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A Manganese in Well Water Risk Map for Nova Scotia

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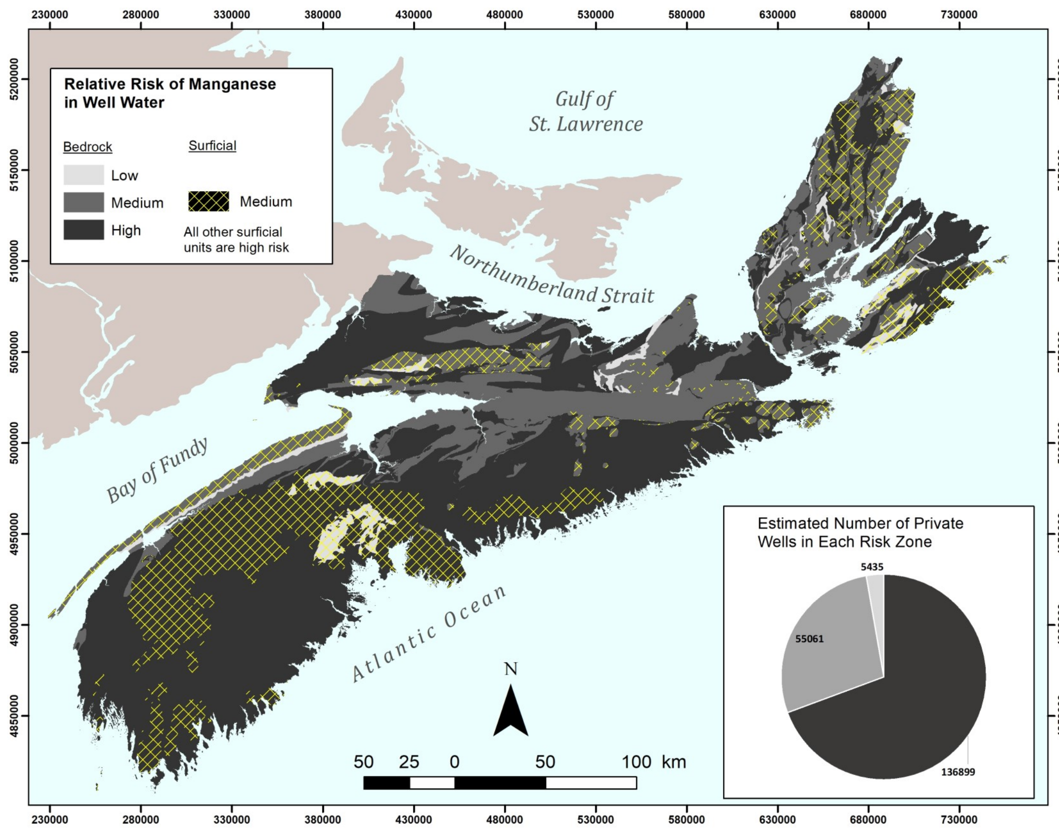

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Cover Illustration

Risk map of manganese in bedrock and surficial aquifers, Nova Scotia, Canada.

Note

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G. W. Kennedy

Abstract

Approximately 42% of Nova Scotians are supplied by private wells, and these water sources are not monitored or regulated with respect to water quality. Effective communication of the health risks associated with the ingestion of manganese in drinking water from private wells is critical for reducing manganese exposure and protecting human health. The relationship between manganese in the province's well water and geology, along with geochemical controls on manganese mobility, such as pH, were investigated to develop a new manganese in well water risk map, which will be used to communicate risk to well owners and to inform groundwater supply development.

Available manganese in well water data were compiled for bedrock (n=3727) and surficial (n=986) aquifers, and classified by the source aquifer (i.e., geological unit). The frequency with which manganese exceeds Health Canada's maximum acceptable concentration (MAC) of 120 µg/L in well water samples was tabulated for the province's five major bedrock groundwater regions, surficial aquifers grouped by the underlying bedrock groundwater region, and over 80 individual bedrock units. Geology was shown to be the most important provincial-scale control on the distribution of manganese concentrations in well water. Province-wide about 22.5% and 45% of well water samples exceeded the Health Canada (2019) MAC and aesthetic objective (20 µg/L), respectively, in their untreated well water.

The highest exceedance rate (33.4%) of the Health Canada MAC for manganese in drinking water was associated with the metamorphic groundwater region of Nova Scotia, likely due to the higher content of manganese present in aquifer materials, such as the manganese-rich Beaverbank and Moshers Island formations (Goldenville Group). Various other bedrock aquifers in all of the province's five groundwater regions were associated with elevated manganese, including various units of the South Mountain Batholith, which may indicate digested inclusions of manganese-enriched Meguma rocks, and Cumberland and Mabou Group aquifers, especially where chemically reduced strata or units are present. In other cases, the relationship between geology and manganese in well water was not evident. For example, some bedrock units associated with known manganese occurrences (e.g., New Ross leucomonzogranite) were not associated with a higher likelihood of manganese in well water, which may be due to the more local scale of the mineralized zones in the host bedrock.

Unlike uranium and arsenic, manganese commonly exceeds the Health Canada MAC in surficial aquifers in Nova Scotia (17% of water samples). Surficial aquifers in sedimentary basins were associated with a higher risk of manganese in well water, which may be due to more alkaline conditions of these aquifers compared to other surficial aquifers in Nova Scotia, or due to the greater availability of manganese in host aquifer materials. The study highlighted other controls on manganese occurrence and mobility, including the influence of the pH and redox environment. Lower concentrations of manganese in groundwater were generally observed where pH was greater than 8, which was attributed to the formation of manganese precipitates with oxygen or carbon.

Based on the percentages of manganese in well water samples exceeding the Health Canada MAC for various geological units, a manganese in well water risk map was developed. Demographic analyses show that approximately 136,899 private wells are in high risk areas (>15% exceedance rate), and the overall percentage of private well water exceeding safe drinking water limits in Nova Scotia may be as high as 23.5% (~90,000 persons). Many of the communities with the greatest risk in terms of number of private well users in a high-risk area for manganese in well water, are also at a high risk for arsenic and/or uranium in well water.

Introduction

Manganese (Mn) is a metallic element that occurs naturally in most rock types. It also occurs in soils and sediment, primarily from the weathering of manganese bearing rocks. Manganese can be leached from overlying soils and sediment, as well as from bedrock minerals, and transported in groundwater and surface water flow systems. After iron, manganese is the second most abundant heavy metal in the natural environment, and although naturally occurring manganese is abundant, it can also occur as a result of human activities, such as mining and other manufacturing and industrial activities.

Manganese is an essential element for humans in small quantities, but can be harmful if it is ingested in high concentrations. The current maximum acceptable concentration of manganese in drinking water is 120 µg/L (Health Canada, 2019).

Uses of Manganese

Global demand for manganese is largely driven by the use of the metal as a hardener in the fabrication of steel alloys. Manganese is also used in the manufacture of products such as batteries, fertilizers, fungicides, cosmetics, fireworks, paints, and in the treatment of drinking water as an oxidizing agent (permanganate).

There has been considerable manganese deposit research and mapping in Nova Scotia. Records indicate that manganese deposits in Nova Scotia were identified as early as 1862, with peak production of manganese ore occurring during the year 1870 (1256 tons) (Bishop and Wright, 1974). A comprehensive review of manganese deposits in Nova Scotia was conducted by the province from 1967 to 1970 (Bishop and Wright, 1974). Presently, there is low interest in prospecting for manganese in Nova Scotia compared to other jurisdictions. This is largely due to the lower economic grades of the province's occurrences or the cost associated with extracting manganese from some of its mineral hosts (e.g,. manganiferous garnet) (White, personal communication). Nonetheless, future interest in manganese exploration in the province may increase with technological advances in manganese extraction, coupled with a decrease in the world's supply of easily exploited manganese deposits.

Sources of Manganese

Manganese comprises approximately 0.085% to 0.095% of the earth's crust and is a component of many rock types, particularly those of metamorphic and sedimentary origin. Manganese can exist in different oxidation states, but it most commonly occurs as the reduced, soluble Mn (II) and the insoluble, oxidized Mn (IV). Manganese has a strong affinity for oxygen and common manganese oxide minerals include pyrolusite (MnO_2), manganite (Mn_2O_3-H_2O), hausmannite (Mn_3O_4) and psilomelane. Other common manganese bearing minerals include manganese carbonates (e.g., rhodochrosite, $MnCO_3$), manganese silicates (e.g., rhodonite, MnCa SiO_4) and ferromagnesian silicates (e.g., hornblende, olivine). The three primary types of manganese occurrences in Nova Scotia are generally considered to be related to: (1) sedimentary processes (oxide, carbonate and bog types), (2) replacement and residual processes, and (3) vein processes (Bishop and Wright, 1974).

Sedimentary environments for manganese include shallow zones where surface water circulates within marine or terrestrial basins. This type of manganese enrichment is observed in Goldenville Group rocks (Fig. 1) as Mn-enriched calc-silicate nodules in laminated slates and siltstones, and as coticule-rich layers consisting of bands of spessartine garnets, manganese carbonate, and quartz-rich laminations near the stratigraphic top of the group (Graves and Zentilli, 1988a; Waldron, 1992, White, 2010). Manganese enrichment has been used as a marker layer of the transition from the older, sand-rich turbidites of the Goldenville Group (uppermost units include the Beaverbank and Mosher's Island formations) to the younger, overlying mud-rich turbidites of the Halifax Group (White, 2010). The Beaverbank Formation, and regional equivalents (e.g., Moshers Island Formation), were deposited during shallow water marine conditions that were becoming progressively anoxic. Manganese became highly concentrated as the

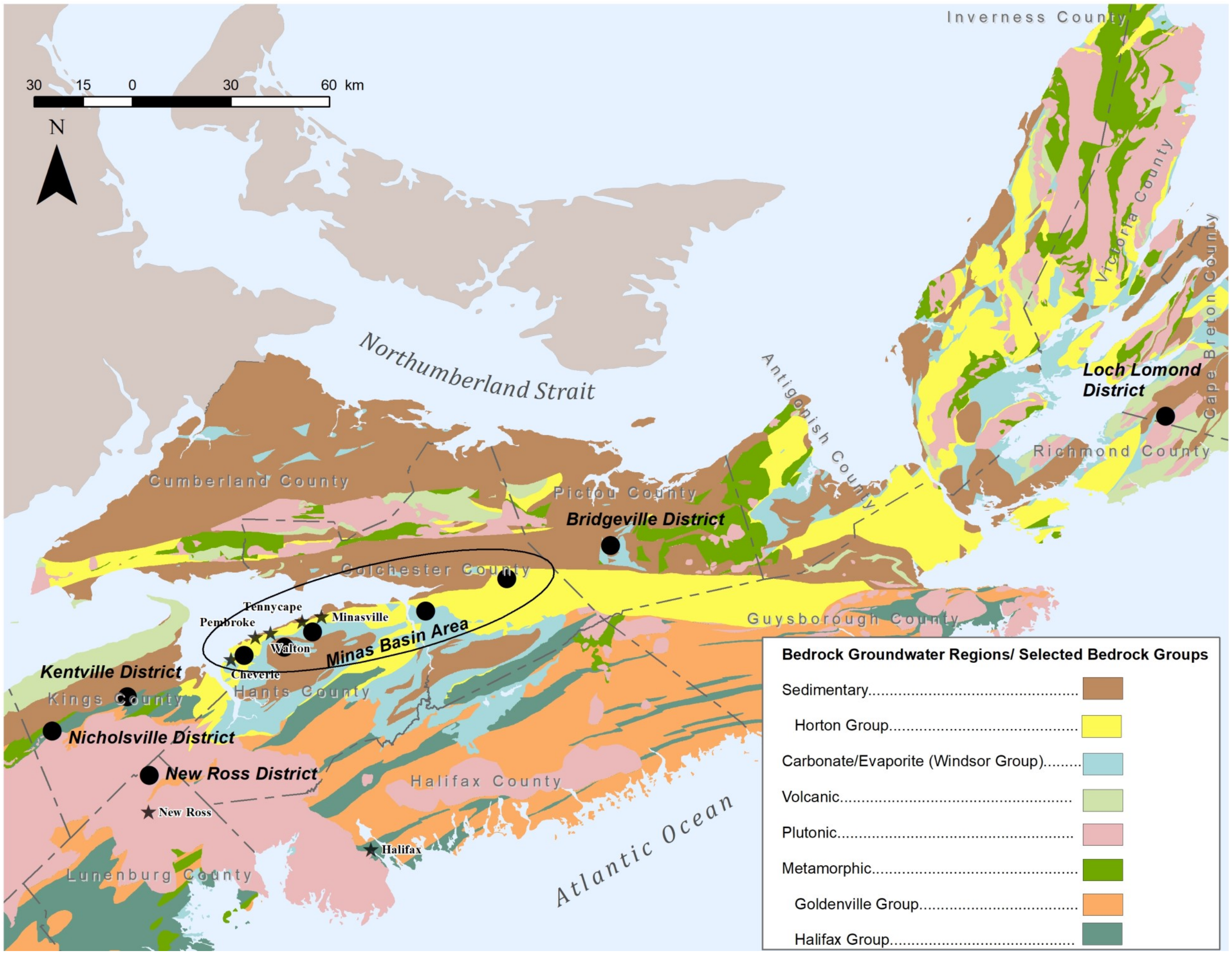

Figure 1. Bedrock geology and location of ten manganese districts in Nova Scotia identified by Bishop and Wright (1974).

anoxic conditions developed. Subsequent oxidation of organic matter near the sediment-water interface during early diagenesis stimulated the precipitation of manganese carbonate minerals from pore fluids (Graves and Zentilli, 1988a). Spessartine garnet in these coticules and nodules subsequently developed during regional and contact metamorphism.

In Nova Scotia most of the known manganese deposits are associated with replacement or vein type processes of hypogene origin (Bishop and Wright, 1974). Manganese ores tend to be associated with carboniferous strata, particularly Windsor Group limestone, or infilling of fissures in crystalline rock. Bishop and Wright (1974) identified ten principal manganese districts in Nova Scotia based on field and laboratory investigation of over fifty manganese occurrences in Nova Scotia (Fig. 1, Table 1). Most of these occurrences are located between the communities of Cheverie and Minasville and are found within the base of Windsor Group rocks at the contact with the underlying Horton Group (Fig. 1).

The most extensive replacement type deposits occur near the communities of Cheverie, Pembroke, Walton and Tennycape (Fig. 1) and are associated with Windsor Group Macumber Formation shaly limestone and overlying ‘Pembroke Formation’ limestone conglomerate rocks (Bishop and Wright, 1974). The Pembroke Formation is no longer considered a geological formation and is now referred to as Pembroke breccia, which describes limestone breccia and conglomerate associated with near surface exposures of Macumber Formation rocks (Murray, 2000).

Table 1. Summary of ten principal manganese districts in Nova Scotia.

