Acid Rock Drainage and Manganese in Rock Units Surrounding the Town of Bridgewater's Water Supply, Lunenburg County, Nova Scotia

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Introduction

Acid rock drainage (ARD) is a common and pervasive concern in southern Nova Scotia due to the presence of abundant sulphide-bearing slates in the Halifax Group (Fig. 1). ARD is produced when pyrite (FeS_2) and/or other sulphide-bearing minerals are excavated, exposing them to surficial oxygen, water, and bacteria. It is characterized by acidic (pH $\leq$5), sulphate (SO_4^{2-})-rich water with high concentrations of dissolved metals. Two of the most common dissolved metals are iron (Fe) and manganese (Mn), and together with ARD they have the potential to impact negatively on the quality of water resources, biodiversity, and metal-concrete infrastructure (e.g. White and Goodwin, 2011; Dvorak et al., 2014; Health Canada, 2016).

ARD has been a continuing environmental problem in the Halifax Regional Municipality (HRM) and several studies have examined the bedrock geology in HRM and its association with the production of acidic waters (e.g. Fox et al., 1997; White and Goodwin, 2011; Trudell and White, 2013a, b). Recently it has been documented that the presence of Mn in drinking water is a potential health hazard, especially in areas where ground and surface waters are more acidic (Heath Canada, 2016).

This report focuses on the ARD potential and related manganese concentrations in rock and water samples from in and around the town of Bridgewater's water supply area, which comprises three lakes (Hebb, Milipsigate, and Minamkeak) and encompasses a natural watershed of approximately 92 km^2 (Fig. 2; Town of Bridgewater, 2018). This area is also the site of the historical Leipsigate Gold District (Fig.2), where abundant mine tailings were produced during gold extraction processes.

This report is the fifth in a series of senior student research projects studying ARD risks in Nova Scotia (e.g. White et al., 2014; Farmer and White 2015; Tarr and White 2016; Hirtle and White, 2017), and the first such study to document manganese concentrations in surface water samples.

Bedrock Geology

Bedrock geology in the Bridgewater watershed area is characterized by rocks of the Cambrian to Ordovician, metasandstone-dominated Goldenville Group and the overlying slate-dominated Halifax Group, exposed in a northeast-trending and northeast-plunging anticline (White, 2010a; White et al., 2012). The Goldenville Group in the area is divided into the older Green Harbour Formation and overlying Government Point and Moshers Island formations (Fig. 2). The Green Harbour Formation consists of grey, thickly bedded and weakly cleaved metasandstone interbedded with minor metasiltstone and rare slate. The conformably overlying Government Point Formation is similar, but the metasandstone is more thinly bedded and interbedded with abundant metasiltstone. The Moshers Island Formation consists of grey to brown to black, cleaved Mn-rich metasiltstone and slate, and rare minor metasandstone. The overlying Halifax Group is represented by the Cunard Formation (Fig. 2; White, 2010a; White et al., 2012), which consists

