr. Fonkwe alone. All collected samples were kept at temperatures below 4°C and analyzed within 4 to 10 days for major and trace elements, inorganic anions and total alkalinity, and 1 or 2 days for THM compounds. Table 2 summarizes the characteristics of the sampling sites and description of the water samples collected with respect to water source, age of the private households and government building, in-house plumbing materials, and distances from the treatment plants or Sandhill reservoir.

At each sampling location, water were collected from the kitchen cold-water faucet, because this is where water is drawn most often for drinking and cooking. Two types of water samples were collected: (*i*) a "first-draw" sample representing water, which has been sitting in the house plumbing system overnight or for at least six hours to determine whether the quality of household-specific tap water was affected by the in-house plumbing; and (*ii*) a "flushed" sample taken after running the cold water faucet for five minutes to flush out the stagnant water in contact with the in-household pipes and other plumbing fixtures in order to access water from the main drinking-water distribution line. This sample determines whether the municipal water distribution system and distances from the Sandhill reservoir or the DND treatment plant influence the tap water quality. Collected samples were in total, 60 samples in Winter 1*, 78 samples in Winter 2, 80 in spring, 81 samples in summer and 78 samples in fall.

Major and trace elements

106 water samples were analyzed for their total content (sum of dissolved and suspended) of 38 major and trace elements. The concentrations are expressed in mg/L for both major and trace elements. The collected samples consist of raw groundwater (12), raw surface water source (4), treated water at the municipal treatment plant (4), treated water at the DND treatment plant (2), municipally-supplied treated water at the Sandhill reservoir before blending (4), DND-supplied treated water at the Sandhill reservoir before blending (6), blended treated water at the Sandhill reservoir (4), tap water (60) in the Valley area, and tap water (10) in the northern sector (see Fig. 8; Table 2). Both "first-draw" and "flushed" samples were collected at the households and government building taps, whereas only "flushed" samples were taken at the treatment plants and at Sandhill reservoir (Table 2). All samples were collected in 125 mL High Density Polyethylene (HDPE) plastic bottles containing 1.5mL of 18% nitric acid (HNO₃) for immediate adjustment of the sample pH to less than 2, in order to preserve trace metals and reduce precipitation, microbial

activity and sorption losses to sampling container walls. Analysis was done by inductively coupled plasma mass spectroscopy (ICP-MS) at ALS Environmental laboratory (Mississauga, Canada), following the United State Environmental Protection Agency (U.S. EPA) method 200.8 (U.S. EPA, 1994). The obtained concentrations of major and trace elements are mg/L.

Total alkalinity and inorganic anions

65 water samples were analyzed for total alkalinity (as CaCO₃) and the concentrations of 7 inorganic anions. The collected samples consisted of raw groundwater source (12), raw surface water source (4), treated water at the municipal treatment plant (4), treated water at the DND treatment plant (2), municipally-supplied treated water at the Sandhill reservoir before blending (4), DND-supplied treated water at the Sandhill reservoir before blending (6), blended treated waters at the Sandhill reservoir (4), tap water (30) in the Valley area, and tap water (5) in the northern Sector (see Fig. 8; Table 2). Only "flushed" samples were collected in 250 mL HDPE plastic bottles. Analysis of inorganic anions was done by ion chromatography following the EPA method 300.0 (Pfaff, 1993), except that orthophosphate content was determined by a colorimetric technique, following the American Public Health Association (APHA) Method 4500-P B.E. (APHA, 1999). Water alkalinity (as CaCO₃) was determined by autoanalyzer following the EPA method 310.2 (U.S. EPA, 1974). All the samples were analyzed at ALS Environmental laboratory (Mississauga, Canada). The obtained concentrations for the total alkalinity and inorganic anions are reported in mg/L.

Trihalomethane compounds

55 water samples were analyzed for the four THM compounds: chloroform (CHCl₃), dibromochloromethane (CHClBr₂), bromodichloromethane (CHCl₂Br) and bromoform (CHBr₃). The focus was on "flushed" treated water samples to investigate the spatial variation of THMs concentrations across the municipality main distribution systems and the relationship between treatment conditions, quality of treated water, blending of treated waters, the location of sampling sites along the distribution systems (distance from Sandhill reservoir and DND treatment plant) and the formation of THMs. In addition, a water sample was collected from one hot water faucet in winter 2 sampling session to compare its THM content with that of water sample from cold water faucet at one household. Samples were collected in duplicate, following the method described by U.S. EPA (1998), at the municipal treatment plant (4), DND treatment plant (2), municipallysupplied treated water at the Sandhill reservoir before blending (5), DND-supplied treated water at the Sandhill reservoir before blending (5), blended treated waters at the Sandhill reservoir (4) and tap water in the Valley area from Sandhill reservoir (24), and tap water (5) in the northern sector (see Fig. 8; Table 2). Flushed samples were collected in 60 mL glass vials containing 1.00 g of a buffer mixture of potassium phosphate and sodium phosphate (KH₂PO₄/Na₂HPO₄ 99:1) and 6.0 mg

Table 2: Characteristics of the sampling sites and description of the collected samples and the measured physical and hydrochemical parameters. Details are given in the text.*Refers to the pipe materials from the wall and connector to the faucets under the kitchen sink. ** From hot water faucet.

Sampling sites		Water source	Sample collected	Type of water sample collected for analyses	Measured physical and hydrochemical parameters									
					Physical parameters					Alkalinity	Major			
					pН	Τ°C	EC	TDS	ORP	and inorganic anions	and trace elements	THMs	Stable isotopes	
DND treatment plant		Surface water, Spring Gulch	A0a	Raw (untreated) water from the impoundment	~	~	~	 	 	\checkmark	\checkmark		\checkmark	
			A0b	Raw water inside the plant - flushed	~	~	~	~	 Image: A start of the start of	\checkmark	\checkmark			
			A1	Treated water - flushed	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark		
Municipal treatment plant		Mix of groundwater from 5 wells	Well #1	Raw water inside the plant - flushed	~	~	\checkmark	~	\checkmark	\checkmark	\checkmark		\checkmark	
			Well #2	Raw water inside the plant - flushed	~	~	>	~	~	\checkmark	\checkmark		\checkmark	
			Mix of Well #3-4-5	Raw water inside the plant - flushed	~	~	~	~	~	\checkmark	~		\checkmark	
			B1	Treated water - flushed	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark		
Sandhill reservoir 7 km from municipal treatment plant/8 km from DND treatment plant		Treated Spring Gulch water	A2	Treated water from DND treatment plant - flushed	~	~	✓	~	~	~	~	~	\checkmark	
		Treated mixed groundwater	B2	Treated water from the municipal treatment plant - flushed	~	~	~	~	~	~	~	~	~	
		Blend of treated Spring Gulch water and treated mixed groundwater	A2+B2	Blend of treated waters from the municipal and DND treatment plants - flushed	~	~	~	~	~	~	~	~		
	H1 Age 2/ 3.5 km from Sandhill reservoir/plastic pipes*	H1 Age 2/3.5 km Blend treated waters	H1-0	First-draw							\checkmark			
Private		from Sandhill from Sandhill	H1-1	Flushed	✓	✓	~	✓	✓	~	✓	✓		
households (age at the		reservon	H1-2	Flushed**								\checkmark		
time of sampling in 2015)	H2 Age ~15-20/4 km from Sandhill reservoir/cooper pipes and metal faucet connector*	/ 4 km Blend treated waters from Sandhill	H2-0	First-draw							~			
,		reservoir/cooper pipes and metal faucet connector*	reservoir	H2-1	Flushed	~	~	✓	~	~	~	~	~	
	H4 Age 15/ 5 km from Sandhill	Blend treated waters from Sandhill reservoir	H4-0	First-draw							~			
--	---	--	------	------------	---	---	---	---	---	---	---	---	---	
	reservoir/ cooper pipes and metal faucet connector*		H4-1	Flushed	~	~	~	~	~	~	~	×		
	H5 Age 65/ 6 km	Blend treated waters from Sandhill reservoir	H5-0	First-draw							~			
	reservoir/copper faucet connector*		H5-1	Flushed	~	~	~	~	~	~	~	~		
	H6 Age 50/ 7km from Sandhill	Blend treated waters	H6-0	First-draw							~			
	reservoir/copper faucet connector*	reservoir	H6-1	Flushed	~	✓	~	~	✓	~	~	✓		
	H7 Age ~40-50/ 6km from DND reservoir/copper faucet connector*	Treated water from DND plant	H7-0	First-draw							~			
			H7-1	Flushed	~	~	~	~	~	~	~	~		
Government building (Age in 2015)	H3 Age 42/ 3 km from Sandhill reservoir/ copper faucet connector*	Blend treated waters from Sandhill reservoir	H3-0	First-draw							~			
			H3-1	Flushed	~	~	~	~	~	~	~	~		
Rainfall													×	
Churchill River													✓	

ammonium chloride NH4Cl for immediate preservation and dechlorination; the vials were closed with polytetrafluoroethylene (PTFE)-lined septa lined screw caps. All the water samples were analyzed at the Stable Isotope Laboratory, Memorial University of Newfoundland in St. John's by Dr. Geert Van Biesen by gas chromatography-mass spectrometry (GC-MS), following a modified EPA Method 551.1, which includes liquid–liquid extraction with Methyl Tertiary Butyl Ether (MTBE) (U.S. EPA, 1998). The concentrations of each individual THMs compound, as well as the sum of these four compounds, are reported in micrograms per litre (µg/L).