Manganese District	Age	Type	Rock Type	Mn content in collected ore specimens (Bishop and Wright, 1974)
Minas Basin area (includes 5 districts)	Mississippian	Mainly replacement type	Limestone, conglomerate, shale, sandstone	48.75%
New Ross district	Devonian	Vein type	Biotite granite	55.12%
Loch Lomond district	Mississippian	Mainly replacement type	Limestone, conglomerate, shale, sandstone	41.90%
Nicholsville district	Silurian	Vein type	Slate, gabbro intrusion	42.70%
Kentville district	Silurian	Vein type	Slate, gabbro intrusion	42.70%
Bridgeville district	Silurian-Mississippian	Mainly replacement type	Limestone	45.85%

Manganese minerals are also found where hydrothermal water has risen from depth. The most well-known vein type manganese deposit in Nova Scotia is found in the New Ross area, where the manganese ore-bodies occur in lenticular masses occupying faults and crushed zones in Devonian granite (O'Reilly, 1992). It is believed that the manganese oxides in the ore-bodies are derived from rising hydrothermal solutions mixing with descending oxygen-rich meteoric water. In addition, there are scattered manganese occurrences throughout the slate-rich Halifax Group, often in association with fault zones (White, personal communication). These occurrences are similar to the New Ross area occurrences, but are more likely the result of reduced water rich in manganese coming in contact with oxygenated meteoric water in the fault zones, and causing manganese to precipitate.

Geochemical Controls on the Mobility of Manganese

Studies on the Distribution of Manganese in Groundwater

Manganese can be leached from soils and minerals in rocks and transported by groundwater flow to well water supplies. Manganese is commonly found in Nova Scotia groundwater and initial estimates suggest that it is detected at levels greater than 120 µg/L in more than 25% of untreated water samples from wells in bedrock aquifers (Kennedy, 2019a), although the distribution of manganese in the province's aquifers is not well understood. Globally, various studies have investigated patterns of manganese in groundwater and have shown that elevated manganese can occur in both surficial and bedrock aquifers (Ayotte et al., 1999; Daughney, 2003; Hasan and Ali, 2010; Homoncik et al., 2010; McMahon et al., 2019; Bondu et al., 2020; Zhang et al., 2020).

An investigation of manganese concentrations in groundwater in the United States showed that the northeastern states, which have similar geology to parts of Nova Scotia, host some of the country's highest concentrations of manganese in groundwater (McMahon et al., 2019). A study that included an assessment of the distribution of manganese in aquifers in New England showed similar rates of detection in glacial till and bedrock aquifers. About 46% of well water samples exceeded 30 µg/L in surficial aquifers (n=145) whereas about 44 % exceeded 30 µg/L in bedrock aquifers (n=607) (Ayotte et al., 1999). Manganese occurred in all aquifer types evaluated in the study but well water samples from metasedimentary aquifers where the rocks were derived from variable sulfidic sedimentary protoliths had higher concentrations of manganese than well water samples from felsic igneous rocks. Similarly, Flanagan et al. (2014) reported that bedrock types in New Hampshire that had over 30% of samples (n=232) exceeding 300 µg/L predominantly consisted of metasedimentary bedrock units.

A regional-scale groundwater geochemical study in southern Quebec found that most high manganese concentrations in well water occurred in less chemically evolved, near-neutral $CaHCO_3$ groundwaters, particularly those associated with metasedimentary and metavolcanic lithologies (Bondu et al., 2020). Manganese concentrations exceeded 120 µg/L in 23% of all water samples (n=2369), and high manganese occurred in both surficial and bedrock aquifers over a wide range of geological settings. High manganese groundwaters were predominantly of $CaHCO_3$ type, moderately mineralized, slightly acidic to slightly alkaline, and mildly reducing. Manganese was strongly positively correlated with iron and silicon and negatively correlated with sodium, boron and chloride. Bondu et al. (2020) suggested that manganese concentrations in groundwater are limited by the precipitation of manganese carbonates above a pH of 7.

Geochemical Controls

The distribution of manganese in groundwater is highly heterogeneous and the result of complex hydrogeochemical processes. There are a wide variety of manganese containing minerals that interact with water, including ferromagnesian silicates, and manganese oxides, carbonates and sulfides and some minerals are more likely to release manganese, such as manganese carbonates and oxides in mineralized areas (Bourg and Bertin, 1994; Bondu et al., 2018).

Due to the widespread availability of manganese in the geological environment, some studies have noted that the conditions for mobilizing manganese are more important than the concentrations present in the source media (Homoncik et al., 2010; McMahon et al., 2019). The concentrations of manganese in groundwater depends on factors such as aquifer lithology, geochemical environment, groundwater flow path and residence time (Homoncik et al., 2010; McMahon et al., 2019; Bondu et al., 2020). On a regional-scale, bedrock composition and mineralogy may be more important in controlling patterns of manganese concentrations in well water, whereas factors affecting manganese mobility, such as groundwater pH and redox potential, and the interaction of manganese with various groundwater constituents, such as dissolved organic carbon (DOC) and iron, may be more important at a local-scale.

Most studies show that the mobility of manganese in groundwater is controlled mainly by pH and redox conditions, with greater manganese mobility associated with oxygen depleted anaerobic systems in near-neutral pH conditions (e.g. Homoncik et al., 2010; McMahon et al., 2019; Bondu et al., 2020) where the reduced form of manganese, Mn(II) is more likely to be present. The oxidized form of manganese (MnIV) has low solubility in near neutral conditions (Daughney, 2003). Manganese has generally been found to be inversely related to pH, with studies suggesting that at higher pH levels, manganese may form precipitates in the presence of oxygen or carbonates (Bondu et al., 2018; Homoncik et al., 2010; Bondu et al., 2020).

Because manganese has been associated with near-neutral pH conditions, some studies have also suggested that elevated manganese concentrations in groundwater are associated with less evolved groundwater chemistry (McMahon et al., 2019; Bondu et al., 2020). For example, McMahon et al. (2019) reported higher manganese concentrations occur near shallow water tables. In contrast, Zhang et al. (2020) showed a positive correlation between increasing manganese and total dissolved solids (TDS) in a floodplain surficial aquifer comprised mainly of glaciofluvial and alluvial deposits in northeastern China and suggested that manganese concentrations may increase with aquifer residence time. The relationship was attributed to enhanced dissolution of manganese from geologic materials along the groundwater flow path due to the increase in ionic strength and decrease in activity coefficient associated with increasing TDS.

Under reducing conditions, the dissolution of iron oxyhydroxides could result in the release of sorbed manganese to groundwater (Daughney, 2003; Homoncik et al., 2010; Bondu et al., 2018; Bondu et al., 2020). Conversely, under oxidizing conditions dissolved manganese may be removed from groundwater by the sorption of manganese to precipitated iron oxyhydroxides. Manganese has been shown to be positively correlated with high NH_3, or low O_2 and NO_3-N groundwater, which are indicators of reducing conditions (McMahon et al., 2019; Zhang, 2020). Uranium is more mobile in oxygenated groundwater, and hence an inverse relationship between uranium and manganese has been detected in some Nova Scotia groundwater (Samolczyk et al., 2012; Finalyson-Bourque et al., 2010).

Microbially mediated redox processes controlled by organic matter can also lead to the mobilization of manganese (Bourg and Bertin, 1994). Organic carbon can be an important electron donor in the Mn(IV) reduction process and various studies have identified DOC as one source of that carbon. DOC is therefore considered an important control on the mobility of manganese in groundwater (Daughney, 2003; Homoncik et al., 2010; McMahon et al., 2019; Zhang et al., 2020). Hence, McMahon et al. (2019) suggested that environments with a greater availability of DOC (hydric soils, river infiltration of aquifers) may be associated with higher concentrations of manganese.

The concentrations of manganese are often studied in relation to iron, owing to similarities in their abundance in the geological environment and the common occurrence of iron-manganese oxyhydroxides (Homoncik et al., 2010; Bondu et al., 2020). Most studies show a positive correlation with iron, although the strength of the correlation is highly variable (Homoncik et al., 2010; Ayotte et al., 1999; Daughney, 2003). The association with iron could be due to overlap of reducing environments but also due to the strong affinity of Mn^{2+} to adsorb to iron oxyhydroxides (McMahon et al., 2019). Arsenic is also often studied in relation to groundwater concentrations of manganese and iron due to the strong geochemical affinity of arsenic with iron-manganese oxyhydroxides (Ayotte et al., 1999; Bondu et al., 2020; Zhang et al., 2020).

Anthropogenic sources can also contribute to elevated manganese in some locations, or anthropogenic impacts can mobilize manganese. For example, McMahon et al. (2019) suggested that NO_3 enriched acidic recharge generated by the oxidation of ammonium found in fertilizer and manure or septic tank leachate can mobilize naturally occurring manganese in shallow groundwater. Alternatively, contaminant releases, such as leaking underground gasoline storage tanks, can result in reducing conditions which are associated with increased manganese mobility (Klinchuch and Delfino, 2000). Manganese can also form inorganic complexes with anions such as chloride, sulphate, bicarbonate and carbonate, and land uses that affect concentrations of these anions can result in increased dissolved manganese concentrations in groundwater (Bondu et al., 2020; Zhang et al., 2020). For example, because manganese forms mobile complexes with chloride, road de-icing salt applications and seawater intrusion can mobilize manganese in groundwater.

Sensitivity of Manganese in Well Water Concentrations to Sampling Protocol

The measured concentration of manganese in water samples is sensitive to the method used in preparing the water sample for analysis. Most drinking water samples are acidified in the lab and analyzed using a total metal digest (dissolved + particulate fractions). Samples with high particulate amounts can result in elevated levels of manganese due to the dissolution of any manganese contained in the particulate matter. Dyck et al. (1976) reported a positive correlation of suspended matter with manganese (as well as zinc and iron) in a large well water sampling program in northern Nova Scotia and concluded that the suspended matter had high levels of iron and manganese oxides. When the samples with the highest suspended matter were excluded, the arithmetic mean manganese concentrations decreased by 10%.

Heath Effects and Exposure

At low concentrations, manganese is an essential element for humans and other animals. Elevated concentrations of manganese, however, are associated with neurological effects in humans, especially infants. Common pathways for human exposure to manganese include air, water, soil and food, with food being the most common. In some locations, such as Nova Scotia, drinking water can be a significant pathway for manganese exposure, and studies have shown that manganese in drinking water is more bioavailable than other routes of exposure (Health Canada, 2019).

The World Health Organization (WHO) does not currently have a health-based limit for manganese in drinking water, although they previously had a guideline of 400 µg/L. According to the latest WHO (2011) guidance, it was not necessary to publish a guideline value because the calculated health-based value of 400 µg/L is above concentrations normally found in groundwater. In 2003, the U.S. Environmental Protection Agency (2003) derived a Health Reference Level for manganese of 300 µg/L. The U.S. Geological Survey (USGS) also uses 300 µg/L as a non-enforceable Health-Based Screening Level for manganese in drinking water (Norman et al., 2018).

A new health-based MAC of 120 µg/L (Health Canada, 2019) was recently adopted by Nova Scotia based on emerging epidemiological and toxicological evidence. Studies have associated prolonged consumption of excessive levels of manganese in drinking water with impaired neurological function in infants and children including cognitive and neurobehavioural impacts, and impaired memory, attention and movement in adults (Bouchard et al., 2011; Woolf et al., 2002; Wasserman et al., 2006; Health Canada, 2019). Health Canada (2019) reported that manganese absorption is greater in infants and children and even short-term exposures to manganese in drinking water can be a health risk to infants.

Health Canada (2019) also recently lowered the aesthetic objective for manganese in drinking water from 50 to 20 µg/L. Aesthetic issues associated with excessive concentrations of manganese include the accumulation of manganese oxides in plumbing fixtures, metallic tasting water, discolouration of water and staining of clothes (Homoncik et al., 2010; Health Canada, 2019).

About 42% of Nova Scotians are supplied by private wells (Kennedy and Polegato, 2017) and these water sources are not regulated with respect to water quality. It is the responsibility of private well owners to ensure that the water is safe to drink and to mitigate any potential health risks associated with their drinking water. Kennedy and Drage (2020a) recently estimated that over 50% of the province's private well owners had never tested, or can't recall testing, the chemical quality of their water, and up to 30% of the province's private water wells have manganese levels above the Health Canada MAC in their untreated well water, while about 50% exceed the revised aesthetic objective of 20 µg/L (unpublished data) . This estimate was based on the distribution of manganese in bedrock aquifers compared to the location of private well users.

Treatment systems commonly used in Nova Scotia for the removal of manganese include cation exchange and point of use or point of entry reverse osmosis. Other less common, but effective treatment methods include distillation and catalyzed oxidation/filtration (Nova Scotia Environment, 2020).

Objectives

A risk map has not been previously produced for manganese because it was not considered a human health hazard in Nova Scotia until the Health Canada health-based MAC was released and adopted in 2019. The objectives of this project are to develop an understanding of the hydrogeological controls of manganese in well water and to develop a risk map for private well users in Nova Scotia to communicate risk, with the aim of encouraging water testing and appropriate treatment which will lead to improved public health outcomes. The risk map will focus only on naturally occurring sources of manganese, and will consider all available well-water chemistry data, and the latest available geology mapping.

Methods

The analysis of manganese in well water is based on data from the Nova Scotia Groundwater Chemistry database (NSGCDB) (n=3443) (Nova Scotia Department of Energy and Mines, 2020) and the Atlantic PATH project (n=1270) (Yu et al., 2014). The NSGCDB is maintained by the Nova Scotia Department of Energy and Mines and consists mostly of non-domestic, untreated (raw) well water sample results collected between 1954 and the present from wells intercepting both bedrock and surficial aquifers. The provincial database was compiled from various federal, provincial and municipal data sources of ambient groundwater chemistry, including water quality monitoring data from government buildings with well water supplies, community well water surveys, and Nova Scotia Department of Environment groundwater chemistry data from registered public drinking water supplies, pumping tests, municipal groundwater supplies, and provincial observation wells. Most of these data are publicly available, however, some data are not public due to privacy considerations. Analytical methods vary, but samples were typically analyzed using ICP-MS as a total metal digest of an unfiltered water sample, as recommended for assessments of drinking water quality.

Atlantic PATH is a longitudinal cohort study that is part of the Canadian Partnership for Tomorrow's Health (CanPath, formerly the Canadian Partnership for Tomorrow) Project, and includes approximately 35,000 adult participants aged 30-74 years from Nova Scotia, New Brunswick, Prince Edward Island, and Newfoundland and Labrador (Sweeney et al., 2017; Dummer et al., 2018). Point of use well water samples were collected in Nova Scotia as part of a sub-study focused on arsenic and heavy metal exposures (Yu et al., 2014). Atlantic PATH's protocol for water sample collection instructed participants to run the tap for 10 minutes to flush the system. Participants were asked to identify the source of the water (e.g., municipal vs. well) and whether water treatment was present. Water samples were filtered in the lab prior to acidification and analysis using ICP-MS (adapted EPA method 200.8).

Only manganese in well water data where the laboratory method detection limit was ≤10 µg/L and where there was adequate confidence in the sample location (i.e., water sample locations accurate to the land parcel scale) and sample type (i.e., only raw or suspected raw water samples) were retained in the combined dataset. The manganese data were plotted on digital versions of the most recent bedrock geology maps for Nova Scotia (e.g. Fisher, 2006a, 2006b; Fisher and Poole, 2006; Horne et al., 2009; White et al., 2012, 2017, 2018; Barr et al., 2017; Nova Scotia Department of Energy and Mines, unpublished data, 2020) in ArcGIS™10 (Esri, Inc.) geographic information system software, and a geologic unit was assigned to each water sample.