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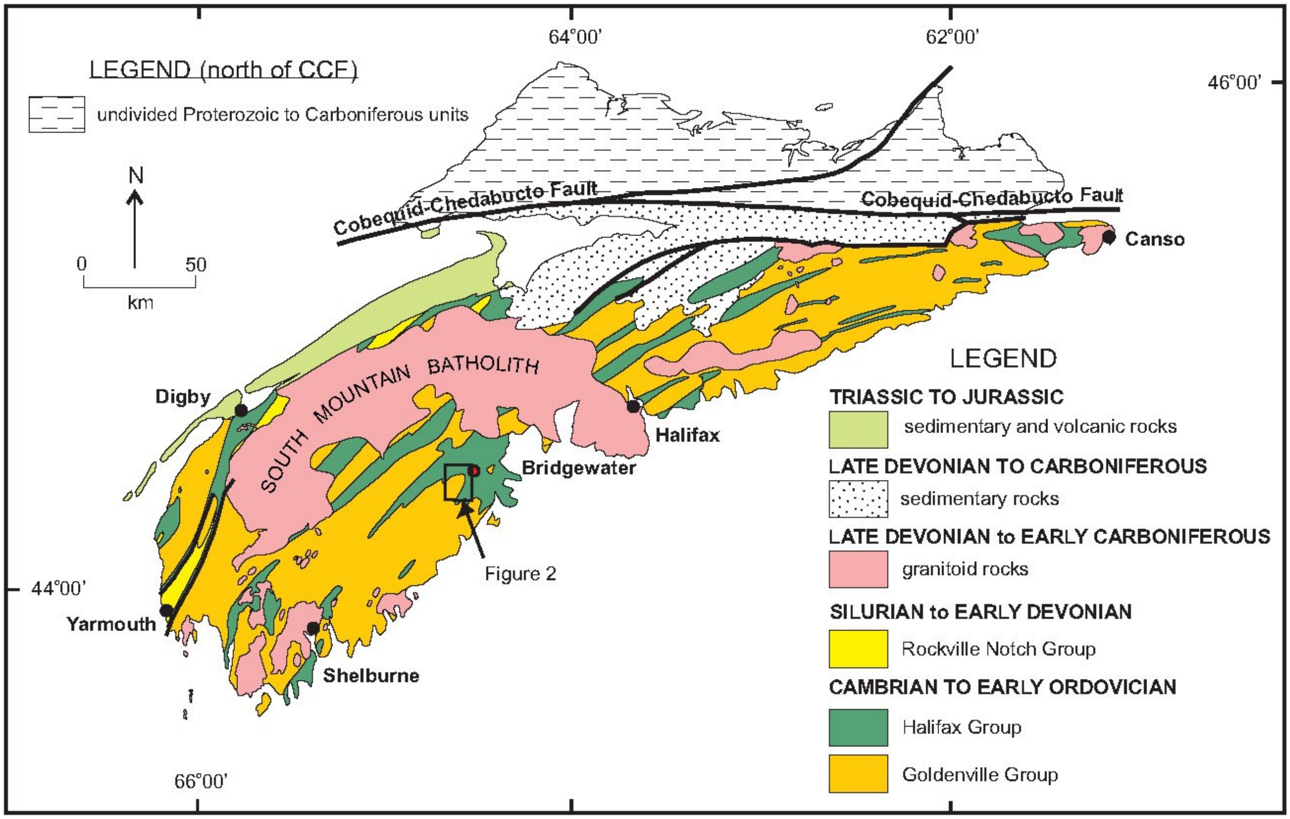

Figure 1. Simplified geological map of the Meguma terrane of southern Nova Scotia, showing the distribution of the Goldenville and Halifax groups and other major units. The area of study is shown in the box and illustrated in Figure 2..

of black to rusty-brown graphitic slate and metasiltstone interbedded with thick, cross-laminated, fine-grained metasandstone. Typically this formation contains abundant pyrite and pyrrhotite, and lesser amounts of arsenopyrite (White and Goodwin, 2011; White et al., 2014).

The Green Harbour Formation hosts the historic Leipsigate Gold District (Fig. 2), where gold-bearing quartz veins were mined from 1884 to 1946. The deposit yielded 13,563.2 Troy ounces of gold (Malcolm, 1976; Bates, 1987). Much of the gold ore was processed on site with the construction of several stamp mills and cyanide plants (Malcolm, 1976).

Methodology

On December 3, 2017, bedrock samples were collected (17NSCC-#s) from twenty-one sites in the study area (Fig. 2). These samples were augmented by 29 samples (W06- and W07-#s) collected from a previous study (Trudell and White, 2013b, c). Thirteen samples are from the Green Harbour Formation, 6 from the Government Point Formation, 13 from the Moshers Island Formation, and 18 from the Cunard Formation (Table 1). In conjunction, the pH of water (ditch, stream, brook, river, lake) at each site was measured in situ using a handheld pH meter (HACH HQ11D portable pH meter), and water samples were collected using 1L polyethylene water bottles for later manganese analysis at NSCC. The bedrock samples were slabbed and multiple spots (3 to 4) on each slab were then analyzed and averaged for total sulphur, calcium, manganese, and a suite of other elements using the Nova Scotia Department of Natural Resources portable X-5000 X-ray fluorescence (pXRF) machine, manufactured by Innov-X (Table 1).