Physical parameters

The physical parameters, pH, temperature (T°C), electrical conductivity (EC), total dissolved solids (TDS) and oxidation-reduction potential (ORP) were measured immediately after the collection of "flushed" samples at the sampling site, because they are unstable and change during storage and transport (see Fig. 8; Table 2). A Hanna Instruments (HI) multiprobe HI 98129 meter was used for pH (±0.05 pH @ 20°C), T°C (±0.5 °C @ 20°C), EC (±2% full scale @ 20°C) and TDS (±2% full scale @ 20°C), whereas an HI 98120 meter was used for ORP (±2 mV @ 20°C). Both testers were calibrated and checked every day before sampling. The HI 98129 was calibrated using calibration solutions, including pH buffer solutions 4.01 (HI 7004) and 7.01 (HI 7007) and conductivity solution 1.413 mS/cm (HI 7031); the meter was not calibrated in TDS, since there is a known relationship between EC and TDS readings. HI 98120 is factory calibrated and was checked using ORP test solutions 240 mV (HI 7021) and 470 mV (HI 7022). Because EC/TDS depends on the measured water temperature, the obtained values were automatically corrected to the standard temperature value of 25°C.



Figure 9: Kyla Penney measures physical parameters of groundwater at the municipal water treatment plant.

Hydrogen and oxygen stable isotopes

Water samples were collected in spring and summer from groundwater wells and Spring Gulch impoundment, as well as from rainfall and the Churchill River bordering the groundwater wells to

determine the importance of precipitation (rainfall and snowfall), with respect of the origin of the recharge water for the groundwater source and its relationships with surface water bodies, i.e. Spring Gulch and the Churchill River (Table 2). All samples were collected in 20 ml scintillation glass vials with rubber-lined screw-top caps. Filled vials had tape wrapped around the caps to prevent caps from coming loose and the sample becoming evapoconcentrated. Hydrogen and oxygen isotopes were measured using a gas stable isotope mass spectrometer at Isotope Tracer Technologies Inc. (IT2) in Waterloo, Canada. Results are expressed in parts per thousand (‰) as ratio of the heavy to light isotope of hydrogen (δ^2 H) and oxygen (δ^{18} O) relative to the Vienna Standard Mean Ocean Water (VSMOW) reference. The precision for δ^2 H and δ^{18} O were ±1.0‰ and ±0.1‰, respectively.

3.3. Quality assurance and quality control

For quality assurance and quality control (QA/QC), "blind" duplicate samples collected at a frequency of 10% of the total number of samples were used to monitor analytical performance in addition to the laboratory quality for alkalinity, inorganic inions, major and trace elements and THMs. For all the analyses, duplicate pairs showed comparable results. Moreover, for THM analysis, trip blanks consisting of vials filled with nano-pure water did not indicate contamination. Furthermore, each of the contracted laboratories independently followed their internal QA/QC programs.

4. **RESULTS AND DISCUSSION**

The physical and hydrochemical parameters of the raw sources, treated waters and tap waters were determined to assess their physical properties and the concentrations of chemical constituents, and to investigate the effects of treatment conditions, distribution arrangements, and seasonal and spatial variations on the quality of drinking water. Tap water results were compared with Canada health- and aesthetic-based guidelines (Health Canada, 2009: 2014), and other international guidelines (WHO 1999: 2004).

4.1. **Physical parameters**

Temperature

The temperature (T°C) of water samples varied widely between 2°C to 24°C across seasons, sources (groundwater and Spring Gulch), and the location (private household vs. government building) (Fig. 10). The Canadian aesthetic-based guideline value of tap water T°C is less than or equal to 15°C (Health Canada, 2014). Tap water T°C at most of the households met the guideline, and the

values were commonly below 10°C in winter and spring and between 10°C and 14°C in fall and summer. Exceptionally, at the government building H3, tap water T°C was above the guideline value in winter, spring and summer. This is probably caused by greater size of the building, smaller demand volumes of water from the kitchen tap, and consequently longer periods of stagnancy of water in the building piping system; these factors seem to have more influence than the ambient/outside temperature in this case. However, the weather forecast information can be used to predict water temperature in drinking water distribution networks (Agudelo-Vera et al., 2014). Moerman et al. (2014) have demonstrated that when water is demanded at the tap, the force that pushes the water through the domestic water supply system (i.e. between the water meter or connection to drinking water distribution network and the tap) also causes a temperature increase between 1°C to 4°C.



Figure 10: Seasonal and spatial changes of water temperature in the distribution systems. See the sampling locations in Figure 8.

Although the water temperature does not have direct health effects, it remains nonetheless an important determinant of water quality because of its influence on the physical and chemical and biological proprieties of drinking water (Health Canada, 2014; Liu et al., 2013; Powell et al., 2000). High temperature accelerates chlorine loss and the formation of disinfection by-products (see section 4.2), and favors bacteria growth and the corrosion of housing plumbing materials. This results in adverse effects on the chemical and aesthetic qualities of drinking water reaching the consumers' taps in comparison with water at the main distribution line.

<u>pH</u>

Measured pH ranged between 6.5 and 7.6, indicating a slightly acidic to slightly basic condition (Fig. 11). No clear trends are observed between seasons or sampling sites. Except for the government building H3 in Winter 2, the samples showed pH values within the recommended desirable range of 6.0 - 8.5 for groundwater, 6.5 - 8.5 for surface water and of 6.5 - 8.5 for tap water (WHO, 2004; Health Canada, 2014).



Figure 11: Seasonal and spatial changes of water pH in the distribution systems. Note: the legend is the same as in Figure 10. Sampling locations are shown in Figure 8.

pH is one of the most important operational parameters of water quality and it should therefore, be checked routinely during water treatment and distribution. There is no direct effect of pH on consumer health. However, improper pH can affect the disinfection action of chlorine, the degree of metals corrosion and the formation and distribution of disinfection by-products (e.g. Rodrigez and Sérodes, 2001; Liang et al., 2003). These outcomes, however, also depend on the composition of the raw water and the nature of the piping materials used in the drinking-water distribution system.

<u>Electrical conductivity</u>

Electrical conductivity (EC) is commonly used as a good indicator of salinity. The variation of EC values during the sampling period is illustrated in Figure 12. Measured EC values of the groundwater source varied widely, between 103 and 2771 μ S/cm. The EC of the groundwater samples were generally higher in winter than those collected during the other seasons. The lowest values were recorded for Well #2 and the highest values for Well #1. Slight variations in the EC values of the wells were observed between the seasons; however, the pattern remained constant, Well #2 having the lowest values follow by Wells #3-4-5 and Well #1 having the highest values. Higher EC values suggest higher concentrations of salts in Well #1, indicating that mixed freshwater and saltwater was pumped from Well #1 into the treatment plant. Pumping of well freshwater from the freshwater-saltwater aquifer depends on the upward movement of saltwater within the aquifer when the well is pumped (Zack, 1988). Given that Well #1 provides most of the raw water into the municipality treatment plant, this implies that the groundwater mix for treatment was salt-enriched and not entirely freshwater. In contrast, EC values for Spring Gulch water, which supplies the DND treatment plant were significantly lower, varying from 41 to 52 μ S/cm; the lowest EC value was obtained in spring and the highest EC value in summer. This suggests lower content of salts.

The EC of treated water ranged between 681 and 1142 μ S/cm at the municipality treatment plant and was strongly influenced by the EC of water from Well #1, whereas lower values of 26 – 38 μ S/cm were obtained for the treated water at DND treatment plant. The EC of the treated waters from the municipality and DND treatment plants varied a little when reaching Sandhill reservoir with values of 553 – 1237 μ S/cm, and 19 – 37 μ S/cm, respectively. After the mixture of the treated waters occurred at the Sandhill reservoir, EC ranged from 304 to 866 μ S/cm. The EC the blend of treated waters was strongly influenced by the proportions of each treated water in the mixture. In the Valley area served by a blend of the treated waters, the EC of tap water varied slightly with increasing distance of the private households H1, H2, H4, H5 and H6, and government building H3 from Sandhill reservoir and between seasons, reaching up to 919 μ S/cm. EC of tap water from the private household H7 in the northern sector (served by DND treatment plant) also varied slightly with seasons, reaching up to 166 μ S/cm.



Figure 12: Seasonal and spatial variations of the electrical conductivity in the distribution systems. Note: the legend is the same as in Figure 10. See the sampling locations in Figure 8.

Total Dissolved Solids

Total dissolved solids (TDS) includes inorganic constituents (salts) and organic matter. TDS values ranged from 51 – 1379 mg/L for the groundwater source (Figure not shown). The lowest values (TDS <1000 mg/L) were recorded for Well #2 and Wells #3-4-5, classified as freshwater, and the highest values (>1000 mg/L) were recorded for Well #1 in winter and spring, classified as brackish water, i.e. a mixture of freshwater and saltwater (Freeze and Cherry, 1979). This implies that the groundwater mix for treatment was salt-enriched or brackish and not freshwater, given that which Well #1 provides most of the raw water into the municipality treatment plant. Therefore, desalination technology should perhaps be considered to remove the dissolved salt content from the brackish groundwater. TDS values of Spring Gulch were much lower, ranging between 20 and 25 mg/L, indicating freshwater (Freeze and Cherry, 1979). The TDS values of the treated waters varied from 339 – 474 mg/L at the municipal treatment plant and from 14 – 19 mg/L at DND treatment plant; these TDS values changed little at the Sandhill reservoir. Blending of the treated waters diluted the TDS content in tap water to a maximum of 461 mg/L in the Valley area, when dominated by treated water from the municipal treatment plant; minimum values were observed in cases of dominance by treated water from DND treatment plant. TDS of tap water at the private

household in the northern sector (served by DND treatment plant) also varied seasonally from 10 - 74 mg/L.