The Groundwater Regions Map of Nova Scotia (Kennedy and Drage, 2008) subdivides the province into five major bedrock groundwater regions based on the dominant rock type in each bedrock unit shown on the compiled provincial bedrock geology map (Keppie, 2000) (Fig. 2). Statistical summaries of manganese in well water concentrations were produced for each of the bedrock groundwater regions, and for each region, summaries of manganese exceedance rates of the Health Canada (2019) MAC of 120 µg/L were generated for constituent bedrock units (or aquifers) that had a minimum of five water-sampling locations. Manganese in well water concentrations in the 60 to 120 µg/L range were also summarized to capture the percentage of samples that were elevated but did not exceed the Health Canada (2019) MAC.

For the purposes of the analysis, each bedrock unit was considered to be a hydrostratigraphic unit (or aquifer) having characteristic hydrogeochemical properties. Where multiple sample results were available for a given well location (i.e., time series), the most recent manganese result was used for the estimation of the exceedance rate of the Health Canada (2019) manganese in drinking water MAC. The use of average values for a given well location would introduce unacceptable uncertainty and bias where method detection limits vary and sample results for a given well location can include values both below and above detection limits. Each bedrock unit was assigned to a low- (<5%), medium- (≥5 to <15%) or high- (≥15%) risk category in terms of the percentage of well water samples exceeding the acceptable limit of 120 µg/L; similar to the risk categorization framework presented in Kennedy and Drage (2017) for arsenic in well water, and in Kennedy and Drage (2020b) for uranium in well water.

A similar approach was adopted for characterizing manganese in surficial aquifers in the province where statistical summaries of manganese in well water concentrations were produced for wells installed in surficial materials (e.g., glacial till, alluvial deposits), including the percentage of well water samples with manganese exceeding 120 µg/L and the percentage of water samples with manganese in the >60 to 120 µg/L range. The number of available samples was insufficient to characterize individual surficial units, and because bedrock geology has been identified as the main control on the variability of regional till geochemistry (Grosz et al., 2004; Goodwin et al., 2009), water samples from surficial units were sub-divided by the underlying groundwater region and exceedance rates were compared.

Due to the non-normal, left-censored distribution of the data, non-parametric statistical tests, such as the Wilcoxon signed rank and Kruskal-Wallis tests, were used to determine whether various groupings of samples came from statistically different populations, with an assumed alpha of 0.05 (95% confidence interval) as an indication of significance. The rejection of the null hypothesis (i.e., all samples originate from the same distribution) indicates that at least one sample stochastically dominates at least one other sample, meaning that a randomly drawn sample from at least one group is more likely to be larger than a randomly drawn sample from a different group. The post-hoc Dunn's pair-wise comparison test (Benjamini-Hochberg correction) was applied following the Kruskal-Wallis test to evaluate stochastic dominance within the groupings (Dinno, 2018). Statistical analyses were conducted using STATA® (StataCorp, LP) and ProUCL 5.0 software (U.S. Environmental Protection Agency, 2013).

Limitations of the Approach

The approach to the risk mapping assumed that areas of the province with adequate control concerning the relationship between manganese concentrations in well water and geology can be extrapolated into areas with limited data control. The spatial coverage is not regularly distributed across the province and is biased towards more developed areas of Nova Scotia, where water wells and chemistry data tend to be more readily available.

Another limitation of the risk-mapping approach includes the assumption that geology is the dominant control, rather than other factors such as the pH and redox environment, or anthropogenic effects, which may be independent of geology. Because maps of varying scales (from 1:10 000 to 1:500 000) were merged to cover the province, the reliability of the derivative provincial-scale manganese risk map at a given location is constrained by the quality (i.e., accuracy, scale, level of detail) of the original bedrock map. The uncertainty associated with the definition of risk zones increases near geologic boundaries due to factors such as map scale, interpolation of geologic boundaries, and gradational contacts between units.

The compiled water chemistry data spans a period of over 50 years and comes from a variety of sources ranging from samples collected by homeowners who have shared their well water chemistry results with government, to well water quality surveys conducted by groundwater professionals. Hence, sampling and laboratory analytical methods are not consistent across the dataset. Field measurements of relevant geochemical parameters, such as dissolved oxygen, pH and Eh, were not part of the dataset. Although the quality of the well water chemistry data used in the analysis varies, it is still considered useful for detecting regional-scale (e.g., >1:50 000) trends.

Results and Discussion

A total of 3727 manganese in well water samples from bedrock aquifers and 986 samples from surficial aquifers were used in the analysis, with the greatest sample density occurring in suburban areas of Halifax and Sydney (Fig. 2). Elevated manganese occurs in both bedrock and surficial aquifers, which is consistent with the findings of other regional manganese in well water surveys (Ayotte et al., 1999; Homoncik et al., 2010; McMahon et al., 2019; Bondu et al., 2020). Statistical summaries of the data classified by groundwater region (Fig. 3, Table 2) shows that the highest mean (Kaplan-Meier) and median concentrations of manganese are associated with the metamorphic groundwater region. Based on the available data, the overall province-wide exceedance rate of the Health Canada (2019) MAC was 22.5%, although as noted in the previous section, sample locations are not randomly distributed and some areas of the province are underrepresented in the dataset. Approximately 45% of water samples had manganese concentrations exceeding the Health Canada (2019) aesthetic objective. The percentages of samples exceeding the Health Canada MAC and aesthetic objective for manganese in drinking water are very similar to the percentages reported in the regional-scale study conducted in southern Quebec (i.e., 23 and 48%, respectively). As was discovered in the Quebec study, most of the elevated (>120 µg/L) manganese in well water results, where major ion and anion data were also available (n=852), were Ca-HCO_3 type (Fig. 4) (Bondu et al., 2020).

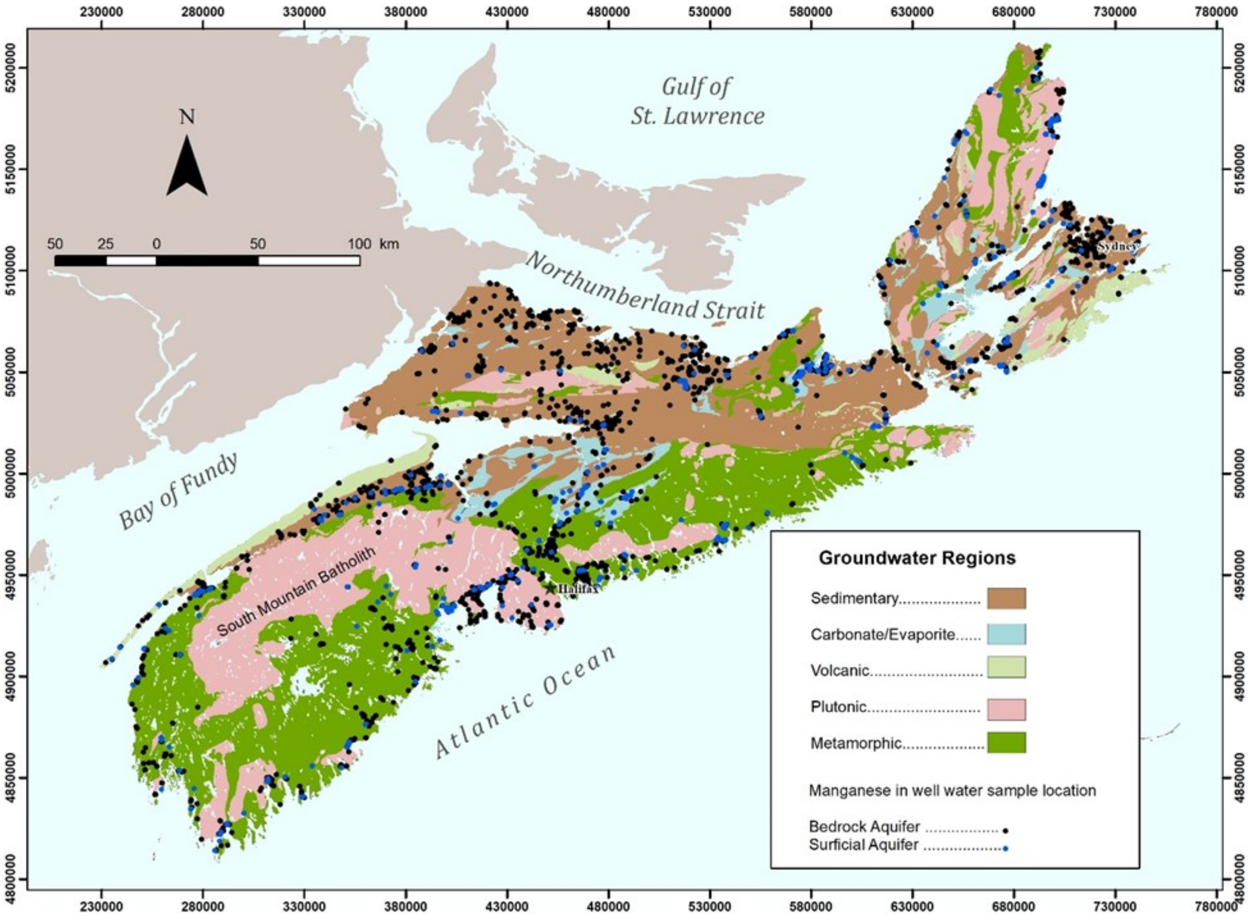

Figure 2. Groundwater regions of Nova Scotia (Kennedy and Drage, 2008) and distribution of manganese in well water data (Atlantic PATH samples excluded from map due to privacy considerations).

The exceedance rate of the Health Canada (2019) MAC for manganese in well water from bedrock aquifers is about 24%, which is less than the 28% exceedance rate reported on the province's most recent map of the distribution of manganese in bedrock aquifers (Kennedy, 2019a). The lower exceedance rate is attributed to the inclusion of the Atlantic PATH water sample data, which has a lower frequency of well water samples exceeding the manganese in drinking water Health Canada (2019) limit (Table 3). It is suspected that underreporting of treatment systems and lab filtration are the main contributing factors for the lower observed exceedance rate in the Atlantic PATH dataset. This underreporting bias may be variable across the province, with water wells in aquifers associated with poor aesthetic quality (e.g., metamorphic rock aquifers) more likely to underreport treatment.

A statistical comparison (Wilcoxon signed rank test) of available samples from the NSGCDB where both filtered and unfiltered samples were collected and analyzed shows that that the filtered sample population has significantly ($p<0.05$) lower concentrations of manganese compared to the unfiltered population (Fig. 5). As noted previously, unfiltered samples with high particulate amounts can result in higher levels of manganese compared to filtered samples due to the dissolution of any manganese contained in the particulate matter.

The Kaplan-Meier mean was highest for metamorphic aquifers and lowest for volcanic aquifers (Table 2). Statistical comparison of manganese in well water concentrations using the Kruskal-Wallis non-parametric test followed by the Dunn test showed that there was no significant difference ($p<0.05$) between surficial and sedimentary region sample populations, and carbonate/evaporite and both sedimentary and plutonic groundwater region sample populations. The metamorphic and volcanic

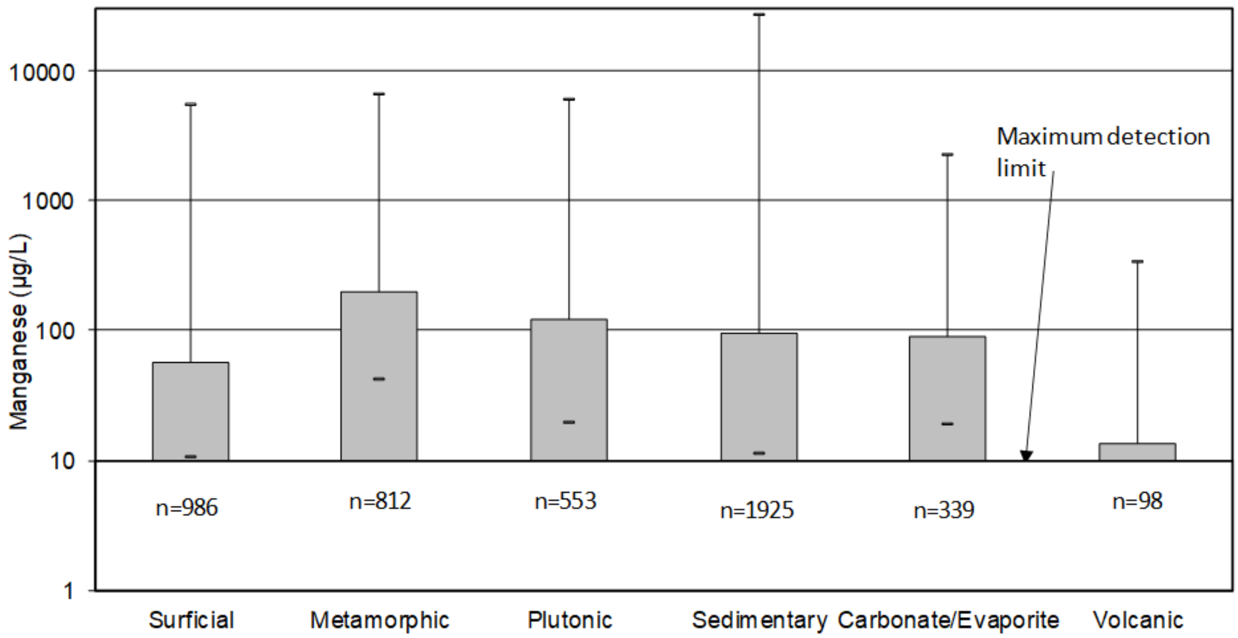

Figure 3. Censored box and whisker plot summarizing the minimum, 25%, median, 75%, and maximum manganese concentrations for the province's surficial aquifers and five bedrock groundwater regions. The portion of the plot below the highest reported detection limit (e.g. 10 µg/L) is not shown.

Table 2. Statistical summary of manganese concentrations classified by groundwater region. The highest reported laboratory detection limit is 10 µg/L. All concentration data are expressed in µg/L.