Testing for manganese in water samples was completed on the HACH DR 2800 Spectrophotometer at the Nova Scotia Community College (NSCC), Dartmouth, following the U.S. Environmental Protection Agency approved

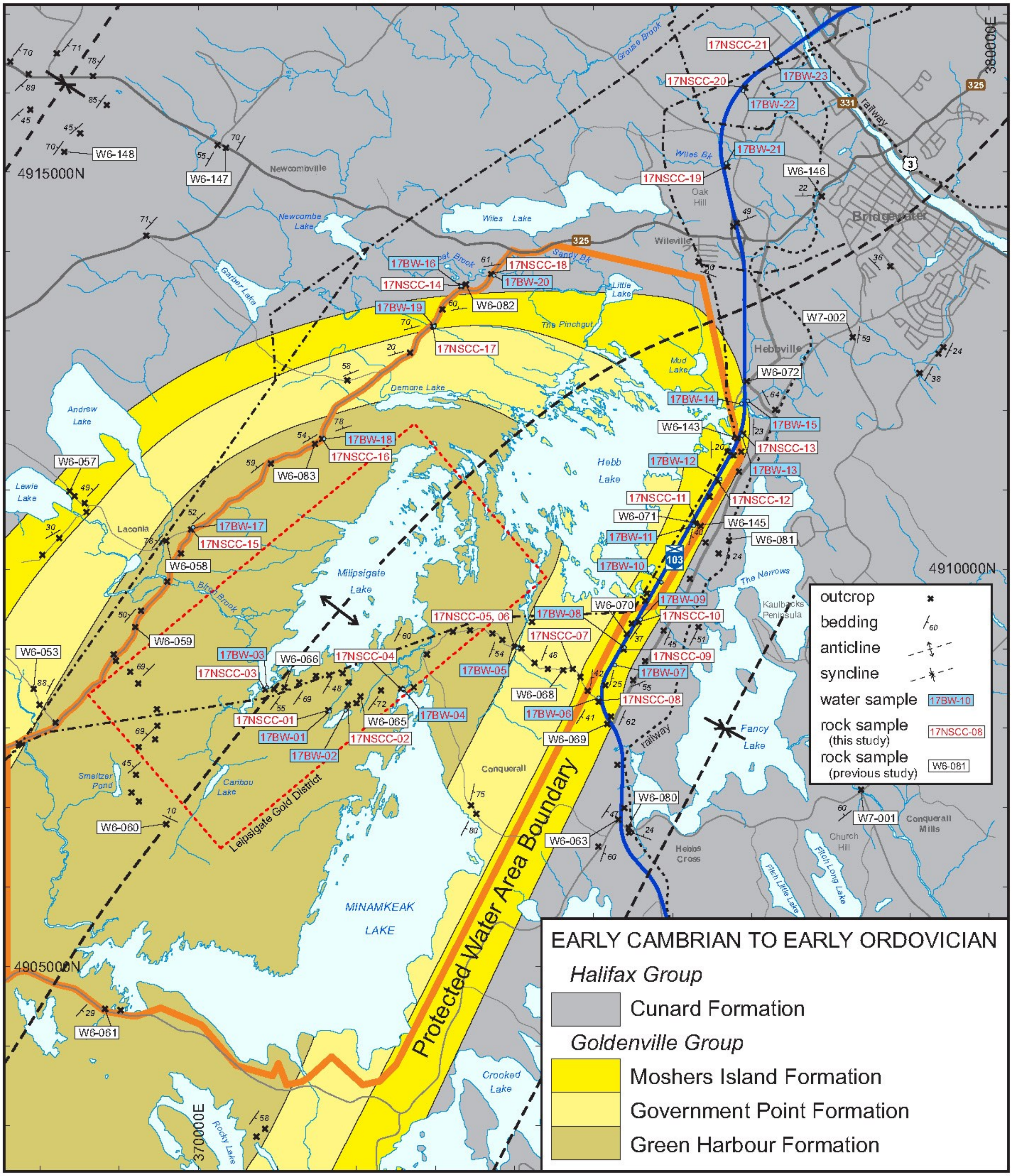

Figure 2. Simplified geology map of the Bridgewater protected water area showing distribution of bedrock and water samples. UTM coordinates for sample locations are in Tables 1 and 2.

"Sample Pretreatment by Digestion" procedure, outlined in the HACH (2013) Water Analysis Guidebook. A manganese standard was used as a check on the quality and accuracy of the analysis, and no adjustments were required.

Results and Discussion

White and Goodwin (2011) showed that the total sulphur (wt.%) versus CaO (wt.%) can be used as a first approximation to determine if a rock is acid producing. When the ratio is greater than 1:1, the rocks can be classified as 'acid producers', whereas below a ratio of 1:2, the rocks are assumed to be 'acid consumers'. When the acid to base ratio falls between 1:1 and 1:2, it is uncertain if the rock is an acid producer or not.