In the Valley area, TDS concentrations were moderate and just below the Canadian aesthetic-based guideline of 500 mg/L. Higher TDS concentrations impart an undesirable salty taste of drinking water, and can cause excessive scaling and corrosion of plumbing materials and household appliances (Health Canada, 2014). Nevertheless, because sensitivity to taste varies from person to person, some people might still detect the salty taste of water at moderate-TDS concentrations (Dietrich and Gallagher, 2003).

Oxidation-Reduction Potential

Oxidation-reduction potential (ORP) or redox potential measures the capacity of water to either lose (oxidation) or gain (reduction) electrons from chemical (redox) reactions. It indicates the oxidizing (aerobic) or reducing (anaerobic) tendency of water; positive values indicate oxidizing conditions, while negative values occur when the water is more reducing. Redox reactions strongly influence the mobilization or immobilization potential of metals (or contaminants) from both natural and anthropogenic sources; the mobility of some metals increases under reducing conditions, while others metals are more mobile under oxidizing conditions (e.g. McMahon and Chapelle, 2008).

The variation of ORP during the sampling period is illustrated by Figure 13. Seasonal changes in reducing and oxidizing conditions of the groundwater source were observed at all the wells. Redox potential alternated from modestly negative values in spring to positive values during the other seasons and ranged between -45 and +106 mV. The ORP concentrations obtained for Spring Gulch water were higher than those for groundwater wells, from +326 and +545 mV in summer and fall, respectively. Groundwater treatment produced positive and higher ORP from +546 to +554 mV, due to the oxidizing nature of the chlorine and permanganate added to the water during the treatment process. A similar trend of higher ORP values between +554 and +658 mV was recorded for treated water from DND treatment plant, as the result of chlorine addition during water disinfection. ORP values for both treated waters at the Sandhill reservoir and tap water in the private households and the government building were variable, but in general decreased with increasing distance along the distribution line in the Valley area. The ORP of drinking water from DND treatment plant showed no change to little increase with distance from the plant, as demonstrated by the ORP concentrations measured at household H7 (Fig. 13).



Figure 13: Seasonal and spatial changes of the redox potential in the distribution systems. Notes: The legend is the same as in Figure 10. The ORP meter was not working during Winter 2** sampling session. See sampling sites in Figure 8.

4.2. Disinfection by-products trihalomethanes

Disinfection by-products (DBPs) result from chlorination in drinking water treatment, and also when other disinfectants, such as ozone and chloramines are used (e.g. Rook, 1974; Williams et al., 1997; Singer, 1994; Rodriguez and Sérodes, 2001; Liang and Singer, 2003; Nikolaou et al., 2004; Rodrigez et al., 2004; Nikolaou et al., 2004; Guilherme and Rodriguez, 2014; Scheili et al., 2015). Although more than 600 different species of disinfection by-products (DBPs) have been identified in tap water (Richardson, 2002; Richardson et al., 2007), only trihalomethanes (THMs) and haloacetic acids (HAAs) are regulated, because of public health concerns. This study focused on the four THM species: chloroform (CHCl₃), dibromochloromethane (CHClBr₂), bromodichloromethane (CHCl₂Br) and bromoform (CHBr₃), because THMs are the most prevalent DBP class in drinking waters and are often used as indicators for all other potentially harmful DBP classes (e.g. Krasner et al. 1989). The sum of these four compounds or total THMs, is regulated at the heath-based guideline value of 0.1 mg/L (or 100 µg/L) in tap water (Health Canada, 2006: 2014).

Figure 14 shows the concentrations and changes of total THMs in treated and tap waters as a function of treatment and distribution conditions (see Table 1), season and residence time in the

distribution systems before reaching the consumer's tap. When comparing the two treatment plants, considerable variability was observed in concentrations of specific THMs species and therefore of total THMs. Total THM levels were higher in treated water at the municipal treatment plant than at the DND treatment plant. A possible explanation is the difference in water source, and therefore in the content of THM precursors (i.e. organic and inorganic material which reacts with chlorine to form THMs) and/or the difference in the chlorine doses. Only the THM species CHCl₃ was found in treated water from DND treatment plant, whereas in treated water from the municipal treatment plant, CHClBr₂, CHCl₂Br and CHBr₃ species dominated with minor amount of CHCl₃. This is probably due to the presence of bromide in groundwater (see section 4.4 of the text).





20.0

0.0

sampling locations are shown in Figure 8.

The levels of total THMs in municipally treated water were higher at the plant and Sandhill reservoir than at DND treatment plant. The highest concentrations of total THMs of 108 and 121µg/L respectively, exceeding the Canada health-risk guideline, were obtained in winter when the plant was operating on a temporary basis after a shutdown for repair. This is likely due to

changes in operational parameters during the period following the repair, indicating a need to verify the potability of threated water upon resuming operations, and prior to pumping water into the distribution system.

Concentrations of total THMs in the treated water at the DND treatment plant remained fairly constant at Sandhill reservoir, reaching 21 µg/L. When dominant in the blend at Sandhill reservoir, the lower total THM levels of the treated water from DND treatment plant caused a reduction (up to 3 times lower) of total THMs content in the mixture of the treated waters before distribution in the Valley area. After the blending, when treated water from the DND treatment plant was dominant, CHClBr₂, CHCl₂Br and CHBr₃ remained the dominant species; however, their concentrations decreased considerably, whereas the level of CHCl₃ slightly increased in blended treated water at Sandhill reservoir. On the other hand, when treated water from the municipal treatment plant dominant species, and their concentrations generally decreased slightly, whereas CHCl₃ content increased considerably.

From site to site across the distribution line in the Valley area, concentrations of total THMs varied slightly, but remained lower (up to 55 μ g/L), when treated water from DND treatment plant accounted for 100 % and 95 % of the mixture at Sandhill reservoir (Fig. 14; Table 1). In contrast, when treated water from the municipal plant dominated in the mixture, total THM levels in tap water remained higher and increased with increasing distance from Sandhill reservoir, and exceeding the Canada health-risk guideline at some households H4, H5 and H6, and the government building H3 (Fig. 14). Higher total THM levels were reported at the beginning of the distribution line at the government building H3 and not toward the end of the distribution line as expected, probably because of higher stagnation times and the higher temperature (see Fig. 10) of water in the plumbing. This building has longer plumbing lines and the kitchen tap is used only periodically, compared to the private households toward the end of the distribution line.

The effect of seasonal changes on total THMs, especially in tap water at the distribution line, could not be inferred with confidence from this study, because of the significant variations in the percent blend of treated waters from the two treatment plants over the timeframe of this study. Constant mixing proportions of the treated waters, and to some extent, similar operational parameters between the seasons are crucial for such evaluation. However, it can be seen in Figure 14 that the concentrations of total THMs were, in general, higher in spring, summer and fall (warmer seasons) than in winter and this corroborates with other studies (e.g. Rodriguez and Sérodes, 2001; Toroz and Uyak, 2005). An increase with travel time and a seasonal variability were observed at household H7, which is served only by the DND treatment plant, with higher levels of total THMs (32 μ g/L) in warmer periods (spring, summer and fall) and lower levels in winter (up to 9 μ g/L).

Higher THM content was observed in kitchen hot water taps than in cold water taps, because of higher water temperature and longer stagnation time in the hot water tank. A difference in the THM species present in water was also observed. For instance, at household H1 during Winter 1 sampling session (when drinking water was supplied solely by DND treatment plant), the level of total THMs in water from the cold faucet tap (at a temperature of 9°C) was 6 µg/L and consisted exclusively of CHCl₃. In contrast, the concentration of total THMs in water from the hot faucet tap (at a temperature of 32°C) was 6.8 times higher than that from the cold faucet tap, reaching 41 µg/L (not shown in Figure 14) and THMs consisted dominantly of CHCl₃ with lesser amounts of CHClBr₂, CHCl₂Br and CHBr₃. This suggests that THM levels increase when cold water stagnates in household pipes and that this increase is even more significant when water sits in hot water tanks. This observation corroborates findings by Dion-Fortier et al. (2009).

There is evidence that long-term exposure to levels of THMs above the guideline value has potential adverse effects on human health (e.g. Canada Health, 2014: Mohamadshafiee and Taghavi, 2012). Although total THMs are monitored under the regulations, the request for specific concentrations of individual THM species is recommended, because potential health effects associated with the exposure to elevated THMs may be different for each THMs species (e.g. IARC, 1999a: 1999b; Hunter et al., 2006). For instance, CHCl₃ and CHCl₂B are considered by the International Agency for Research on Cancer (IARC) to be possibly carcinogenic in humans (IARC, 1999a: 1999b). Moreover, epidemiologic studies suggest possible relationships between exposure to CHCl₃ and increased risk of cancer, especially of the urinary bladder and colorectum (e.g. King and Marrett, 1996; IARC, 2004; Richardson et al., 2007; Villanueva et al., 2004: 2007). Furthermore, exposure to high concentrations of DBPs has been associated with significant increases in risks of reproductive, developmental and birth defects (e.g. Nieuwenhuijsen, et al., 2000; Tardiff et al., 2006; Chisholm et al., 2008; Smith et al., 2016). Humans are exposed to THMs by drinking tap water, as well as through dermal absorption and inhalation during showering and bathing (Lin, 2000; Backer, 2000; Nuckols et al., 2005).

4.3. Total alkalinity and total hardness

Total Alkalinity

Alkalinity measures water's capacity to resist to pH changes. Adequate alkalinity, typically above 100 mg/L, will protect pH from fluctuation and therefore, will keep it stable. Alkalinity is primarily

a function of the presence of naturally-occurring carbonates, bicarbonates and to a lesser degree, hydroxides and phosphates (e.g. Griggs and Ficke, 1977). It is influenced by local geology and by the percolation of rain and surface water along with the dissolved carbon dioxide of the atmosphere. Alkalinity is a commonly used indicator in the interpretation and control of water processes.