										Detects Only	
Groundwater Region	**Count Observa-tions**	**Count Detects**	**Percent Detects**	**Percent Exceed[1]**	**K-M[2] Mean**	**Min**	**Median**	**95%ile**	**Max**	**Mean**	**Median**
Metamorphic	812	735	90.5%	33.4%	220.2	<2	42.0	929.3	6610.0	243.2	58.0
Plutonic	553	487	88.1%	25.5%	187.0	<2	19.5	877.6	5980.0	212.2	30.0
Sedimentary	1925	1462	75.9%	21.4%	168.2	<2	11.3	709.0	26800.0	221.1	31.0
Carbonate/ Evaporite	339	252	74.3%	19.2%	104.9	<2	19.0	543.3	2220.0	140.7	40.0
Volcanic	98	62	63.3%	7.1%	26.9	<2	-	181.5	337.5	42.0	8.0
Surficial	986	840	85.2%	16.8%	129.2	<2	10.6	736.0	5500.0	151.4	18.0
TOTAL	**4713**	**3103**	**65.8%**	**22.5%**							

1. Per cent of manganese in well water results exceeding the maximum acceptable concentration of 120 µg/L
2. Kaplan-Meier

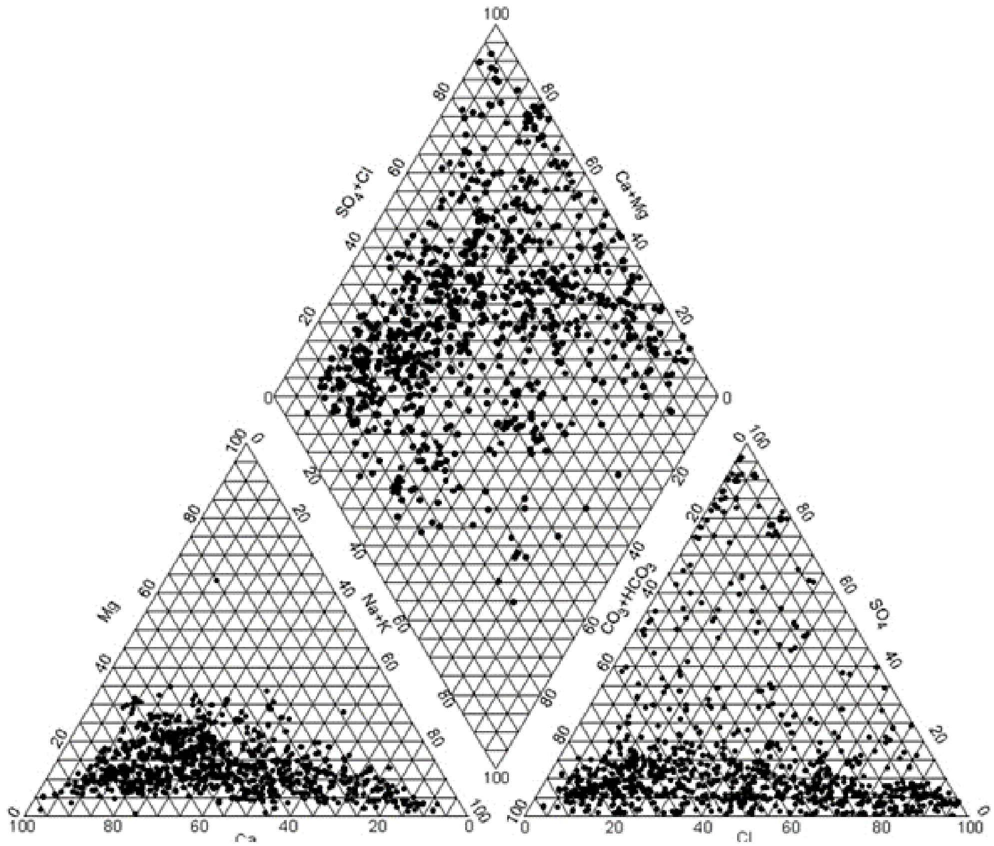

Figure 4. Piper diagram of major cation and anion composition of well water samples in bedrock aquifers with Mn>120 µg/L.

Table 3. Comparison of exceedance rates of the Health Canada (2020) MAC for manganese in drinking water for the Nova Scotia Groundwater Chemistry Database (NSGCDB) and the Atlantic PATH dataset for each groundwater region.

	Count of observations		Per cent of results exceeding 120 µg/L	
	NSGCDB	**Atlantic PATH**	**NSGCDB**	**Atlantic PATH**
Surficial	626	360	20.1%	11.1%
Sedimentary	1468	457	22.1%	18.6%
Carbonate/Evaporite	285	56	20.7%	12.5%
Metamorphic	598	209	38.8%	18.2%
Plutonic	386	170	28.2%	19.4%
Volcanic	80	18	7.5%	5.6%
TOTAL	**3443**	**1270**	**24.9%**	**16.1%**

groundwater region sample populations were significantly higher, and lower, respectively than all other groundwater regions.

A summary of manganese in well water exceedance rates of the Health Canada (2019) MAC for various bedrock aquifers within each of the five bedrock groundwater regions and a more detailed exploration of the potential controls on manganese occurrence in groundwater with respect to lithogeochemistry and aquifer geochemistry are presented in the following sections.

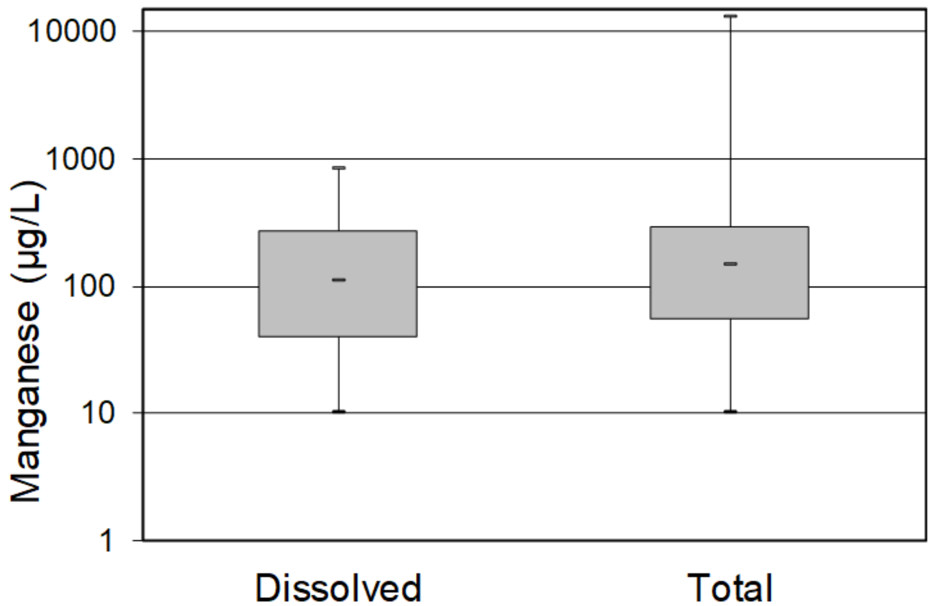

Figure 5. Boxplot of manganese concentrations showing filtered and unfiltered sample populations (detects only, i.e. >10 µg/L). The Wilcoxon signed matched pair test shows a significant difference between the two populations.

Metamorphic Groundwater Region

Distribution of Manganese and Summary of Exceedance Rates

Low to very high concentrations (<1 to >6,000 µg/L) of manganese were observed in the metamorphic groundwater region of Nova Scotia (Table 4, Fig. 6). The overall exceedance rate of the Health Canada (2019) manganese in drinking water MAC for metamorphic aquifers was about 33% (n = 812), and ranges from 8 to 70% for individual bedrock units (Table 4). For Halifax Group aquifers, the Feltzen and Glen Brook formations were associated with the greatest percentage of samples exceeding the Health Canada (2019) MAC. The Beaverbank Formation, and its regional equivalent in southwestern Nova Scotia, the Moshers Island Formation, along with the Government Point Formation were associated with the highest exceedance rates for Goldenville Group aquifers.

Relation of Manganese in Well Water to Lithogeochemistry and Aquifer Geochemistry

Manganese commonly occurs in metamorphic rocks in Nova Scotia, especially within the Meguma terrane. A compilation of manganese contents in Meguma rocks in southwestern Nova Scotia showed average concentrations of 0.79% (6011 ppm) as MnO (White, 2010), with much higher concentrations detected in manganese rich beds in the transition zone from the Halifax Group to the Goldenville Group (Graves and Zentilli, 1988b; Waldron, 1992, O'Beirne-Ryan, 1996; White, 2010). For example, O'Brien (1988) reported concentrations as high 18.9% MnO by weight in coticules of the Moshers Island Formation. Patterns of elevated manganese levels in rock generally correspond to observed patterns in well water, with a high percentage of samples in Beaverbank and Moshers Island formation aquifers, which contain manganese-rich concretions, exceeding the Health Canada (2019) MAC for manganese in drinking water. Similarly, Keefe et al. (2018) found elevated (>11,000 ppb) manganese in surface waters over Moshers Island Formation rocks.

Despite lower documented whole rock concentrations in Halifax Group rocks compared to Goldenville Group rocks (White, 2010), groundwater concentrations of manganese are elevated in some Halifax Group aquifers (Table 4). It is not clear whether manganese detected in Halifax Group aquifers is

Table 4. Percentage of water samples exceeding 60 and 120 µg/L of manganese in well water, based on available data for various metamorphic bedrock units with at least five samples.

Bedrock Unit	Count	Per cent of Mn results >60 µg/L	Per cent of Mn results >120 µg/L
METAMORPHIC GROUNDWATER REGION	**812**	**44.09%**	**33.37%**
Georgeville Group	**11**	**9.09%**	**9.09%**
Goldenville Group	**456**	**37.72%**	**30.26%**
Goldenville Group - Undivided	268	33.96%	27.61%
Beaver Bank F.	10	80.00%	70.00%
Church Point F.	46	30.43%	23.91%
Government Point F.	43	51.16%	44.19%
Green Harbour F.	46	41.30%	28.26%
Moses Lake F.	8	62.50%	25.00%
Moshers Island F.	14	50.00%	50.00%
Taylors Head F.	18	27.78%	22.22%
Halifax Group	**326**	**54.91%**	**38.96%**
Halifax Group - Undivided	57	64.91%	45.61%
Acacia Brook F.	21	38.10%	33.33%
Bear River F.	12	16.67%	8.33%
Cunard F.	165	61.21%	40.00%
Feltzen F.	45	57.78%	48.89%
Glen Brook F.	9	44.44%	44.44%
Lumsden Dam F.	7	14.29%	14.29%
Rock Notch Group	**17**	**29.41%**	**23.53%**
White Rock F.	14	21.40%	21.40%

originating from groundwater flow through adjacent Goldenville Group aquifers, or whether there is sufficient disseminated manganese in Halifax Group rock units that can be mobilized, resulting in elevated concentrations of the metal in well water. About 64% of elevated manganese in well water results (<120 ug/L) from Cunard Formation aquifers are located within 1.5 km of a bedrock contact with the Goldenville Group.

In addition to manganese carbonate type mineralization, some vein type deposits have been identified in gabbro dikes hosted by Halifax Group rocks near the contact with the South Mountain Batholith in the Nicholsville/Kentville area (Bishop and Wright, 1974, Fig. 1). As noted earlier, the area also hosts manganese mineralization in fault zones (White, personal communication). Although conditions favourable for manganese mobilization (reducing environment, near neutral pH) are common in metamorphic aquifers, it is expected that the geochemical environment has an important role in controlling local variability in the distribution of manganese in groundwater. Comparison of manganese in well water exceedance rates in metamorphic aquifers for various pH ranges shows that the frequency of manganese in well water samples exceeding the Health Canada (2019) MAC decreases at pH levels above 8 (Fig. 7). This finding is consistent with other studies that showed manganese was less mobile in alkaline conditions, forming precipitates with oxygen or carbonate (Bondu et al., 2018; Homoncik et al., 2010; Bondu et al., 2020).

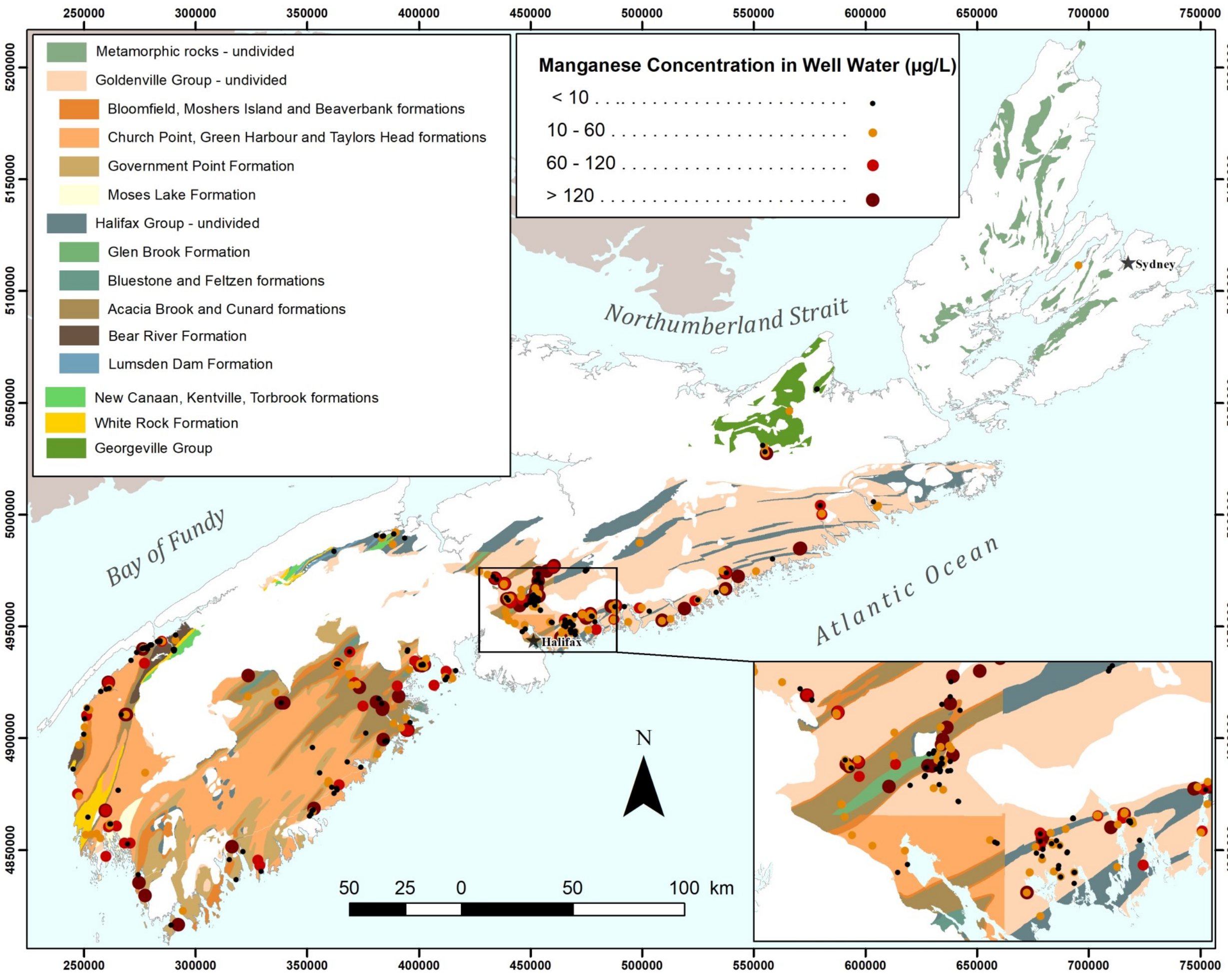

Figure 6. Concentrations of manganese in well water in the metamorphic groundwater region compared to bedrock geology. Atlantic PATH sample locations not shown on the map due to privacy considerations.

Delineation of Risk Zones

Based on the data shown in Table 4, all metamorphic bedrock aquifers were assigned to the high-risk category (≥15%) with the exception of the Bear River and Lumsden Dam formations of the Halifax Group and the Georgeville Group aquifers, which were assigned to the medium-risk category.

Plutonic Groundwater Region

Distribution of Manganese and Summary of Exceedance Rates

Low to very high concentrations (<1 to 6,000 µg/L) of manganese are observed in the plutonic groundwater region of Nova Scotia (Table 5, Fig. 8). The overall exceedance rate of the Health Canada (2019) manganese in drinking water MAC for plutonic aquifers is about 25% (n = 553), and ranges from 0 to 64% for individual bedrock units (Table 5). The highest manganese in well water exceedance rates were associated with the Peggys Cove biotite monzogranite, the Shelburne pluton, the Tantallon leucomonzogranite and the Black Brook granitic suite, including the adjacent intruded Neils Harbour orthogneiss.