Based on these criteria all the samples from the Cunard Formation and about half of those from the Moshers Island Formation are acid producers (Fig. 3a, b; Table 1). The S/CaO ratios in the Cunard Formation average around 250 and range from 4 to 1400. Although S/CaO ratios are lower in the Moshers Island Formation (average of 2.8 with a range of 0 to 9.6) half the samples are still considered acid producers. Samples in the Moshers Island Formation that are not acid producers have elevated CaO (up to 8 wt.%) and hence lower S/CaO ratios. Four of the 19 samples from the Government Point and Green Harbour formations are acid producing because these specific samples have pyrite-rich laminations. However, the majority of samples have S/CaO ratios lower than 0.4 due to lower sulphur content and the presence of abundant carbonate cement to buffer the acidity (Fig. 3a, b; Table 1). Samples collected from within the Leipsigate Gold District showed no significant acid-producing potential.

The ARD results are consistent with previous studies conducted in HRM (White et al., 2014; Farmer and White, 2015; Tarr and White, 2016; Hirtle and White, 2017) that showed all rocks from the Cunard Formation are major contributors to ARD, whereas about half of the rocks from the Moshers Island Formation (Beaverbank Formation in HRM) are acid producing. Rocks in the underlying Government Point and Green Harbour formations are typically non-acid producing.

The pH of water was measured in the field in a variety of settings ranging from standing water to lakes and fast-running rivers (Table 2; Fig. 3d) and range from 3.21 to 6.89. A water pH value of ≤ 5 is considered to indicate the presence of ARD (U.S. Environmental Protection Agency, 1994). As predicted from previous studies (e.g. Farmer and White, 2015; Tarr and White, 2016; Hirtle and White, 2017), the lowest pH values (3.21, 3.24, and 3.56; Fig. 3d) are from water samples overlying the Cunard Formation and the highest pH values (5.80 to 6.78) are from water samples in the Green Harbour Formation (Table 2). Water samples from the Moshers Island Formation had pH values of 4.10 to 5.88 with an average of about 5. This is consistent with the whole rock ARD values (Table 1; Fig. 3b) where half the samples are acid-producing. In all formations where water samples were taken from relatively fast-flowing streams and rivers, or from large lakes, the pH ranged from 5.8 to 6.9, above the acidity benchmark.

Manganese concentrations in the water samples in this study range from 0.078 to 11.270 mg/L (Table 2; Fig. 3). Not surprisingly, the highest concentrations show a strong correlation with the underlying manganese-rich Moshers Island Formation. The data also show that the more acidic the rock (i.e. high S/CaO ratios), the higher the manganese concentration in the water. Although manganese in water can be the result of mining, industrial discharges, and landfill leaching (e.g. Stokes et al., 1988) or reducing conditions related to decomposition of organic matter (Kohl and Medlar, 2006), in this case the source is likely from the weathering of the underlying manganese-rich Moshers Island Formation (Fig. 3c). Compared to national and regional levels, the mean background manganese concentration for soils and rocks from five major geological areas of Canada was measured at 0.52 mg/L, with a range of 0.10 to 1.2 mg/L (McKeague and Wolynetz, 1980). The higher levels are more prevalent in metamorphic and sedimentary rock (Stokes et al., 1988; Michaelke et al., 2007). Compared to Mn concentrations in raw (untreated) drinking water from across Canada, the Mn concentrations in this study are significant higher than most recorded levels summarized in the Canadian Manganese in Drinking Water Guidelines (Health Canada, 2016).

Table 1. Portable XRF (pXRF) analyses of rock samples from the Bridgewater watershed area.