Total alkalinity (as CaCO₃) values of the groundwater vary from 31 to 79 mg/L between the wells. Except for summer, a very narrow variation range was observed in each individual well. In summer, total alkalinity was significantly lower for Well #1 and higher for Well #2 and Wells #3-4-5. The total alkalinity of Spring Gulch water was lower than that of the groundwater, with values of 17 and 15 mg/L in summer and fall. Treated groundwater showed total alkalinity values of 40 – 55 mg/L at the municipal treatment plant and a comparable range at the Sandhill reservoir. Treated water from DND treatment plant had slightly lower total alkalinity, ranging from 10 to 14 mg/L at both the plant site and Sandhill reservoir. The low total alkalinity obtained (below 100 mg/L) suggests poor buffering capacity in both groundwater and surface water sources. This is possibly due to the fact that the sedimentary rocks through which the groundwater and surface water move through contain little carbonate or bicarbonate minerals or compounds. The total alkalinity of the mixture of the treated waters varied between 21 and 51 mg/L and was strongly influenced by the proportion of treated water from each of the treatment plants in the blend: the higher the proportion of treated water from DND treatment plant in the blend, the lower the total alkalinity of the mixed treated waters; the opposite was observed when treated water from the municipal treatment plant dominated in the mixture. The total alkalinity of tap water samples varied little along the distribution line in Valley area compared to corresponding treated water mixtures at the Sandhill reservoir. "First-draw" and "flushed" samples from individual households and the government building showed either similar values of total alkalinity or narrow variation ranges. Similarly, the total alkalinity of tap water supplied by DND treatment plant at household H7 varied little, ranging between 12 and 15 mg/L, and was comparable to the values for corresponding treated water at the DND treatment plant.

Total hardness

Water hardness is caused primarily by the presence of dissolved calcium- and magnesiumcarbonates, bicarbonates and hydroxides (namely carbonate hardness) and dissolved noncarbonate salts, calcium- and magnesium- chlorides and sulphates (namely non-carbonate hardness) with to some extent, several other dissolved metals forming divalent or multivalent cations, such as aluminum, barium, strontium, iron, zinc, and manganese in water. Carbonate hardness is equivalent to total alkalinity and any excess of hardness above total alkalinity is considered to be non-carbonate hardness (e.g. Rice et al., 2012). Carbonate hardness can be removed by boiling and as such is referred to as temporary hardness, whereas non-carbonate hardness is permanent in water. Its constituents are from natural sources and are expected to occur in higher concentrations in groundwater compared to surface water, because groundwater moves through sedimentary rocks and is contaminated by seawater intrusion. Drinking water is classified based on total hardness (TH) as CaCO₃, which represents the sum of carbonate hardness and non-carbonate hardness as: soft (TH less than 60 mg/L), moderately hard (TH between 60 and 120 mg/L), hard (TH between 120 and 180 mg/L), and very hard (TH above 180 mg/L) (Durfor and Becker, 1964; Health Canada, 1979). Total hardness (as CaCO₃) of water was calculated using the formula below:

Total hardness as CaCO₃ (mg/L) = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

The variability of TH in water presented in Figure 15 is similar to that of total alkalinity (figure not shown). It can be seen in Figure 15 that groundwater samples from the wells fall within different water hardness zones. With the exception of fall, water from Well #1 was very hard and had TH of 277 – 323 mg/L, whereas water from Well #2 and Well #3-4-5 was within the soft water zone (TH >60 mg/L) in summer, spring and winter. In the fall, although slightly higher, water from Well #2 remained soft. On the contrary, water from Well #1 became soft with a substantial decline in TH to 23 mg/L, while a significant increase in TH of water from Well #2 was observed and reached 292 mg/L. The difference and seasonal changes in groundwater TH quality from the wells can possibly be explained by the pumping of a mixture of freshwater and saltwater (i.e. brackish water) into the treatment plant; saltwater is enriched in magnesium and sodium salts and non-carbonate salts, such as chloride (see Figs. 17, 19 and 20).

The surface water source (Spring Gulch) supplying the DND treatment plant was soft, having a TH of 12 mg/L. Treated water at the municipal treatment plant was hard and remained so, in general, at the Sandhill reservoir (between 109 and 152 mg/L). On the other hand, treated water from DND treatment plant remained soft with TH of 12 mg/L after treatment and after reaching the Sandhill reservoir. Due to the high proportions in the blend of treated water distributed in the Valley area, the hardness characteristic of the treated water from the municipal treatment plant dominated the tap water TH in spring, summer and fall (also see Table 1). Tap water TH along the distribution system was between moderately hard and hard, ranging between 99 and 138 mg/L, and in general was above the Canada aesthetic-based guideline range of 80 - 100 mg/L (Health Canada, 2014). In winter (Winter 1 and Winter 2), the percent blends of the treated waters were, in contrast, dominated by treated water from DND treatment plant (also see Table 1). As result, tap water showed TH range of 12 - 42 mg/L, indicating soft water. At household H7, supplied only by the

DND treatment plant, TH levels ranged from 11 to 16 mg/L, indicating soft water. Only negligible changes were observed within the households and the government building.



Figure 15: Seasonal and spatial changes of the total hardness in the distribution systems. The classification of the hardness in water is shown. See Figure 8 for the sampling locations.

Depending on pH and alkalinity, water with hardness above 100 mg/L may cause problems, such as incrustation of pipes and deposition of off-white chalky scale in in-house plumbing fixtures and water use appliances (Fig. 16); in the long term, this can shorten the operational lives or otherwise damage domestic water-use machinery (e.g. Hudson and Gilcreas, 1976; Gray, 2008; Spellman, 2013). In addition, hard water may have corrosion tendencies and also, reduce the effectiveness of soaps and detergents and thereby, increasing soap consumption. The breakdown of major appliances such as dishwashers, washing machine and water boilers have prompted frequent complaints from residents living in the Valley area (See Fig. 1), where TH concentration at the taps ranged between 99 and 138 mg/L. Therefore, the reduction and monitoring of drinking-water hardness is necessary to avoid not only more frequent cleaning, but also expensive repair and/or replacement of household water-use appliances. Softening processes are common practices in water treatment (Curtis and El-Midany, 2006; Spellman, 2013). The type of chemical used depends on the type of hardness in the water.



Figure 16: The electric kettle at one household shows a build-up of off-white, chalky scale from tap water.

4.4. Nutrients and inorganic anions

Nutrients, nitrate-nitrogen (NO₃-N), nitrite-nitrogen (NO₂-N) and orthophosphate-phosphorus (PO₄-P) were not present in detectable levels (i.e. obtained concentrations were below their lower limits of detection) or were present only at very low concentrations in all samples.

<u>Bromide</u>

Bromide (Br⁻) was detected only in groundwater and in tap water at the private households and the government building in the Valley area (figure not shown). Groundwater from Well #1 contained Br⁻ only in winter, spring and summer and the concentrations ranged from 1.79 to 1.95 mg/L. Well #2 contained Br⁻ at 0.15 mg/L only in fall and Br⁻ levels detected in groundwater Well #3-4-5 were 0.15 and 0.41 mg/L in summer and fall, respectively. Br⁻ in groundwater typically originates from natural sources (Davis et al., 2004; Magazinovic et al., 2004). Although

anthropogenic sources of Br⁻ have also been identified (e.g., Br⁻ containing pesticides and fuel additives), their contribution to overall Br⁻ levels are, in general, expected to be negligible (Price et al., 1988; Magazinovic et al., 2004). Given their similar physical and chemical properties, Br⁻ is commonly found in groundwater with sodium and chloride in coastal settings, such as Happy Valley-Goose Bay (Davis et al., 1998; Davis et al., 2004). Therefore, the presence of Br⁻ in raw groundwater was likely the result of pumping a mix of saltwater and freshwater into the treatment plan; it is also possible that sedimentary rocks made contributions. When present in raw groundwater, Br⁻ can react with chlorine and naturally-occurring organic matter, leading to increasing formation of the brominated and mixed chlorinated–brominated species of THMs (CHClBr₂, CHCl₂Br and CHBr₃) and HAAs in drinking water (Chang et al., 2001; Chowdhury et al., 2010). The presence of Br⁻, therefore, explained the dominance of these brominated and mixed chlorinated–brominated and mixed chlorinated and mixed chl

The content of Br- varied across the distribution line in the Valley area. With the exception of household H3, Br- in tap water was commonly found in "first draw" samples at the households closer to Sandhill reservoir (H1 and H2), while it was present in both "first draw" and "flushed" samples towards the end of the distribution line at households H4, H5 and H6. The concentrations of Br- were higher in "first draw" (up to 0.45 mg/L) than "flushed" samples (up to 0.25 mg/L). At the government building H3, bromide was detected in both "first draw" and "flushed" samples and its levels were either higher in "first draw" or in "flushed"; in both cases, the highest Br- level obtained was 0.42 mg/L in "flushed" sample. There are no adverse health effects due to the presence of Br- in drinking water (WHO, 2009).