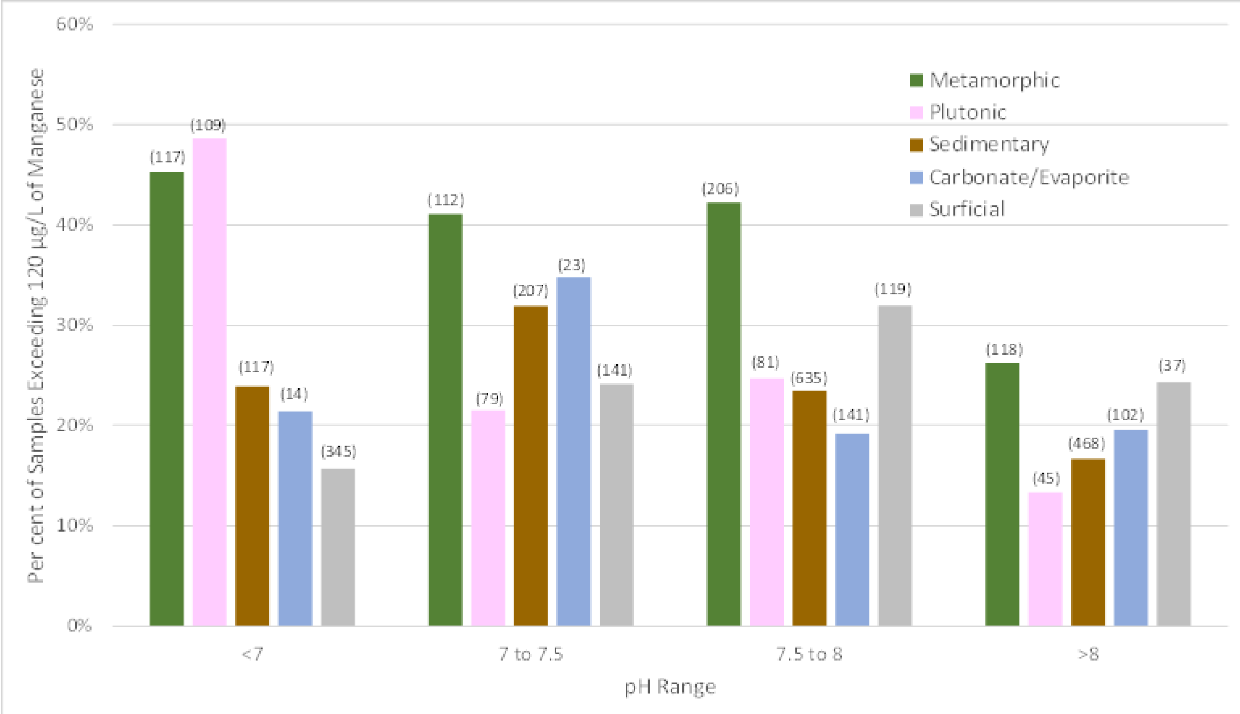

Figure 7. Per cent of water samples exceeding the Health Canada (2019) manganese in drinking water MAC for various pH ranges and aquifer types. Bracketed values indicate sample population size. Due to the small population size, pH data from volcanic aquifers are not included in the figure.

Relation of Manganese in Well Water to Lithogeochemistry and Aquifer Geochemistry

Average whole rock concentrations of manganese were reported to be 478 ppm (0.06% MnO) (n=475) and 465 ppm (0.06% MnO) (n=61) in the South Mountain Batholith (MacDonald et al., 1992) and selected plutons of Cape Breton Island (Barr et al., 1982), respectively. Enriched concentrations of manganese in plutonic rocks have been associated with vein type hydrothermal deposits or infilling of fissures (Bishop and Wright, 1974), with the most well known manganese deposit occurring near the community of New Ross (Fig. 1), where manganese oxides represent more than 40% of the rock by weight in the identified ore zone (O'Reilly, 1992).

Similar to arsenic mineralization, enrichment of manganese in granitoid rocks of the South Mountain Batholith (SMB) may be related to the digestion of inclusions of Goldenville and Halifax group bedrock or from hydrothermal quartz veins in the granite (Ryan and Smith, 1998). A higher percentage of samples from the SMB satellite pluton aquifers in southwest Nova Scotia (Table 5) exceeded acceptable manganese limits compared to the rest of the South Mountain Batholith, which may be because these satellite plutons tend to host more inclusions of Mn-enriched Meguma rocks. The Peggys Cove monzogranite, another unit associated with high percentages of well water samples exceeding the Health Canada (2019) MAC for manganese, has been observed to contain xenocrysts with Mn-rimmed garnet mineralization (Lackey et al., 2011) indicating the digestion of Goldenville group country rock (e.g., Moshers Island Formation) may have contributed to the increased Mn-content. Contamination of plutonic rocks by manganiferous Goldenville Group country rocks has been observed in other areas of the Meguma terrane that host granitoid plutons (e.g., Governor Lake area, Scallion et al., 2011); however, there are few well water sample data available for comparison in these areas.

MacDonald et al. (1992) did not show a clear trend in whole-rock concentrations of manganese in the six major rock types associated with the SMB, and whole rock concentrations of manganese do not appear

Table 5. Percentage of water samples exceeding 60 and 120 µg/L of manganese in well water based on available data for various plutonic bedrock units with at least five samples.

Bedrock Unit	Count	Per cent of Mn results >60 µg/L	Per cent of Mn results >120 µg/L
PLUTONIC GROUNDWATER REGION	**553**	**35.08%**	**25.50%**
Plutonic Rocks - Cape Breton Island	**91**	**16.48%**	**13.19%**
Cameron Brook granodiorite	47	2.13%	2.13%
Black Brook Granitic Suite and Neils Harbour orthogneiss	13	69.23%	53.85%
Remainder of Cape Breton Island granites	31	16.13%	12.90%
Plutons Related to South Mountain Batholith in Southwest NS	**60**	**51.67%**	**38.33%**
Barrington Passage Pluton	21	52.38%	38.10%
Port Mouton Pluton	15	40.00%	33.33%
Shelburne Pluton	16	50.00%	43.75%
Wedgeport Pluton	6	100.00%	50.00%
South Mountain Batholith	**378**	**37.57%**	**27.25%**
Granodiorite (unnamed biotite granodiorite)	10	40.00%	20.00%
Gaspereau Lake biotite granodiorite	5	20.00%	0.00%
Halifax Peninsula leucomonzogranite	89	40.45%	26.97%
Harrietsfield muscovite-biotite monzogranite	55	40.00%	32.73%
New Ross leucomonzogranite	15	6.67%	0.00%
Panuke Lake leucomonzogranite	5	20.00%	20.00%
Peggys Cove biotite monzogranite	11	63.64%	63.64%
Quarry Lake granodiorite	8	12.50%	12.50%
Sandy Lake biotite monzogranite	99	29.29%	17.17%
Tantallon leucomonzogranite	70	52.86%	45.71%
Musquodoboit Batholith	**5**	**40.00%**	**20.00%**
Kinsac Pluton	**8**	**12.50%**	**12.50%**
Plutonic Rocks - Remainder of Mainland Nova Scotia	**11**	**27.27%**	**9.09%**

to predict occurrences of elevated manganese in groundwater. For example, despite a known mineral occurrence in New Ross, a lower exceedance rate of the Health Canada limit for manganese in drinking water was detected in wells completed in New Ross leucomonzogranites (Table 5). This result may indicate that the vein-type manganese mineralization is localized, and does not have a regional influence on groundwater chemistry or that the geochemical environment is limiting manganese mobilization in these aquifers. The percentage of water samples exceeding the Health Canada (2019) MAC decreases with pH in plutonic aquifers, with a much higher percentage of samples exceeding 120 µg/L at pH levels less than 7 compared to pH levels greater than 8 (Fig. 7).

Delineation of Risk Zones

Based on the data shown in Table 5, only Cameron Brook granodiorite, Gaspereau Lake granodiorite and New Ross leucomonzogranite aquifers were assigned to the low-risk category (<5%). Aquifers assigned to the medium-risk category included undivided plutonic rock aquifers throughout Nova Scotia (mainly Cape Breton Island and Cobequid and Antigonish highlands), and the Quarry Lake granodiorite of the SMB and the Kinsac pluton. All other plutonic bedrock aquifers were assigned to the high-risk category (≥15%). There are significant areas where data coverage is sparse, especially on Cape Breton Island, parts of the South Mountain Batholith, eastern areas of the Meguma terrane and the Cobequid Highlands (Fig. 7). Additional well water sampling is recommended in these areas to refine the risk map zones.

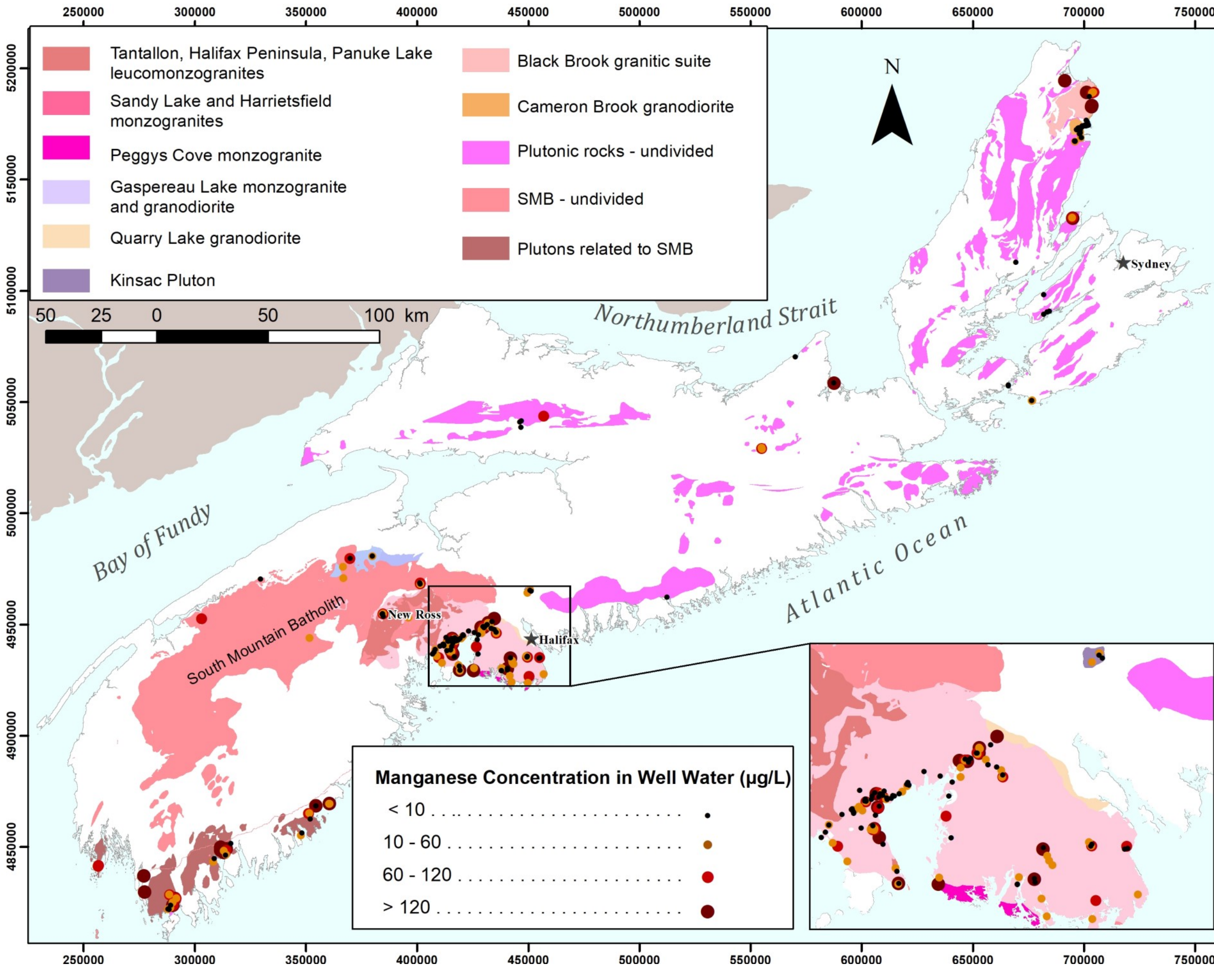

Figure 8. Concentrations of manganese in well water in the plutonic groundwater region compared to bedrock geology. The South Mountain Batholith is denoted as SMB. Atlantic PATH sample locations not shown on the map

Sedimentary Groundwater Region

Distribution of Manganese and Summary of Exceedance Rates

Low to very high concentrations (<1 to >10,000 µg/L) of manganese are observed in the sedimentary groundwater region of Nova Scotia (Table 6, Fig. 9). The overall exceedance rate of the Health Canada (2019) manganese in drinking water MAC for sedimentary aquifers is about 21% (n = 1925), and ranges from 0 to 85% for individual bedrock units (Table 6). The highest manganese in well water exceedance rates were associated with Cumberland and Mabou Group aquifers.

Relation of Manganese in Well Water to Lithogeochemistry and Aquifer Geochemistry

Manganese oxides are commonly deposited in shallow surface water basins, oxygen-poor environments, and tend to be associated with reducing zones in sedimentary bedrock. There are few regional datasets showing whole-rock concentrations of manganese in sedimentary bedrock in Nova Scotia, although several mineral occurrences and one of the ten principal manganese districts identified by Bishop and Wright (1974) occur in sedimentary basins (Fig. 1). The Minas Basin manganese district mineralization occurs along the contact between Horton and Windsor Group bedrock units. Mineral occurrences of manganese (up to >45% by weight) typically occur as replacement type veinlets in fractures within the Cheverie Formation sandstones or within brecciated zones of the contact zone. Boyle (1972) published

Table 6. Percentage of water samples exceeding 60 and 120 µg/L of manganese in well water, based on available data for various sedimentary bedrock units with at least five samples.