SO[1]	Sample number	Lithology	Formation	UTM[2] Easting	UTM[2] Northing	SiO_2 (wt%)	CaO (wt%)	TiO_2 (wt%)	MnO (wt%)	$Fe_2O_3^T$ (wt%)	S (wt%)	As (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	U (ppm)	Zn (ppm)	ARD[3] potential	
50	17NSCC-21	black slate	Cunard	377484	4916530	68.88	0.01	0.43	0.07	9.02	4.28	178	16	5	6	0	79	612.42	y
49	W06-148	grey siltstone	Cunard	368315	4915458	65.61	0.11	0.81	0.02	2.10	1.48	1	22	44	25	12	15	13.23	y
48	17NSCC-20	grey slate	Cunard	377003	4916151	80.76	0.01	0.43	0.02	3.00	2.01	3	30	15	11	0	39	287.38	y
47	17NSCC-20	black slate	Cunard	377004	4916150	85.49	0.01	0.63	0.04	3.08	0.65	3	3	5	1	0	41	92.88	y
46	17NSCC-20	grey sandstone	Cunard	377005	4916151	76.63	0.01	0.83	0.01	2.27	3.35	3	66	30	11	0	15	478.68	y
45	W06-147A	black siltstone	Cunard	370456	4915532	64.51	0.01	0.96	0.04	4.60	0.07	4	15	2	14	3	51	6.53	y
44	W06-147B	grey siltstone	Cunard	370458	4915530	71.16	0.00	0.67	0.05	5.01	0.43	3	19	2	7	1	63	386.61	y
43	17NSCC-19	grey sandstone	Cunard	376749	4915194	85.28	0.01	0.37	0.06	7.16	3.54	96	16	9	4	0	99	505.58	y
42	W07-002	grey siltstone	Cunard	378330	4912945	65.50	0.01	0.81	0.17	6.30	0.35	4	15	0	6	1	90	30.66	y
41	W07-001	grey siltstone	Cunard	378296	4907249	64.79	0.14	0.48	0.05	6.40	2.57	9	28	0	0	2	66	18.78	y
40	W06-080	black slate	Cunard	375371	4906797	52.12	0.03	1.45	0.03	4.68	0.35	3	19	2	12	3	37	11.12	y
39	W06-063	black slate	Cunard	375247	4906924	67.51	0.04	0.90	0.03	2.37	1.74	2	11	10	11	5	21	42.92	y
38	W06-081a	grey sandstone	Cunard	376706	4910422	75.42	0.00	0.65	0.10	3.90	1.53	69	13	2	27	1	33	1368.65	y
37	W06-081b	black slate	Cunard	376706	4910421	68.38	0.00	0.90	0.17	4.83	0.19	8	8	2	6	3	50	49.65	y
36	17NSCC-18	black slate	Cunard	373778	4913853	58.90	0.01	1.10	0.39	8.78	0.03	4	3	9	1	0	86	4.29	y
35	W06-082	black slate	Cunard	373386	4913739	66.08	0.00	1.06	0.18	3.35	0.07	8	8	2	10	3	43	60.12	y
34	17NSCC-14	black slate	Cunard	373344	4913696	67.85	0.01	0.75	0.28	5.69	2.85	9	31	40	35	0	397	407.26	y
33	W06-072	black slate	Cunard	376959	4912397	60.00	0.00	1.25	0.15	2.91	0.15	5	9	2	9	4	41	137.49	y
32	W06-069	black siltstone	Moshers Island	375132	4908167	64.11	0.18	1.03	1.48	11.03	0.15	57	25	16	3	3	83	0.80	m
31	W06-057	brown siltstone	Moshers Island	368458	4911176	57.98	0.14	1.15	4.27	24.69	0.23	173	15	278	85	4	191	1.58	y
30	W06-145	black siltstone	Moshers Island	376312	4910451	62.66	0.03	0.85	0.73	10.21	0.12	9	23	2	0	2	87	3.88	y
29	17NSCC-13	grey siltstone	Moshers Island	376858	4911707	51.33	4.67	0.99	4.09	13.49	0.03	43	3	102	1	0	98	0.01	n
28	W06-143	grey siltstone	Moshers Island	376921	4912060	85.21	1.40	0.85	6.77	6.62	0.28	70	7	248	207	6	40	0.20	n
27	17NSCC-12	brown siltstone	Moshers Island	376527	4911134	58.15	7.90	1.10	3.59	10.63	0.03	39	3	67	8	0	71	0.00	n
26	17NSCC-11	grey siltstone	Moshers Island	376231	4910653	66.11	0.01	0.96	0.71	9.62	0.07	22	86	62	1	0	84	9.56	y
25	17NSCC-10	brown siltstone	Moshers Island	375485	4909376	68.86	0.01	0.93	0.44	6.72	0.03	5	3	69	1	0	93	4.29	y
24	17NSCC-09	grey siltstone	Moshers Island	375287	4909043	62.61	0.20	0.84	2.25	7.94	0.03	7	48	54	1	0	77	0.15	n
23	W06-071	grey siltstone	Moshers Island	376187	4910548	65.99	1.22	0.79	1.05	9.02	0.48	0	11	8	0	1	78	0.39	n
22	W06-070	grey siltstone	Moshers Island	375416	4909255	64.14	0.52	0.99	0.88	8.15	0.12	4	13	6	2	0	74	0.22	n