<u>Chloride</u>

The variation of chloride (Cl⁻) levels in groundwater, surface water, treated and tap waters is presented in Figure 17. The trend of Cl⁻ is comparable to that of total hardness with regards to the seasonal and local variations. In raw groundwater, Cl⁻ concentrations varied over a wide range among the wells, with the highest concentrations in Well #1 (2.29 – 715 mg/L), followed by Well #3-4-5 (58.7 – 145 mg/L) and Well #2 (2.60 – 56.1 mg/L). As for EC and TDS, this suggests that mixed saltwater and freshwater was pumped from Well #1 into the treatment plant. Lower Cl⁻ level in Well #1 was observed in the fall, whereas the level was higher during the other seasons. The opposite was observed in Well #3-4-5, where Cl⁻ content was lower in winter, spring and summer, and higher in fall. Well #2 displayed similar Cl⁻ seasonal evolution as in Well #3-4-5; however, the obtained Cl⁻ concentration range was narrower (Fig. 17). The seasonal changes in Cl⁻ levels in raw groundwater were likely due to the variation of saltwater proportion in water pumped into the

plant. Cl⁻ was not present in raw surface water at the DND treatment plant, but it was found at lower concentrations of 1.7 and 2.1 mg/L in treated water. This sudden appearance of Cl⁻ in treated water was likely due to reactions between the chlorine used for disinfection and elements in water to form Cl⁻ compounds.



Figure 17: Seasonal and spatial variations of chloride concentrations in the distribution systems. Note: The legend is the same as in Figure 15. See sampling locations in Figure 8.

After the treatment process, Cl⁻ content in treated water at the municipal treatment plant varied between 233 and 292 mg/L. In the Valley area, when the blended treated water at Sandhill reservoir included higher proportion of the water were from the municipal treatment plant in (also see Table 1), its Cl⁻ content had a significant impact on the Cl⁻ concentrations of tap water (spring, summer and fall). The levels of Cl⁻ in tap water along the distribution line showed a narrow range of variability, from 199 to 250 mg/L. Because the percent blends of the treated waters were, in contrast, dominated by treated water from DND treatment plant in winter (Winter 1 and Winter 2; also see Table 1), Cl⁻ content in tap water was significantly lower and ranged between 2.25 and 64.7 mg/L. At Household H7, which was supplied only by DND treatment plant, Cl⁻ concentrations ranged from 1.79 to 3.41 mg/L (Fig. 17). Negligible intra-household changes in the levels of Cl⁻ were observed.

Because of the taste concern posed by high levels of Cl⁻ in tap water, Health Canada (2014) has established an aesthetic-based guideline of 250 mg/L. Above that limit, consumer acceptability of drinking-water can be hampered by the salty taste. Nevertheless, acceptability depends on the sensitivity of the consumer and therefore, may vary among consumers. Cl⁻ levels in treated water from the municipality treatment plant exceeded the permissible limit in winter, spring and summer (Fig. 17). On the other hand, Cl⁻ concentrations in tap water, across all the seasons, distances from the Sandhill reservoir, and sampling locations, tended to clusters near or at the permissible limit (Fig. 17).

Chloride also has a significant influence on the corrosion of materials in the distribution system, as well as household pipes and other plumbing materials. This may lead to detrimental consequences by permitting the leaching of toxic metals into tap water (see section 4.5 of the text), and also may shorten the life of household plumbing materials and water-use appliances. As already pointed out, desalination should perhaps be considered for implementation to remove the salts, including Cl- from the brackish groundwater.

<u>Sulphate</u>

Based on taste considerations, Health Canada (2014) recommends the aesthetic-based guideline value of 500 mg/L for sulfate (SO₄^{2–}) in drinking water. Moreover, SO₄^{2–} concentrations exceeding 500 mg/L may cause diarrhea (Heizer et al., 1997). SO₄^{2–} occurs naturally in groundwater and surface water from the dissolution and/or oxidation of sulfate minerals in mineral deposits, soils and rocks (e.g. shales), from seawater intrusion, or due to human activities, such as power plants and industrial wastes (e.g., Krouse and Mayer, 1999; Seller and Canter, 1980).

Sulphate concentrations showed seasonal, intra-household/government building changes similar to those observed for chloride concentrations and total hardness (figure not shown). $SO_{4^{2-}}$ concentrations in groundwater varied among the wells, with the highest concentrations in Well #1 (1.73 – 86.6 mg/L), followed by Well #3-4-5 (7.42 – 82.6 mg/L) and Well #2 (1.86 – 7.47 mg/L). The lower $SO_{4^{2-}}$ level in Well #1 was observed in the fall, while levels were high for the other seasons. The opposite was observed in Well #3-4-5, where $SO_{4^{2-}}$ content was lower in winter, spring and summer, and higher in fall. Well #2 showed similar $SO_{4^{2-}}$ seasonal change as in Well #3-4-5, but with a much narrower range of $SO_{4^{2-}}$ concentrations. $SO_{4^{2-}}$ content in treated water at the municipal treatment plant and Sandhill reservoir varied from 27.1 to 37.2 mg/L. Like chloride and the total hardness, $SO_{4^{2-}}$ is likely from a natural source, i.e. the mixture of freshwater and saltwater pumped into the plant. $SO_{4^{2-}}$ in raw surface water at DND treatment plant was very low and

reached up to 1.05 mg/L; this remained constant after treatment and at Sandhill reservoir and at household H7 in the northern sector of the town. The level of $SO_{4^{2-}}$ in tap water at the distribution line in the Valley area was influenced by the percent blend of the treated waters from the municipal and DND treatment plants at Sandhill reservoir (see Table 1). With higher proportions of treated water from the municipal treatment plant in spring, summer and fall, $SO_{4^{2-}}$ concentrations in tap water were between 22.4 and 30.0 mg/L. In contrast, when the percent blend of the treated waters was dominated by treated water from DND treatment plant in winter (Winter 1 and Winter 2), the $SO_{4^{2-}}$ content in tap water was much lower, between 1.09 and 8.27 mg/L. Intra-household variations were insignificant. Concentrations of $SO_{4^{2-}}$ were well below the Canadian aesthetic-based guideline.

<u>Fluoride</u>

Fluoride (F⁻) occurs naturally in groundwater and surface water from many types of sedimentary and igneous rocks. Health Canada (2014) suggests an aesthetic-based guideline value of 1.5 mg/L for F⁻ in drinking water. Although today exposure of humans to F⁻ is through a variety of sources, fluoridated drinking-water remains the principal source of the daily F- intake (WHO, 2004). The benefits for dental health of drinking water fluoridation to increase naturally low fluoride concentrations F⁻ in water sources is still a matter of debate (e.g. Canadian Dental Association, 2012; Peckham and Awofeso, 2014). Nevertheless, since fluoridation of drinking water was introduced in 1945, it has been agreed that a fluoride level of 0.7 mg/L represents the best balance of F⁻ in drinking water to promote dental health in both children and adults, while minimizing the risk of excess F- intake through multiple daily sources of exposure (e.g. Griffin et al., 2007; Loskill et al., 2013; Rabb-Waytowich, 2009; Yeung, 2007; WHO, 2004). Increase in the rates and severity of dental caries may occur when levels fluoride in drinking water are less than 0.7 mg/L, whereas the development of dental fluorosis (pitting and yellow to brown staining of teeth) has been linked to long-term ingestion of higher levels of fluoride above the aesthetic-based guideline; and skeletal and crippling fluorosis at much higher concentrations, above 4.0 mg/L (e.g. DenBesten and Li, 2011; Health Canada, 2014; Rabb-Waytowich, 2009).

Figure 18 shows F⁻ concentrations in groundwater, surface water (Spring Gulch), and treated and tap water samples. When detected, F⁻ concentrations in groundwater were, in general, very low in all the wells and ranged from 0.04 to 1.00 mg/L. This observed range in raw groundwater remained unchanged after the treatment process, since the municipality does not add F⁻ to its treated water. At the DND treatment plant, F⁻ in raw Spring Gulch water was also low with concentration of 0.04 mg/L. However, this level increased (up to 0.58 mg/L) in treated water due to addition of a F⁻

compound, and this level remained constant in tap water served by the DND treatment plant only (i.e. household H7, see Fig. 18). F- content at Sandhill reservoir and in tap water at the distribution line in the Valley area was influenced by the percent blend of the treated waters from the municipal and DND treatment plants (see Table 1). With the higher proportions of treated water from the DND treatment plant in winter (Winter 1 and Winter 2; see Fig. 17), F- concentrations in tap water were higher and varied between 0.34 and 0.43 mg/L. In contrast, when the percent blend of the treated waters was dominated by treated water from the municipal treatment plant in spring, summer and fall, the F- content in tap water was much lower and ranged from 0.09 to 0.22 mg/L. Intra-household variations of fluoride content appears almost negligible.



Figure 18: Fluoride concentrations in the distribution systems. Note: The legend of the sampling locations is the same as in Figure 15. Sampling locations is presented in Figure 8.

Overall, the concentrations of F⁻ in tap water in the distribution systems at the Valley area and the northern sector were well below the aesthetic-based guideline, below optimal promotion of dental health (Fig. 18). For this reason, residents should be encouraged by the appropriate authorities to use topical fluoride (e.g. fluoridated toothpaste, varnish, gel or mouth rinse) or other measures to protect dental health, as recommended by the Canadian Dental Association (2012).

4.5. Major and trace elements

The following elements were either not detected (obtained concentrations were below their limits of detection) or were present only in trace quantities (concentrations were close to their limits of

detection) in groundwater and surface water sources, and treated waters and tap water samples: antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), lithium (Li), molybdenum (Mo), phosphorus(P), selenium (Se), nickel (Ni), silver (Ag), tellurium (Te), thallium (Tl), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V) and Zirconium (Zr).

Elements actually detected in the analyzed water samples have been divided into three groups based on their origin: (*i*) naturally-occurring elements, barium (Ba), magnesium (Mg), potassium (K), sodium (Na), calcium (Ca), sulfur (S), strontium (Sr) and silicon (Si); (*ii*) Natural- and plumbing corrosion-induced metals, iron (Fe) and manganese (Mn), and (*iii*) plumbing corrosion-induced metals, copper (Cu), lead (Pb) and zinc (Zn).