Bedrock Unit	Count	Per cent of Mn results >60 ug/L	Per cent of Mn results >120 ug/L
SEDIMENTARY GROUNDWATER REGION	**1925**	**30.29%**	**21.35%**
Arisaig Group	**8**	**25.00%**	**0.00%**
Cumberland Group	**784**	**47.07%**	**35.71%**
Boss Point F.	29	44.83%	31.03%
Claremont F.	11	36.36%	18.18%
Joggins F.	31	54.84%	35.48%
Malagash F.	171	40.94%	29.82%
New Glasgow F.	64	25.00%	10.94%
Parrsboro F.	7	42.86%	28.57%
Polly Brook F.	6	33.33%	16.67%
Port Hood F.	81	22.22%	14.81%
Ragged Reef F.	14	57.14%	50.00%
South Bar F.	238	60.92%	49.58%
Springhill Mines F.	33	60.61%	48.48%
Stellarton F.	25	28.00%	28.00%
Sydney Mines F.	49	51.02%	36.73%
Waddens Cove F.	20	90.00%	85.00%
Fundy Group	**448**	**6.47%**	**4.91%**
Blomidon F.	33	0.00%	0.00%
McCoy Brook F.	11	9.09%	9.09%
Wolfville F.	404	6.93%	5.20%
Guysborough Group	**8**	**25.00%**	**12.50%**
Horton Group	**359**	**18.11%**	**10.31%**
Ainslie F.	14	7.14%	0.00%
Cheverie F.	23	30.43%	13.04%
Clam Harbour River F.	19	31.58%	21.05%
Caledonia Mills F.	39	15.38%	7.69%
Creignish F.	10	20.00%	10.00%
Grantmire F.	140	7.86%	5.71%
Horton Bluff F.	51	33.33%	17.65%
Tracadie Road F.	21	38.10%	28.57%
Mabou Group	**180**	**47.78%**	**27.78%**
Hastings F.	43	41.86%	30.23%
Lismore F.	15	73.33%	46.67%
Pomquet F.	63	52.38%	25.40%
Watering Brook F.	14	35.71%	14.29%
Pictou Group	**126**	**22.22%**	**15.08%**
Balfron F.	86	17.44%	12.79%
Cape John F.	21	23.81%	14.29%
Tatamagouche F.	16	43.75%	31.25%

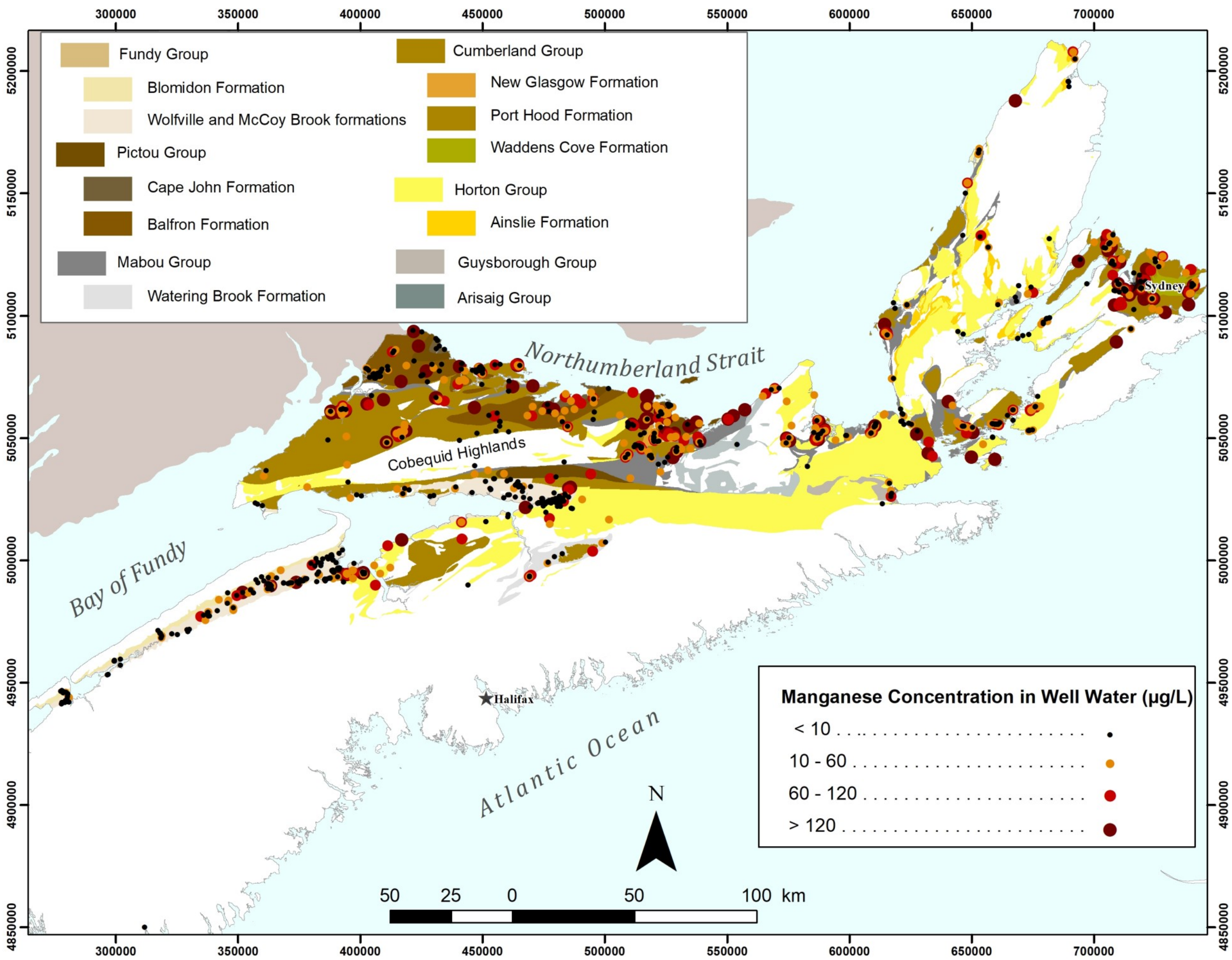

Figure 9. Concentrations of manganese in well water in the sedimentary groundwater region compared to bedrock geology. Atlantic PATH sample locations not shown on the map due to privacy considerations.

MnO levels for various sedimentary units in the Walton-Cheverie area, with composite sample concentrations ranging from 0.1 (775 ppm) to 0.7% (5421 ppm). Ore grade concentrations of manganese (>40%) have also been detected as replacement type deposits in these rocks (Boyle, 1972).

Studies reporting on the geochemistry of coal beds in Nova Scotia indicate average manganese concentrations in the 23 ppm to 1223 ppm range (Kaplan et al., 1985; Zodrow and Zentilli, 1979). In Joggins Formation coal beds, Kaplan et al. (1985) attributed enriched heavy metal trace element concentrations, including manganese (average 184 ppm, n=7), to the redeposition of sediments derived from the Cobequid highlands. Similarly, Dyck et al. (1976) attributed anomalies in heavy metals concentrations in groundwater, such as manganese, to known mineral occurrences in up-gradient mineralized zones of the Cobequid highlands.

There are insufficient whole-rock geochemistry data to determine whether there is an association between concentrations of manganese in well water and manganese in the host bedrock. Based on Table 6, however, many of the aquifers with lower rates of manganese exceeding drinking water limits are associated with a greater proportion of fluvial red beds indicating more oxygenated depositional conditions (e.g., Blomidon, Ainslie, Cheverie, Wolfville, Balfron, Cape John, Port Hood formations, Guysborough Group). The Waddens Cove Formation (Table 6, Fig. 9) was associated with the highest percentage of well water samples exceeding the Health Canada (2019) MAC for manganese in drinking water and is composed of a mixed redbed and coal-bearing section of sandstone and mudrocks (Boehner and Giles, 2008). These reduced coal-bearing stata, or the overlying Sydney Mines Formation, which contains extensive coal resources (Boehner and Giles, 2008), may be a source of elevated manganese in well water.

Given that manganese is widely available in sedimentary bedrock aquifers, it is likely that the geochemical environment has an important role in controlling local variability in the distribution of manganese in groundwater. Comparison of manganese in well water exceedance rates in sedimentary aquifers for various pH ranges shows that the frequency of manganese in well water samples exceeding the Health Canada (2019) MAC is greatest at pH levels between 7 and 7.5 and is lowest at pH levels above 8 (Fig. 7).

Delineation of Risk Zones

Based on the data shown in Table 6, only Arisaig Group and Ainslie and Blomidon Formation aquifers were assigned to the low-risk category (<5%). Aquifers assigned to the medium-risk category included the Guysborough Group and New Glasgow and Port Hood formations of the Cumberland Group, the McCoy Brook and Wolfville formations of the Fundy Group, the Cheverie, Caledonia Mills, Creignish, and Grantmire formations of the Horton Group, the Watering Brook formation of the Mabou Group, and the Balfron and Cape John formations of the Pictou Group. All other sedimentary bedrock aquifers were assigned to the high-risk category (≥15%).

Carbonate/Evaporite Groundwater Region

Distribution of Manganese and Summary of Exceedance Rates

Low to high concentrations (<1 to 2,220 µg/L) of manganese are observed in the carbonate/evaporite groundwater region of Nova Scotia (Table 7, Fig. 10). The overall exceedance rate of the Health Canada (2019) manganese in drinking water MAC for carbonate/evaporite aquifers is about 19% (n = 339), and ranges from 3 to 43% for individual bedrock units (Table 7). The highest manganese in well water exceedance rates are associated with Carrolls Corner and Hood Island formations.

Relation of Manganese in Well Water to Lithogeochemistry and Aquifer Geochemistry

There are few regional datasets showing whole-rock concentrations of manganese in carbonate/evaporite bedrock in Nova Scotia, although several mineral occurrences and most of the principal manganese districts identified by Bishop and Wright (1974) occur in carbonate bedrock (Fig. 1).

Table 7. Percentage of water samples exceeding 60 and 120 µg/L of manganese in well water based on available data for various carbonate/evaporite bedrock units with at least five samples.

Bedrock Unit	Count	Per cent of Mn results >60 µg/L	Per cent of Mn results >120 µg/L
CARBONATE/ EVAPORITE GROUNDWATER REGION	**339**	**30.09%**	**19.17%**
(Windsor Group)			
Carrolls Corner F.	14	64.29%	42.86%
Green Oaks F.	17	29.41%	11.76%
Hood Island F.	39	51.28%	38.46%
Meadows Road F.	36	38.89%	22.22%
Pugwash Mine F.	16	37.50%	31.25%
Sydney River F.	98	21.43%	12.24%
Woodbine Road F.	31	16.13%	3.23%
Mainland Nova Scotia - all	**132**	**34.85%**	**27.27%**
Cape Breton Island - all	**207**	**27.05%**	**14.01%**

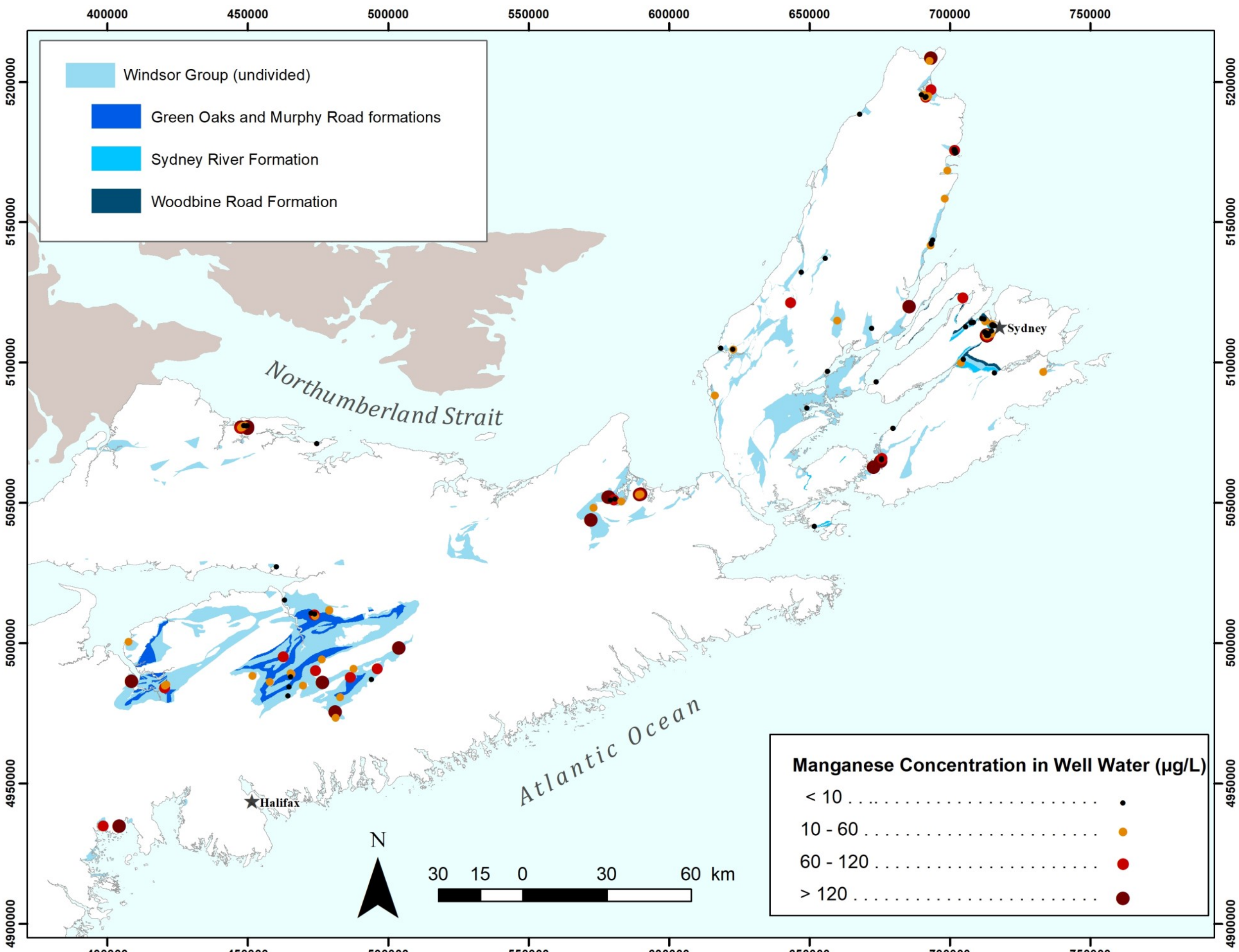

Figure 10. Concentrations of manganese in well water in the carbonate/evaporite groundwater region compared to bedrock geology. Atlantic PATH sample locations not shown on the map due to privacy considerations.

Manganese mineralization is often hosted in dark manganiferous limestones with manganese ores generally occurring as soft-grained pyrosulite or siderite. Pyrolusite occurs in strings and pockets in the limestone at its contact with the underlying Devonian sandstones in Hants and Colchester counties. These replacement type manganese deposits have been associated with Windsor Group's Macumber Formation and Pembroke breccias (Fig. 1) where concentrations of manganese oxides in ore zones can be as high as 48% by weight (Bishop and Wright, 1974). Concentrations of composite manganese samples from limestone rocks in the Walton-Cheverie area published by Boyle (1972) were 0.2% (1549 ppm), whereas manganese was not detected in evaporite rocks in this area. Several manganese deposits in eastern Cape Breton Island were described by Bishop and Wright (1974), occurring as beds and irregular layers and nodules in soft shales which are also associated with dark manganiferous limestones (Fig. 1).

Few well water samples from Macumber Formation aquifers are available so it is not clear whether manganese mineralization in this unit imparts significant concentrations of manganese to groundwater. Although favourable conditions (circumneutral pH, reducing environment) for manganese mobilization could develop in carbonate/evaporite aquifers in Nova Scotia, these aquifers are associated with a higher pH compared to other aquifer types in the province (Kennedy, 2019b), which may limit manganese mobility. As noted earlier, manganese may form manganese carbonate precipitates above a pH of 7 (Bondu et al., 2020). Comparison of manganese in well water exceedance rates in carbonate/evaporite aquifers for various pH ranges shows that the frequency of manganese in well water samples exceeding the Health Canada (2019) MAC is greatest at pH levels between 7 and 7.5 and is lowest at pH levels above 7.5 (Fig. 6).

Delineation of Risk Zones

Based on the data shown in Table 7, only the Woodbine Road Formation was assigned to the low-risk category (<5%). Aquifers assigned to the medium-risk category included the Green Oaks (and regional equivalent Murphy Road Formation) and Sydney River formations, and all undivided Windsor Group aquifers in Cape Breton Island. All other carbonate/evaporite bedrock aquifers were assigned to the high -risk category (≥15%).

Volcanic Groundwater Region

Distribution of Manganese and Summary of Exceedance Rates

Low to moderate concentrations (<1 to 338 µg/L) of manganese are observed in the volcanic groundwater region of Nova Scotia (Table 8, Fig. 11). The overall exceedance rate of the Health Canada (2019) manganese in drinking water MAC for volcanic aquifers is about 7% (n = 98), and ranges from 0 to 40% for individual bedrock units (Table 8). The highest manganese in well water exceedance rates are associated with the Fourchu Group, although there were few available well water sample results (n=5).

Relation of Manganese in Well Water to Lithogeochemistry and Aquifer Geochemistry

There are various regional datasets showing whole-rock concentrations of manganese in volcanic bedrock in Nova Scotia. Dostal et al. (1983) reported average manganese oxide concentrations for various Paleozoic rhyolites to range from 77.5 ppm (0.01%) to 2170 ppm (0.28%) with the highest whole rock concentrations associated with the Arbuckle Brook Formation in the Antigonish Highlands. In eastern Cape Breton Island, Barr et al. (1996) reported manganese oxide concentrations in late Precambrian volcanic belts to range from 155 ppm (0.02%) to 4495 ppm (0.58%). The highest MnO concentrations were observed in Fourchu Group rocks (Barr et al., 1996), which is consistent with the observed patterns of elevated manganese in well water. Data published by MacHattie and MacMullen (2018) shows average concentrations of manganese in volcanic rocks of the eastern Cobequid Highlands to be 838 ppm, ranging from 15 ppm to 4163 ppm (n=1851).

Manganese is a common constituent of volcanic rocks in Nova Scotia, though there are few known manganese containing mineral occurrences in these rocks (Bishop and Wright, 1974). Otherwise, it is not clear why volcanic rocks aquifers generally have lower levels of manganese compared to other groundwater regions in the province. It could be related to factors such as the susceptibility of manganese minerals hosted in volcanic rocks to weathering or the geochemical environment limiting the mobility of manganese in these aquifers.

Table 8. Percentage of water samples exceeding 60 and 120 µg/L of manganese in well water, based on available data for various volcanic bedrock units with at least five samples.

Bedrock Unit	Count	Per cent of Mn results >60 µg/L	Per cent of Mn results >120 µg/L
VOLCANIC GROUNDWATER REGION	98	12.24%	7.14%
East Bay Hills Group	8	0.00%	0.00%
Fourchu Group	5	40.00%	40.00%
Fountain Lake Group	18	11.11%	0.00%
Fundy Group (North Mountain Formation)	47	10.64%	6.38%
Stirling Group	9	0.00%	0.00%

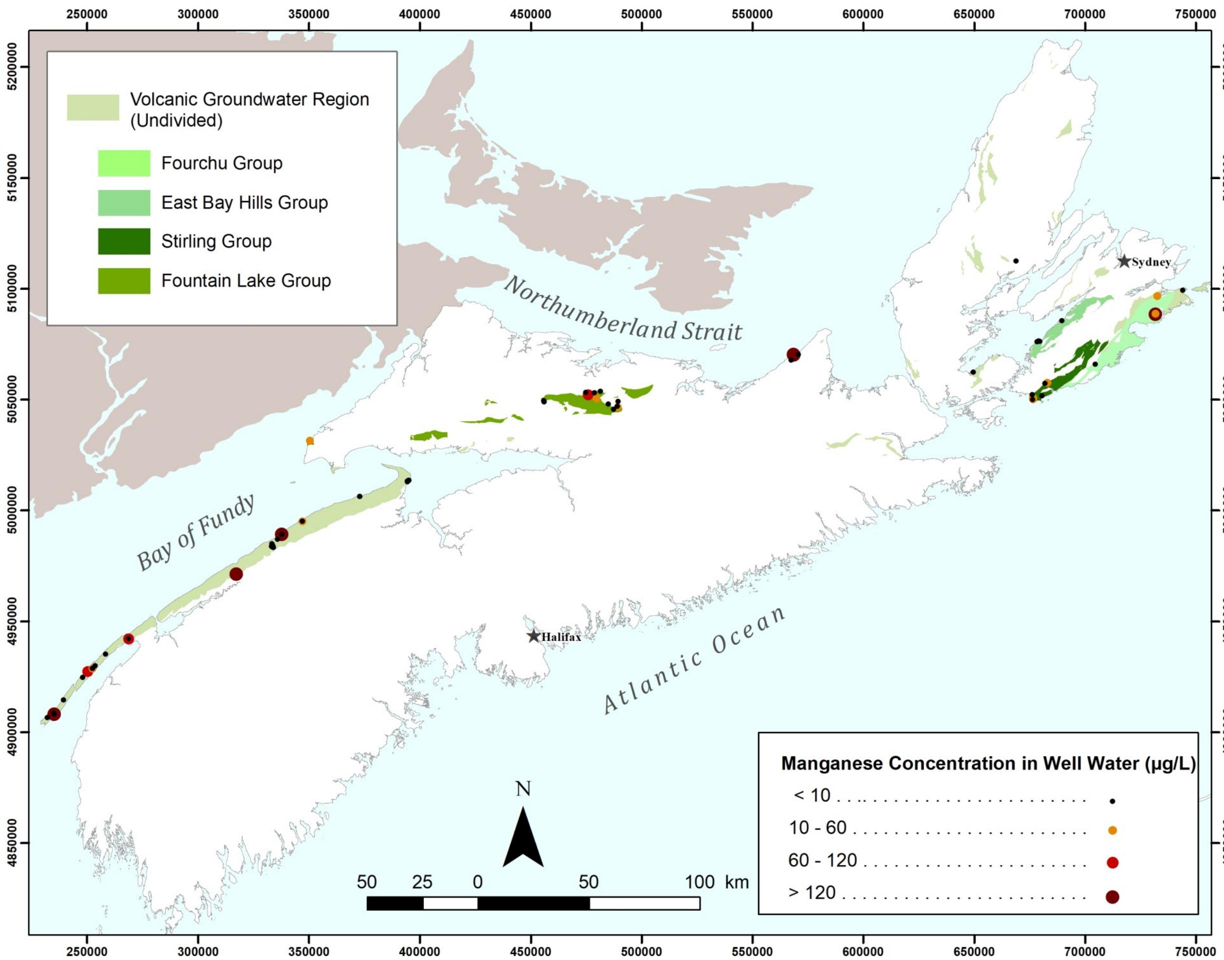

Figure 11. Concentrations of manganese in well water in the volcanic groundwater region compared to bedrock geology. Atlantic PATH sample locations not shown on the map due to privacy considerations.

Delineation of Risk Zones

Based on the data shown in Table 8, the East Bay Hills, Fountain Lake and Stirling groups were assigned to the low-risk category (<5%), whereas the North Mountain basalt aquifers of the Fundy Group were assigned to the medium-risk category and the Fourchu Group was assigned to the high-risk category. All other undivided volcanic rock aquifers were assigned to the medium-risk category (≥5 and <15%). There are fewer well water samples available in volcanic rock aquifers compared to other groundwater regions, and additional sampling is recommended to refine the risk map zones, especially in the western parts of the Cobequid Highlands and Cape Breton Island (Fig. 11).

Surficial Groundwater Regions

Distribution of Manganese and Summary of Exceedance Rates

Low to very high concentrations (<1 to 5500 µg/L) of manganese are observed in surficial aquifers of Nova Scotia (Table 9, Fig. 12). The overall exceedance rate of the Health Canada (2019) manganese in drinking water MAC for surficial aquifers is about 17% (n =986) (Table 9). The highest manganese in well water exceedance rates are associated with wells installed in surficial materials (e.g., till, glaciofluvial, alluvial deposits) overlying the carbonate/evaporite bedrock aquifers.

Relation of Manganese in Well Water to Lithogeochemistry and Aquifer Geochemistry

Large regional till surveys were conducted in Nova Scotia between 1977 and 1982 over mainland Nova Scotia and between 1984 and 1989 over the South Mountain Batholith (Nova Scotia Department of Natural Resources, 2006a, 2006b). The median concentrations of manganese in till samples were greatest in sedimentary basins of mainland Nova Scotia and lowest over the South Mountain Batholith (Table 9). A similar trend was observed with respect to well water concentrations of manganese, suggesting that the availability of manganese in these materials partly explains manganese concentrations in groundwater.

Statistical comparison of manganese in well water concentrations showed a significant difference ($p<0.05$) between populations grouped by groundwater region, however, due to relatively small sample population sizes, pairwise comparisons adjusted for multiple comparisons could differentiate few groupings at a 0.05 significance level. The median manganese concentration of water samples in surficial aquifers overlying the metamorphic groundwater region was shown to be significantly higher than the median manganese concentration of samples from surficial aquifers overlying the plutonic groundwater region.

Although there is evidence of spatial patterns with respect to the distribution of manganese in surficial aquifers in Nova Scotia, there is insufficient data to investigate the relationship between the geochemistry of the province's surficial geology units and concentrations of manganese in well water. The higher concentration of manganese in well water samples from surficial aquifers overlying carbonate/evaporite rocks may also be due to the more circum-neutral conditions associated with these aquifers compared to other surficial aquifers in the province (Kennedy, 2019b). In general, the lower pH typically associated with shallow surficial aquifers, compared to bedrock aquifers, may limit the mobility of manganese. Some unconfined surficial aquifers are also less likely to be associated with reducing conditions because these shallow groundwater systems receive oxygenated recharge, which may limit the release and mobilization of manganese.

Delineation of Risk Zones

Based on the data shown in Table 9, surficial aquifers overlying the carbonate/evaporite and sedimentary groundwater regions groups were assigned to the high-risk category (≥15%) whereas surficial aquifers overlying the plutonic and volcanic groundwater regions were assigned to the medium-risk category (≥5 <15%). Although the exceedance rate of the Health Canada (2019) manganese MAC for surficial aquifers overlying the metamorphic groundwater region corresponds to the medium risk category, these aquifers were conservatively assigned to the high-risk category in consideration of the results of the post-hoc Dunn's multiple comparison test and the higher interpreted mean (Kaplan-Meier) manganese concentration of these aquifers relative to volcanic and plutonic aquifers (Table 9).

Table 9. Percentage of water sample results exceeding 60 and 120 µg/L of manganese in well water, based on available data for various surficial aquifer units with at least five samples. [1]K-M=Kaplan-Meier.

Bedrock Unit	Count water samples	K-M[1] Mean (Mn µg/L)	Per cent of Mn results >60 µg/L	Per cent of Mn results >120 µg/L	Count of till samples	Median concentration of Mn in till (ppm)
SURFICIAL AQUIFERS	**986**	**129.2**	**24.24%**	**16.84%**		
Surficial Aquifers within Metamorphic Groundwater Region	335	110.60	22.69%	13.43%	823	690.0
Surficial Aquifers within Plutonic Groundwater Region	141	75.84	18.44%	12.06%	1948	310.0
Surficial Aquifers within Sedimentary Groundwater Region	348	153.60	24.71%	18.39%	760	1062.5
Surficial Aquifers within Carbonate/ Evaporite Groundwater Region	141	176.70	34.04%	26.24%	72	955.0
Surficial Aquifers within Volcanic Groundwater Region	21	58.40	14.29%	14.29%	40	857.5

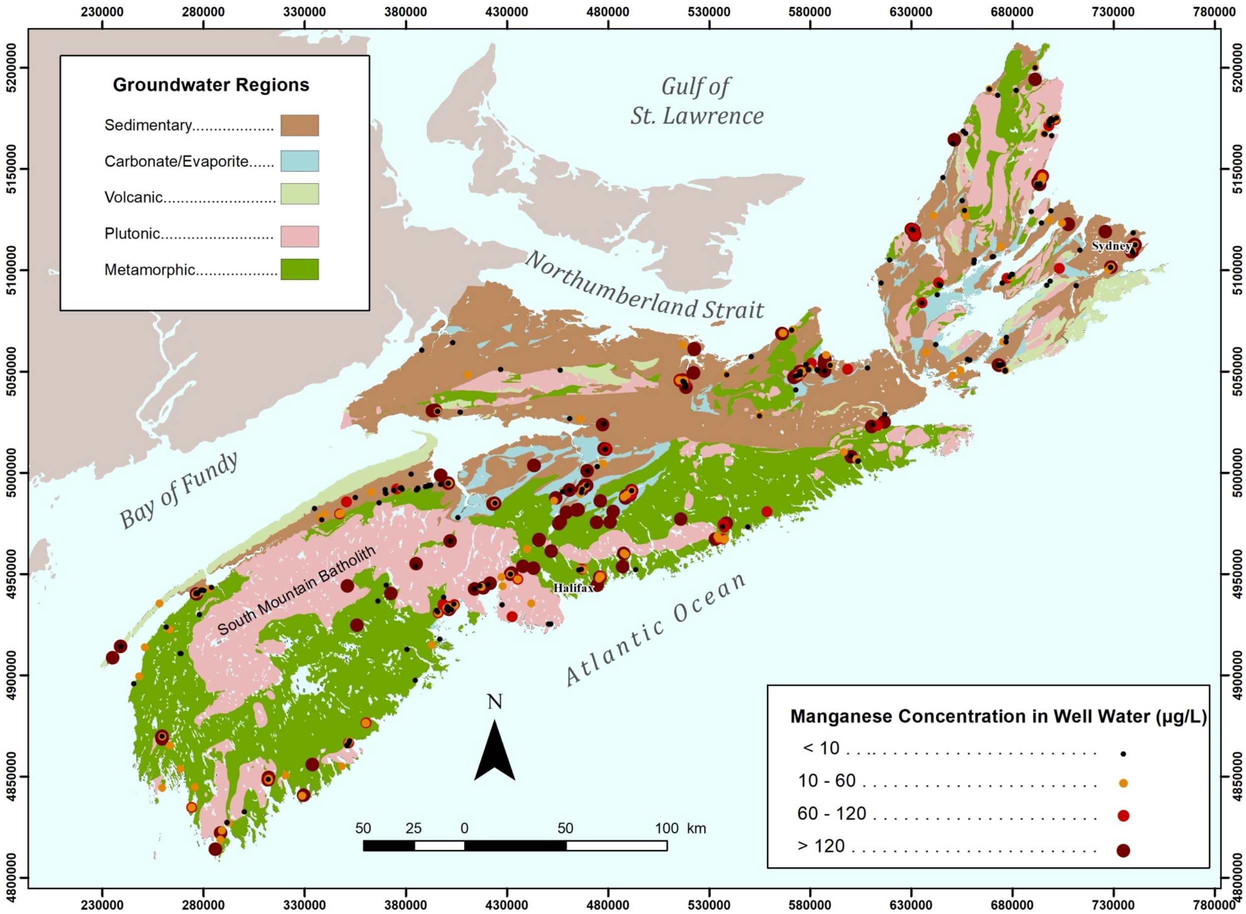

Figure 12. Concentrations of manganese in well water in the surficial aquifers compared to bedrock groundwater regions. Atlantic PATH sample locations not shown on the map due to privacy considerations.