4.5.1 Naturally-occurring elements

The variations of Ba, Mg, K, Na, Ca, S, Sr and Si in water samples are presented in Figure 19, 20 and 21. Their seasonal and special variations were similar to those of total hardness (Fig. 15), Cl- (Fig. 17), and SO₄^{2–} and Br[–] (figures not shown). The variations in Ba, Mg, and K (Fig. 19), Na, Ca and S (Fig. 20) and Sr and Si (Fig. 21) were predominantly controlled by seasonal differences in concentration in groundwater from Well #1, Well #2 and Well #3-4-5. In addition, the percent blend of the treated waters from the municipal and DND treatment plants at Sandhill reservoir (given in Table 1) influenced the concentrations of these elements at taps in the Valley area. Except for Si, the concentrations of the other elements were considerably higher in Well #1 in winter, spring and summer compared to Well #2 and Well #3-4-5 (Figs. 19, 20 and 21). The opposite was observed in fall, with groundwater from Well #3-4-5 containing substantially higher concentrations of Ba, Mg, K, Na, Ca, S and Sr, followed by Well #2 and finally Well #1 (Figs. 19, 20 and 21). Groundwater Si concentrations showed a less pronounced seasonal variation (Fig. 21). The treatment process at the municipal treatment plant resulted in considerable reduction of these elements in the treated water. On the other hand, the surface water source (Spring Gulch) had considerably lower contents of Ba, Mg, K, Na, Ca, S, Sr and Si compared to groundwater supply wells; equivalent lower concentrations were observed after treatment and in tap water supplied by the DND treatment plant only, i.e. household H7 (Figs. 19, 20 and 21). After the mixture of the treated water occurred at Sandhill reservoir, a higher percentage of treated water from DND treatment plant in winter resulted in a significant dilution of Ba, Mg, K, Na, Ca, S, Sr and Si in tap water at the distribution line in the Valley area. In contrast, the dominance in the mixture of treated water from the municipality treatment plant in spring, summer and fall maintained the elevated concentrations in these elements in water reaching the consumer's taps (Figs. 19, 20 and 21).



Figure 19: Seasonal and spatial changes of barium, magnesium and potassium concentrations in the distribution systems. Note: The legend of the sampling locations is the same as in Figure 15. See the sampling locations in Figure 8.



Figure 20: Seasonal and spatial variations of sodium, calcium and sulfur concentrations in the distribution systems. Notes: Sulfur was not determined in Winter 1 and Winter 2 samples. The legend of the sampling locations is the same as in Figure 15. Sampling locations are shown Figure 8.



Figure 21: Seasonal and spatial variations of strontium and silicon concentrations in the distribution systems. Note: The legend of the sampling locations is the same as in Figure 15. See the sampling locations in Figure 8.

There are no documented adverse health effects due to the presence of Mg, Ca, K, S, Sr and Si in drinking water and, therefore, no guidelines values have been issued for these elements (Health Canada, 2014). Sr is, however, being reconsidered and evaluated further for establishment of regulatory levels in drinking water by the U.S. EPA (Alfredo et al., 2014). An aesthetic-based guideline level has been established at 200 mg/L for Na (Health Canada, 1992: 2014), because of possible noticeable salty taste at higher concentrations; however, this limit may varies substantially among people. For people on salt (or sodium)-restricted diet, it is suggested to consume drinking water with less than 20 mg/L Na (Health Canada, 1992; U.S. EPA, 2003). Higher sodium

concentrations in tap water in the Valley area were observed (average 120 mg/L) compared to that at household H7 (1.2 mg/L) at the northern sector, which was served only by DND treatment plant; but all were below the Canadian aesthetic-based guideline.

4.5.2 Natural- and plumbing corrosion-induced metals

Natural- and plumbing corrosion-induced metals here refer to iron (Fe) and manganese (Mn). High concentrations of Fe and Mn in drinking water are associated with colored (orange, red-brown or black-brown) stains, which were one of the main reasons for drinking-water quality complaints from customers (Fonkwe, 2015: Fonkwe and Schiff 2016; also see Fig. 1). Fe and Mn often occur together and in higher concentrations in groundwater than surface water. While, naturally occurring Fe and Mn in groundwater is generally the major source, because of weathering minerals in the bedrock, human contamination from landfill leachate, sewage, and industrial wastewater may also occur. It has also been demonstrated that depending on the chemical compositions of the water, corrosion of cast iron and ductile iron pipes in drinking water distribution systems can cause the formation of internal corrosion scales, especially as the pipes' age increase, resulting in the release of Fe and Mn into drinking water (Hallam et al., 2001; Maneesha et al., 2011; Sun et al., 2014). The pipe materials of the water main supply line in Happy Valley-Goose Bay are made of cast iron and ductile iron (F. Brown, pers. comm. June 09, 2014). Moreover, household pipes and other plumbing materials can also contribute to the Fe and Mn load into tap water.

The variability of Fe and Mn in analyzed water samples is shown in Figures 22 and 23, respectively. As expected, Fe and Mn concentrations were negligible in surface water from Spring Gulch, reaching up to 0.10 mg/L for Fe and 0.014 mg/L for Mn. On the other hand, Fe content was much higher in groundwater from Well #1 (up to 10.9 mg/L), followed by Well #2 (up to 6.6 mg/L) and Well 3-4-5 (1.7 mg/L) in winter, spring and summer. In fall, the higher concentration of Fe in groundwater was found in Well #3-4-5 (10.8 mg/L), followed by Well #1 (6.2 mg/L) and Well #2 (1.5 mg/L). This indicates seasonal variability of Fe in the groundwater supply wells. Similarly, Mn showed higher concentrations in groundwater from Well #1 (up to 0.95 mg/L), whereas Well #2 and Well 3-4-5 had similar Mn content, up to 0.4 mg/L in winter, spring and summer. A different Mn trend in groundwater was observed in spring; higher concentration occurred in Well #3-4-5 (0.94 mg/L) and similar low concentration of 0.34 mg/L in Well #1 and Well #2.

Treated water (B1; see Fig. 22) had very low levels of Fe (up to 0.072 mg/L) and Mn (up to 0.034 mg/L) compare to raw groundwater (Figs. 22 and 23), demonstrating removal efficiencies higher than 90% during treatment. Levels in tap water, however, increased with increasing distance from

the treatment plants or Sandhill reservoir. In general, the further a location in the Valley area was from Sandhill reservoir, the higher the concentrations of Fe and Mn in its tap water. At the households and the government building, the obtained concentrations of Fe and Mn were nearly equal or equivalent in both the "first-draw" and "flushed" samples. This suggests that Fe and Mn were released in tap water from corroded cast iron and ductile iron pipes of the main water line (Figs. 22 and 23), and that in general, household/government building pipes and fixtures contributed only to a small extent; this also depended upon the stagnation times of the water in the pipes. As shown in Figure 23, much higher Mn concentrations in "first draw' samples at household H4 during winter and spring were due to significantly longer-stagnation times (more than 24 hours), compared to about 6 hours (or overnight) at the other locations. Fe and Mn concentrations varied from season to season, but showed no clean trends (Figs. 22 and 23). In general, seasonal maximum levels occurred during winter and fall for Fe and spring and fall for Mn; minimum levels were observed during summer and fall for Fe and winter and summer for Mn.



Figure 22: Seasonal and spatial changes of iron concentrations in the distribution systems. Note: The legend of the sampling locations is the same as in Figure 15. See the sampling locations in Figure 8.



Figure 23: Seasonal and spatial changes of manganese concentrations in the distribution systems. Note: The legend of the sampling locations is the same as in Figure 15. See the sampling locations in Figure 8.

4.5.3 Plumbing corrosion-induced metals

Plumbing corrosion-induced metals in this study include copper (Cu), lead (Pb) and Zinc (Zn). These elements were either not detected or found to be present only at very low concentrations (close to their limits of detection) in groundwater, surface water from Spring Gulch and treated waters from the municipal and DND treatment plants (Figs. 24, 25 and 26). However, Cu, Pb and Zn were found at varied concentrations in tap water at the households and the government building, depending upon housing ages in the Valley area and the northern sector (Figs. 24, 25 and 26; also see Table 2). This indicates that these metals were released by the corrosion of pipes and/or other plumbing materials. Therefore measures to reduce water corrosivity and the exposure of tap water to these metals should be evaluated and implemented.

<u>Copper</u>

Copper was detected in the "first draw" samples at concentrations well above the aesthetic-based guideline value of 1.0 mg/L (Fig. 24; Health Canada, 2014) in all the households/government

building, except for household H1. The households/government building have Cu pipes and other metal plumbing materials, whereas household H1 has plastic pipes and metal plumbing materials. This explains the elevated levels of Cu in "first draw" samples in the former locations. Cu concentrations did not show clear seasonal differences, whereas significant spatial (intra- and inter-household/government building) variations in Cu content were observed (Fig. 24).



Figure 24: Seasonal and spatial changes of copper concentrations in the distribution systems. Note: The legend of the sampling location is the same as in Figure 15. See the sampling locations in Figure 8.

On the other hand, "first draw" samples from household H1 with the plastic pipes contained lower Cu, but higher than Cu content in the "flushed" samples, demonstrating a contribution of brass fixtures and/or faucets to the load of Cu released in tap water (Fig. 24). In general, Cu content in "flushed" samples increased with increasing distance from the DND treatment plant at household H7, and from Sandhill reservoir in the Valley area at households H1, H2, H4, H5 and H6, and the government building H3 (Fig. 24). Except at the government building H3, flushing was effective in reducing the levels of Cu below the aesthetic-based guideline, but still in general, above the Cu content in the blended treated water at the Sandhill reservoir. This indicates that Cu also entered drinking water before reaching consumers' household plumbing, while travelling through the municipal copper pipes that connect the water main line to customers' property lines throughout

the town (F. Brown, pers. comm. June 09, 2014). The nearly constant high Cu levels in both the "first draw" and "flushed" samples from the government building H3 indicate that the allowed flushing time of five minutes did not successfully clear all the standing water in the building's plumbing and was therefore, ineffective in reducing the levels of Cu exposure, as observed at the households. This is due to the greater size of the building. The effectiveness of flushing therefore varies between the locations.