Manganese in Well Water Risk Map for Bedrock Aquifers and Demographics of Risk

Based on the analysis of the distribution of manganese in Nova Scotia's aquifers and exceedance rates of manganese in well water, compared to the Health Canada MAC for various bedrock units, a new risk map showing low- (<5% water samples exceeding Health Canada MAC), medium- (≥5 to <15%) and high- (≥15%) risk zones was developed (Fig. 13). The risk mapping followed a similar methodology as the approach used in the development of the arsenic and uranium in bedrock water well risk map (Kennedy and Drage, 2017; 2020b). The risk map of manganese in well water was developed based on geological mapping and does not consider anthropogenic influences.

Statistical comparison of the sample populations associated with the three zones using the Kruskal Wallis non-parametric test found a significant difference ($p<0.05$) between the three categories of risk. The high-risk category covers about 69% of the province (Table 10) and captures approximately 86% of the exceedances of the Health Canada (2019) manganese in drinking water MAC in the overall dataset (Table 10).

The distribution of private wells in Nova Scotia was inferred from the distribution of residential unserviced civic address points (see Kennedy and Polegato, 2017). The distribution of private wells compared to the risk zones shows that 69% of private wells (~136,899 households or ~266,514 persons) in the province are located in the high-risk zone for manganese in well water, whereas only 3% are located in the low-risk zone for manganese in well water (Table 10, Fig. 13).

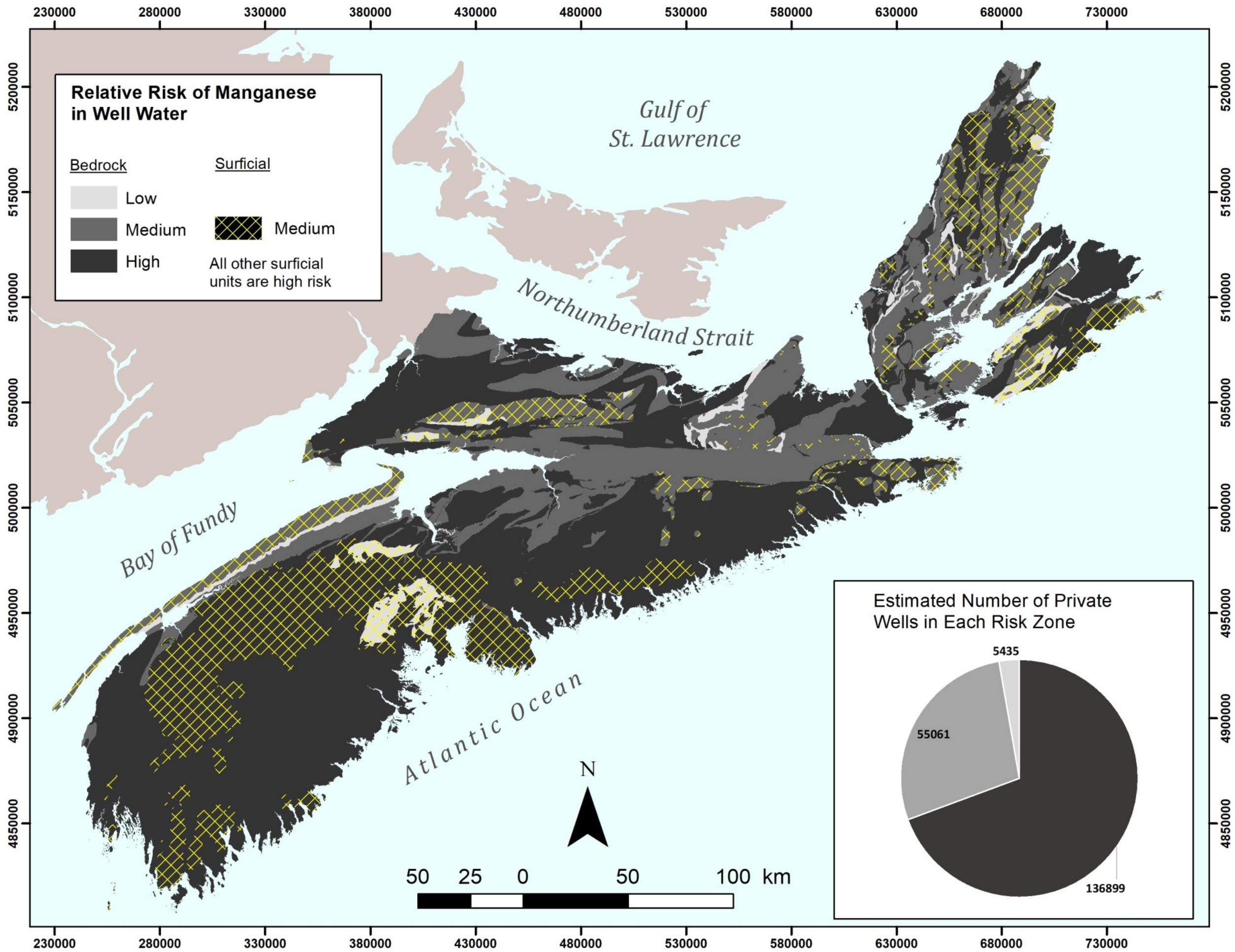

Figure 13. Risk map of manganese in bedrock and surficial aquifers.

Table 10. The area of coverage, estimated number of private wells using bedrock aquifers, and per cent of well water sample results exceeding 60 and 120 µg/L of manganese for each of the three risk zones. The analysis assumes that 91% of private wells are supplied by bedrock aquifers in Nova Scotia (see Kennedy and Polegato, 2017).

Risk classification	Area of coverage (km^2)	Per cent of samples >60 µg/L (n=1250)	Per cent of samples >120 µg/L (n=895)	Estimated number of private wells	Per cent of private wells in risk zone
High	41,993	83%	86%	136,899	69%
Medium	17,961	16%	14%	55,061	28%
Low	2,250	0.3%	0.3%	5,435	3%

The ten communities with the greatest number of private wells in a high-risk zone for manganese are located in suburban Halifax or Sydney (Table 11). Many of the communities with the greatest number of private wells in the high-risk zone for manganese in well water are also located in a high-risk zone for arsenic or uranium in well water (Table 11; Kennedy and Drage, 2017, 2020b). The percentage of private wells with manganese exceeding the Health Canada (2019) acceptable limit of 120 µg/L was estimated by multiplying the calculated exceedance rate for each groundwater region (Table 2) by the approximate number of private wells located within each region. In total, approximately 23.5% of all private wells (~46,000 wells or 90,000 persons) across Nova Scotia may have manganese concentrations exceeding Health Canada limits in their raw well water (Fig. 14), which is similar to the proportion of water samples exceeding the Health Canada (2019) MAC in a regional survey conducted in southern Quebec (Bondu et al., 2020).

Table 11. The ten communities with the largest number of private wells located in a high-risk zone for manganese in well water.

Community	Underlying High-Risk Bedrock Unit	County	Estimated Number of Private wells
Hammonds Plains[1,2]	Halifax and Goldenville groups and South Mountain Batholith	Halifax	2054
Fall River	Halifax and Goldenville groups and Kinsac Pluton	Halifax	1658
Middle Sackville	Halifax and Goldenville groups	Halifax	1361
Upper Tantallon[1,2]	South Mountain Batholith	Halifax	1342
Porters Lake[1]	Halifax and Goldenville groups and Musquodoboit Batholith	Halifax	1276
Lawrencetown[1]	Halifax and Goldenville groups	Halifax	1245
Sydney River	Mabou and Cumberland groups	Cape Breton	1072
Albert Bridge	Mira River and Cumberland groups	Cape Breton	953
Lake Echo[1]	Halifax and Goldenville groups and Musquodoboit Batholith	Halifax	875
Stillwater Lake[2]	South Mountain Batholith	Halifax	843

[1] Also appeared in the list of the ten communities with the largest number of private wells in a high-risk zone for arsenic (Kennedy and Drage, 2017).
[2] Also appeared in the list of the ten communities with the largest number of private wells in a high-risk zone for arsenic (Kennedy and Drage, 2020).

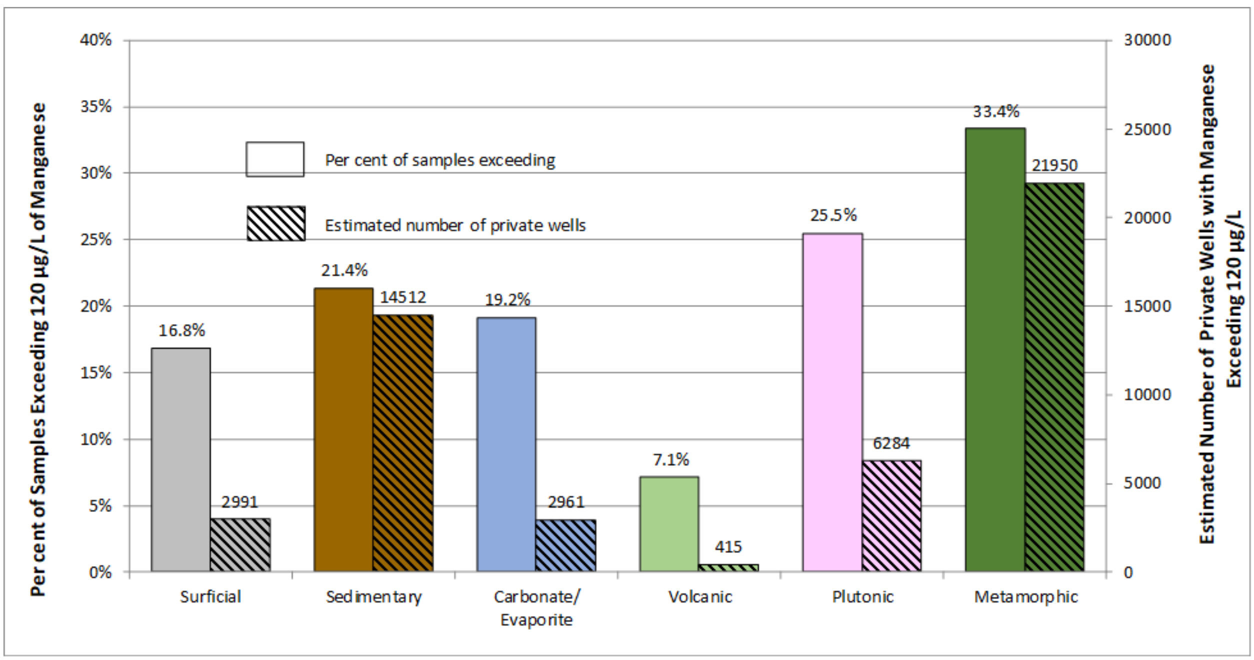

Figure 14. Exceedance rates of Health Canada's maximum acceptable concentration (MAC) of 120 µg/L manganese in drinking water for Nova Scotia's major groundwater regions. Based on these exceedance rates, the number of affected private well owners (households) in each groundwater region is estimated.

Summary

At the levels of manganese found in some well water supplies in Nova Scotia, ingestion of manganese can adversely affect neurological function, which is especially a concern for infants and children, but longer-term ingestion is also a concern for adults.

Elevated manganese occurred in both surficial and bedrock aquifers and geology was shown to be an important provincial-scale control on the distribution of manganese concentrations in well water. Elevated levels of manganese in groundwater can occur throughout the province but the highest exceedance rate of the Health Canada (2019) MAC for manganese in drinking water was associated with the metamorphic (33.4%) groundwater region of Nova Scotia, likely due to the higher content of manganese present in aquifer materials. For example, the Beaverbank and Moshers Island formation (Goldenville Group) aquifers were associated with high concentrations of manganese in the host bedrock and were also associated with a high percentage of well water samples exceeding the Health Canada (2019) manganese MAC in drinking water. The highest exceedance rates (i.e. >50%) of the Health Canada (2019) MAC were observed in bedrock geological units of the Goldenville and Cumberland groups, and granites associated with the South Mountain Batholith and Black Brook Granitic suite in Cape Breton Island. The highest mean concentrations of manganese in well water in surficial aquifers were observed in the Province's sedimentary basins, which may be due to the greater availability of manganese in host aquifer materials or the more circum-neutral pH conditions, which favor manganese mobilization, associated with these aquifers compared to other surficial aquifers in Nova Scotia.

The present analysis demonstrated regional-scale trends, although it should be noted that there is significant spatial heterogeneity of manganese concentrations, which may be attributed to such factors as the availability of manganese containing minerals in contact with groundwater flow and the susceptibility of these minerals to weathering, along with variability in the geochemical conditions influencing manganese mobility (e.g,. pH, redox conditions, availability of complexing ions). The focus of the present analysis with respect to geochemical controls on manganese mobility was the influence of pH and it was generally observed that higher concentrations of manganese in groundwater were associated with circum-netural to slightly alkaline pH (i.e., 6.5 to 8), and lower manganese concentrations at pH levels greater than 8 due to the formation of manganese precipitates with oxygen or carbonates.

It is estimated that about 23.5% (90,000 persons) of private well users province-wide may have manganese exceeding the Health Canada (2019) MAC in their raw water. The largest number of private wells users tend to occur in communities surrounding Halifax and Sydney, where residential growth is concentrated. Many suburban Halifax communities are underlain by the South Mountain Batholith and Meguma rocks (e.g., Goldenville and Halifax Groups), which are also associated with an elevated risk of arsenic and/or uranium in well water.

The manganese in well water risk map (Fig. 13) offers a characterization of relative risk across Nova Scotia. The risk zones, however, should be subject to continuous evaluation as new groundwater chemistry data become available. Approximately 136,899 private wells (69%) or 266,514 persons in Nova Scotia are in the high-risk zone for manganese in well water.

The manganese in well water risk map will be used as a tool to raise risk awareness amongst private well users in Nova Scotia, and to promote appropriate testing and treatment of well water. Effective risk communication is essential to manage the risk of manganese exposure, and to reduce associated adverse health impacts and health care system costs. The manganese in well water risk map will be published as a web map application with an accompanying webpage and story map, targeting private well owners and making it easier for them to access information about risk levels, water testing, and strategies to mitigate elevated manganese in their well water. The map may also be used to inform epidemiological research and land/groundwater supply planning and development.

Further Research

Given the importance of pH, redox and DOC on the mobility of manganese in groundwater, the collection of these field measurements during well water sampling would improve our understanding of the geochemical controls on the release and mobilization of manganese in groundwater. In addition, lab-scale analyses of how manganese is mobilized from various types of manganese minerals may be helpful in explaining patterns of manganese occurrence in groundwater. Additional manganese in well water sampling is recommended to refine the delineation of the risk zones where there are gaps in data coverage, especially where there is a coincident large number of private well users relying on the aquifer for domestic water supply. Additional well water sampling in areas of known manganese mineralization (e.g., manganese districts) would also be useful in understanding the distribution of manganese in well water.

An important aspect of understanding the risk of manganese exposure to private well owners is quantifying the extent to which private well owners are implementing successful mitigation strategies (e.g., water treatment, bottled water). Additional research is therefore warranted to investigate population exposure to manganese in well water. Additional research is also warranted to improve our understanding of the behavioural patterns and barriers to well water testing and treatment across socioeconomic categories in Nova Scotia. Hence behavioural insight analysis could help inform the design of effective risk communication and public health intervention measures.

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