Corrosion of copper pipes can leave obvious bluish-green stains around sinks and bathroom fixtures. At levels at or above the guideline 1.0 mg/L, Cu can also give a bitter, metallic taste to tap water. Small amounts of Cu are essential to human health, but excess intake can cause adverse health effects (e.g. Dietrich et al., 2004). Exposure to elevated Cu concentrations (4.0 - 7.0 mg/L) in drinking water has been associated with gastrointestinal symptoms such as nausea, abdominal pain, diarrhea, and vomiting in the short term (e.g. Potera, 2012). Based on limited evidence from studies in humans, ingestion of very high concentrations of Cu over long period of time can lead to liver and kidney damage (de Romaña et al., 2011; Stern, 2010). The long-term health effects of copper at moderately high intake, as observed in the present study, are still not well defined.

<u>Lead</u>

The health-based guideline value for Pb in drinking water is 0.010 mg/L (Health Canada, 2014). Pb was detected primarily in all "first draw" tap-water samples; but was also present in "flushed" samples in two households, H5 and H7 and the government building H3 (Fig. 25). Pb content was higher in the "first draw" samples than in "flushed" samples. No clear seasonal variations in Pb concentrations were observed (Fig. 25). In contrast, the difference in lead levels within and between the households and the government building was substantial in the Valley area, influenced mainly by the types of plumbing materials (see Table 2). At household H5 (Winter 1 data was excluded from analysis, because flushing instructions were not followed), Pb concentrations in "first draw" tap water samples were up to 3.5 times higher than the health-based guideline. Pb exceedance in "first draw" samples from the other households and the government building was sporadic and occurred in both the Valley area and northern sector, during one sampling session in each case. At household H1 with plastic pipes, Pb likely entered tap water from corrosion of the brass faucets or other metallic plumbing fixtures. On the other hand, lead was, in general, not detected in "flushed" samples. But at two households, H7 in the northern sector and H5 in the Valley area, Pb was found in "flushed" samples at concentrations considerably less that than their corresponding "first-draw" samples, but still exceeding the health-based guideline value in spring for H5 and fall for H7. The results suggest that Pb in tap water solely arises from plumbing pipes and/or fixtures and faucets in the households and the government building. They also demonstrate that although effective in



some cases, flushing for five minutes may not always reduce the level of lead and therefore, the effectiveness of flushing should be verified and tailored to each household.

Figure 25: Seasonal and spatial changes of lead concentrations in the distribution systems. Notes: The legend of the sampling location is the same as in Figure 15. Winter 1 result of household H5 was excluded because flushing instruction was not followed. See the sampling locations in Figure 8.

Because Pb is a known cumulative toxicant (meaning that it remains in the body following exposure), elevated lead in drinking water is a significant public health concern (Health Canada, 2007). Water lead levels have been shown to contribute significantly to blood lead levels in humans; children under the age of 6 are especially vulnerable to the harmful health effects of Pb (Edwards et al., 2009; Levallois et al., 2014; Ngueta et al., 2016). Lead exposure in children has been linked to anemia, renal dysfunction, impaired hearing and postnatal growth, intellectual deficit (in Ngueta et al., 2016). In adult, long-term lead exposure have been linked to renal dysfunction (Loghman-Adham et al., 1997) and hypertension (Navas-Acien et al., 2007).

Lead is released in drinking water from Pb pipes (commonly in houses built before 1950), galvanized (zinc-coated) pipes and/or lead solders (commonly in houses built before 1990), and/or

brass fittings or faucets, which are also found in newer houses/buildings with plastic pipes (Clark et al., 2015; Elfland et al., 2010; Ng and Lin, 2016).

<u>Zinc</u>

Zinc in drinking water is not regarded as a health hazard to humans; however, the aesthetic-based guideline level has been set at 5.0 mg/L, because of potential problems associated with taste, milky appearance (opalescence), and the formation of greasy films at water surface upon boiling (Health Canada, 2014).

Zinc (Zn) was found, in general, in "first draw" tap-water samples in significant amounts, whereas "flushed" water samples typically contained small amounts, mostly below 0.1 mg/L (Fig. 26). Zn content in "first draw" tap-water samples varied significantly, but irrespectively of the seasons and Sandhill reservoir-to-household/government building distances in the Valley area (Fig. 26). At household H2 and government building H3, "first draw" samples exceeded the Canadian aesthetic-based guideline in fall, spring and summer, respectively (a "first draw" sample was not collected for analysis in the fall at H3). The concentrations of Zn at other households were within the aesthetic-based guideline. This suggests that the observed differences in Zn levels in tap-water were solely controlled by the types of plumbing materials inside the households and the government building (see Table 2). Zinc typically enters drinking water from the corrosion of galvanized (zinc-coated) pipes and brass fittings. Flushing for five minutes was effective in reducing the Zn level in tap water in all the households and the government building.

4.6. Stable hydrogen and oxygen isotopic compositions

Stable isotopes of hydrogen (δ^2 H) and oxygen (δ^{18} O) of water have been widely used, as complements to hydrochemical and physical data, in order investigate the origin of groundwater and its interactions with surface water to assess groundwater recharge and vulnerability to pollution (e.g. Clark, 2015; West et al., 2014; Yeh et al., 2014). In general, groundwater originates from direct infiltration of water runoff from rainfall and snowmelt, or via infiltration of surface water (lakes or rivers), or a combination of both. Groundwater recharge can also be impacted by human activities. Since hydrogen and oxygen are components of the water molecule H₂O, their isotopic compositions in water tend to be conserved and thus ideal indicators of the origin of water resources and the presence of potentially contaminating water sources. The water stable isotope ratios provide a unique means to assess the long-term viability of water resources in terms of both quantity and quality, and they are therefore essential indicators for the implementation of strategies to achieve sustainable management (Clark, 2015; Elliot, 2014).



Figure 26: Seasonal and spatial changes of zinc concentrations in the distribution systems. Notes: The legend of the sampling locations is the same as in Figure 15. "First draw" sample was not collected for analysis in the fall at H3. See the sampling locations in Figure 8.

The results of the δ^2 H and δ^{18} O analysis of groundwater, Spring Gulch water, the treated waters at Sandhill reservoir, the Churchill River water and rainwater are plotted on a conventional δ^2 H and – δ^{18} O diagram (Fig. 27). For comparison the variation trend of Global Meteoric Water Line (GMWL; δ^2 H = 8 δ^{18} O + 10; Craig, 1961), a global average of several local meteoric water lines, is also indicated in Figure 27. The δ^2 H and δ^{18} O values of rainwater averaged respectively –76.1‰ ± 0.99‰ and –11.5‰ ± 0.32‰ and were significantly different from those of wells' groundwater (average –110.4‰ ± 0.47‰ δ^2 H and –15.1‰ ± 0.11‰ δ^{18} O), Spring Gulch (–110.9‰ δ^2 H and –15.5‰ δ^{18} O) and the Churchill River (average –118.3‰ ± 0.37‰ δ^2 H and –16.1‰ ± 0.15‰ δ^{18} O). δ^2 H and δ^{18} O data of rainwater lies along but slightly above the GMWL, indicating contribution of the local re-evaporated (recycling) water vapor to the raining cloud. This corroborates with the deuterium excess (or *d*-excess) values of rainwater, which range between 14‰ and 18‰ with a mean value of 16‰. These values are higher than the *d*-access value GMWL of 10‰, which is indicative of un-evaporated water (Craig, 1961). The *d*-excess, defined as *d* = δ^2 H – $8\delta^{18}$ O (Dansgaard, 1964), has been widely used as isotopic indicator to assess the effect of evaporation in

modifying the isotopic compositions of rainwater prior to recharge of groundwater or surface water (e.g. Clark, 2015; Lai and Ehleringer, 2010).



Figure 27: The relationships between $\delta^2 H$ and $\delta^{18}O$ of the water samples. For comparison, the dashed line shows the Global Meteoric Water Line (Craig, 1961).

The stable isotopes data of groundwater, Spring Gulch and the Churchill River are clustered on the GMWL to the lower left corner, indicating precipitation recharge by rainfall (summer precipitation) or snowfall (winter precipitation) or a combination of both. Their isotopic similarity may reflect the hydraulic interconnections amongst the groundwater, Spring Gulch and the Churchill River. The substantial depletion of δ^2 H and δ^{18} O (most negative) in groundwater, Spring Gulch and the Churchill River compared to water from rainfall likely indicates that in addition to rainwater, there was a significant contribution from another sources of water with depleted isotopic signatures, possibly water from snowmelt runoff in spring 2015. On the other hand, stable isotopic compositions of both treated waters from the municipal and DND treatment plants were representative of their groundwater and Spring Gulch sources (Fig. 27), possibly suggesting that water had a short residence time in these reservoirs. δ^2 H and δ^{18} O measurement in tap waters has been successfully used to describe the flow of water in the human-hydrological system (Bowen et al., 2007; Leslie et al., 2014).

This initial δ^2 H and δ^{18} O results provide a basis of isotopic characteristics of groundwater, Spring Gulch, the Churchill River and treated waters; however, considerable insight can still be gained from this limited data. Further study is necessary to achieve a better understanding of the local isotope hydrological characteristic and seasonality.

5. CONCLUDING REMARKS AND RECOMMENDATIONS

The results of this project lead to the following conclusions:

- Groundwater showed a heterogeneous composition across supply wells and seasons. Water pumped into the municipal treatment plant was a mixture of freshwater and saltwater, hard to very hard with nearly a neutral pH range. The redox state of groundwater changed between mildly reducing (negative ORP) and oxidizing (positive ORP) conditions.
- Spring Gulch water was very distinct from groundwater, as expected; it was soft, moderately alkaline, and characterized by oxidizing conditions.
- The hydrochemical comparison between the two water sources indicates higher concentrations of Cl⁻, SO₄²⁻, Ba, Mg, K, Na, S, Ca, Sr, Si, Fe, Mn and Br⁻ in groundwater, compared to Spring Gulch water, and very low levels of F⁻ in both water sources.
- The absence of typical landfill leachate contaminants (e.g. NO₃-N, NO₂-N, PO₄-P, Cu, Pb and Zn) in groundwater suggests that the former landfill located up-gradient of the groundwater supply wells did not affect the quality of groundwater over the timeframe of this study.
- Stable isotopic compositions indicate that most recharge of groundwater, Spring Gulch, and the Churchill River is from snowmelt runoff in spring 2015, with a small amount from rainfall of the following summer; isotopic similarity possibly reflects hydraulic interconnections between the groundwater, Spring Gulch and the Churchill River.
- Treated waters at the municipal treatment plant shared similar trends with the "parent" groundwater. However, treated water showed significantly lower levels of elements than found in "parent" groundwater, while THMs dominated by CHCl₃, CHCl₂Br and CHBr₃ with lesser amount of CHClBr₂ were formed during the treatment process. The removal efficiencies for Fe and Mn were higher than 90%.
- Raw and treated Spring Gulch water shared similar physical and chemical characteristics, except that the concentrations of F⁻ were higher in treated water as the result of fluoridation applied at the DND treatment plant to help promote dental health, and CHCl₃ was formed during the treatment process (the only THM species to arise).
- The physical and chemical properties of the blended treated waters at Sandhill reservoir, as well as those of the tap water along the distribution line in the Valley area, typically reflected the proportions of the treated water that dominated in the mixture.

- The elements with the lowest variation (both seasonal and spatial) in tap water were Cl⁻, SO_{4²⁻}, Ba, Mg, K, Na, S, Ca, Sr, Si, Br⁻ and F⁻, all originating from natural sources, except for F⁻, which related to the treatment process at the DND treatment plant.
- Among the elements, which displayed considerable variations (mostly spatial, i.e. within and between the private households and the government building) were THMs formed by the reactions between the organic matter and chlorine in water, and Fe, Mn, Cu, Pb and Zn released by corrosion reactions with the materials of the distribution systems and plumbing inside sampling locations. Both treated waters were corrosive, but the water from the DND treatment plant seemed to be less corrosive than that from the municipal treatment plant.
- Chloride levels at the Canada aesthetic-based guideline, in combination with high hardness and elevated of Fe, Mn, Cu, and Zn, which locally exceeded the aesthetic-based guidelines, likely explained the aesthetic problems detected by the consumers.
- The levels of fluoride in tap water are lower than optimal for the promotion of dental health.
- Concentrations of THMs in tap water increased with increasing distance from Sandhill reservoir in the Valley area or from the DND treatment plant in northern sector with exceedance of the health-risk guidelines for THMs (in the Valley area) and Pb (locally in both the Valley area and northern sector).
- Although flushing, as a mitigation strategy to lower metal exposure, effectively reduced the levels of Cu and Zn, it did not always lower the levels of Fe and Mn below the aesthetic-based guidelines, or those of THMs and Pb below health-based guidelines.

Based on the findings of the present study, the following recommendations are appropriate:

- Seasonal variability of the quality of groundwater supply wells should be taken into account during the treatment operations.
- Systematic evaluation of groundwater quality would be beneficial to better understand how the quality of water pumped from the wells changes over (*i*) short (daily to monthly) and (*ii*) long (seasonal to yearly) time period, so that plant operators may adjust the treatment to changes in raw water quality. Given that the groundwater wells are located down gradient of a former landfill, its quality must be continually monitored for contamination.
- The appropriate authorities should encourage residents to use topical fluoride (e.g. fluoridated toothpaste, varnish, gel or mouth rinse) or other measures to promote dental health, as recommended by the Canadian Dental Association.
- Giving that the groundwater source does not contain high levels of naturally-occurring fluoride, the decision whether or not to add fluoride compound to drinking water at the municipality treatment plant might warrant a re-examination and systematic reviews.
- Mitigation strategies to further reduce the formation of THMs (and other DBPs) in the treated water leaving the municipal treatment plant should be evaluated and implemented for consistent protection from DBPs and to ensure compliance across the entire distribution line in the Valley area.
- Desalination technology should perhaps be considered to remove the dissolved salt content from the brackish groundwater.
- Measures to reduce or prevent tap water corrosivity and hardness should be evaluated and implemented with the objectives to: (*i*) lower exposure to toxic metals; (*ii*) improve aesthetic quality (e.g. chloride, hardness, iron and manganese); and (*iii*) improve consumer satisfaction.
- Since household pipes and plumbing materials are most likely to be the source of Pb (as shown in this research), homeowners should be encouraged by the appropriate authorities to do a two-sample test at an authorized laboratory to determine whether the tap water contains lead (and other metals) and whether exposure can be avoided or reduced by flushing the cold water tap for a specified length of time (e.g., five minutes).

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APPENDIX

Letters of support from partners organizations



Town of Happy Valley-Goose Bay

P.O. Box 40 Station B
Happy Valley-Goose Bay, Labrador, Newfoundland
AOP IE0
709-896-3321
Fax: 709-896-9454

March 24, 2014

To Whom It May Concern,

On behalf of the Town of Happy Valley-Goose Bay, I would like to extend our support of Merline Fonkwe's research project on the evaluation for the quality of the drinking water in our community. The town is currently re-examining our water system and how we can best move forward with providing a high-quality water resource to our residents. The more information that our town can obtain the better, which is why we are feel so strongly in favor of this project.

This study would be crucial to the decision-making process in the design of sustainable management strategies of our water treatment plants, not only for the prevention public health hazards, but also for the improvement of communication leading to amelioration of public perceptions and attitudes towards the quality of our tap water. We feel that partnering with the Labrador Institute for this project will lead us as a municipality in achieving this exact goal.

If you would like to discuss this further with a representative of the town please feel free to contact the Chair of our Municipal Services Committee, Councillor Shannon Tobin. He can communicate Council's support of this project.

Sincerely yours,

Jamie Snook, His Worship The Mayor



370 Hamilton River Road P. O. Box 460, Station C Happy Valley-Goose Bay, NL A0P 1C0

Phone: 1-709-896-0592, Ext. 229 Fax: 1-709-896-0594 Email: grussell@nunatukavut.ca Website: www.nunatukavut.ca

April 2, 2014

MERLINE FONKWE, PhD | EARTH SCIENTIST/MINERAL DEPOSITS Exploration & Environmental Geochemistry, Applied Mineralogy Labrador Institute, Memorial University of Newfoundland PO Box 490, Stn. B 219 Hamilton River Rd., Rm. 113 Happy Valley-Goose Bay, NL, A0P 1E0 T 709 896 8589 | F 709 896 2970

Dear Dr. Fonkwe;

NunatuKavut Community Council Inc. (known as NunatuKavut) is pleased to offer this letter of support, confirming our support for research on rural and remote drinking water issues in Newfoundland and Labrador. NunatuKavut represents approximately 6000 Southern Inuit members, primarily living in southern and central Labrador.

Water-related research and decision-making that effectively and appropriately engages Indigenous Knowledge and Indigenous methodologies is important to NunatuKavut because water is always a concern for our organization. One of our communities, Black Tickle, doesn't have consistent access to clean water and several other NunatuKavut communities face various water related challenges. A research study that will focus on better understanding water quality, supply and access in the community and its impact on local community members' lives will be beneficial for future community development and advocacy purposes. It is hoped that such a study will also serve to increase community capacity in the area of future economic and social development.

On behalf of NunatuKavut, I look forward to partnering with you and helping out in what capacity we can. Best wishes in the upcoming proposal.

Sincerely,

George Russell, Jr. Natural Resources Manager



Government of Newfoundland and Labrador Department of Environment and Conservation Water Resources Management Division

Dr. Merline Fonkwe Research Scientist Labrador Institute, Memorial University of Newfoundland PO Box 490, Station B 219 Hamilton River Road, Room 113 Happy Valley-Goose Bay, NL, AOP 1EO, Canada

March 24, 2014

Re: Letter of Support, Drinking Water Research Project

Dear Dr. M. Fonkwe:

This letter is in response to your request for the NL Department of Environment and Conservation (ENVC), Water Resources Management Division (WRMD), to support a research project on the assessment of physiochemical characteristics of raw water sources and municipal drinking water systems within the province of Newfoundland and Labrador. This project aims to investigate operational parameters in municipal water distribution systems to improve and maintain water quality throughout the system.

The WRMD will contribute to the project by providing publically available drinking water data collected during routine sampling programs in the province. Other than responding to general inquiries about sampling schedules, measured parameters, or knowledge regarding community distribution systems, the WRMD cannot provide resources for the collection of water samples or specific work as part of the research team. No monetary contribution will be made.

Please accept this letter of support from the NL ENVC WRMD, subject to the above conditions.

Sincerely,

Grace de Beer Environmental Scientist Water Resources Management Division Department of Environment and Conservation 2 Tenth Street, P.O. Box 3014, Stn. B Happy Valley-Goose Bay, NL, A0P 1E0 Office: 709.896.5542 Cell: 709.899.3861 Fax: 709.896.9566 Email: gracedebeer@gov.nl.ca