21	17NSCC-08	brown siltstone	Moshers Island	375037	4908477	67.55	0.01	0.92	0.54	7.26	0.03	7	9	66	1	0	73	4.29	y
20	17NSCC-17	brown siltstone	Moshers Island	373012	4913235	70.49	0.05	0.84	1.15	7.35	0.03	23	15	98	1	0	103	0.62	m
19	17NSCC-07	grey siltstone	Government Pt.	374789	4908764	58.09	0.01	0.78	0.92	9.82	0.03	40	3	10	1	0	72	4.29	y
18	W06-068A	grey slate	Government Pt.	374610	4908855	51.70	0.40	0.88	0.77	12.04	0.13	9	160	2	4	1	138	0.31	n
17	W06-068C	grey siltstone	Government Pt.	374610	4908854	80.52	0.57	0.71	0.47	1.92	0.04	2	20	3	7	1	11	0.07	n
16	W06-068B	grey sandstone	Government Pt.	374610	4908853	91.40	0.15	0.35	0.28	3.15	0.06	1	93	1	0	1	43	0.42	n
15	17NSCC-06	grey siltstone	Government Pt.	373949	4909138	61.69	0.01	0.89	0.46	8.22	0.03	18	14	47	1	0	77	4.29	y
14	17NSCC-05	grey sandstone	Government Pt.	373949	4909137	83.08	0.39	0.39	0.23	3.65	0.03	7	15	19	16	0	36	0.08	n
13	W06-058	grey siltstone	Green Harbour	369261	4909731	64.85	0.81	0.76	0.10	8.23	0.10	9	26	2	0	1	86	0.12	n
12	17NSCC-16	grey slate	Green Harbour	371471	4911761	80.75	0.01	0.53	0.05	5.01	0.03	29	14	34	4	0	61	4.29	y
11	W06-083	grey sandstone	Green Harbour	371560	4911831	73.91	0.11	0.49	0.06	7.41	0.11	19	29	2	0	0	87	1.01	y
10	17NSCC-15	grey siltstone	Green Harbour	369904	4910701	80.37	0.16	0.96	0.06	4.98	0.03	9	10	34	1	0	57	0.19	n
9	17NSCC-15	grey sandstone	Green Harbour	369904	4910700	78.50	1.60	0.51	0.06	5.04	0.03	8	9	34	1	0	60	0.02	n
8	W06-058	grey sandstone	Green Harbour	369465	4907005	64.85	1.98	0.34	0.04	1.90	0.31	0	6	2	0	1	19	0.16	n
7	17NSCC-04	grey sandstone	Green Harbour	372531	4908655	81.99	0.23	0.58	0.10	7.47	0.08	22	7	51	1	0	81	0.32	n
6	17NSCC-02	grey sandstone	Green Harbour	371860	4908449	90.76	0.39	0.43	0.02	2.30	0.03	3	12	10	7	0	24	0.08	n
5	17NSCC-01	grey sandstone	Green Harbour	371629	4908409	81.98	1.59	0.37	0.05	2.54	0.03	13	3	22	1	0	23	0.02	n
4	W06-066	grey sandstone	Green Harbour	371056	4908718	84.90	0.73	0.43	0.05	2.71	0.49	9	5	2	0	0	17	0.68	m
3	17NSCC-03	grey sandstone	Green Harbour	370776	4908688	85.81	3.56	0.60	0.07	3.26	0.03	15	3	5	1	0	19	0.01	n
2	W06-060	grey sandstone	Green Harbour	369465	4907005	82.69	0.17	0.45	0.06	3.66	0.07	11	7	2	7	2	30	0.41	n
1	W06-061	grey sandstone	Green Harbour	368552	4904791	85.33	0.25	0.37	0.03	2.57	0.06	3	9	2	1	1	20	0.26	n

Notes: [1] SO = stratigraphic order from oldest (1) to youngest (50); [2] UTM = NAD83, Zone 20; [3] ARD = acid rock drainage potential expressed as ratio (S/CaO), y = yes (>1.0), m = maybe (0.5 to 1.0), n = no (<0.5)

These high Mn levels are of some concern given that the Canadian Manganese in Drinking Water guidelines (Health Canada, 2016) considers the maximum acceptable concentration (MAC) and the aesthetic objective (AO: how the water looks and tastes) for total manganese in drinking water to be 0.1 mg/L and 0.02 mg/L, respectively. In addition, this high manganese unit occurs throughout southern Nova Scotia from Yarmouth to Canso (Fig. 1) and can have MnO levels greater than 30 wt% in some areas (White and Barr, 2010; White 2010b), so the problem could be worse in some other places.

Nova Scotia Environment (NSE) regulates water quality at municipal and registered public drinking

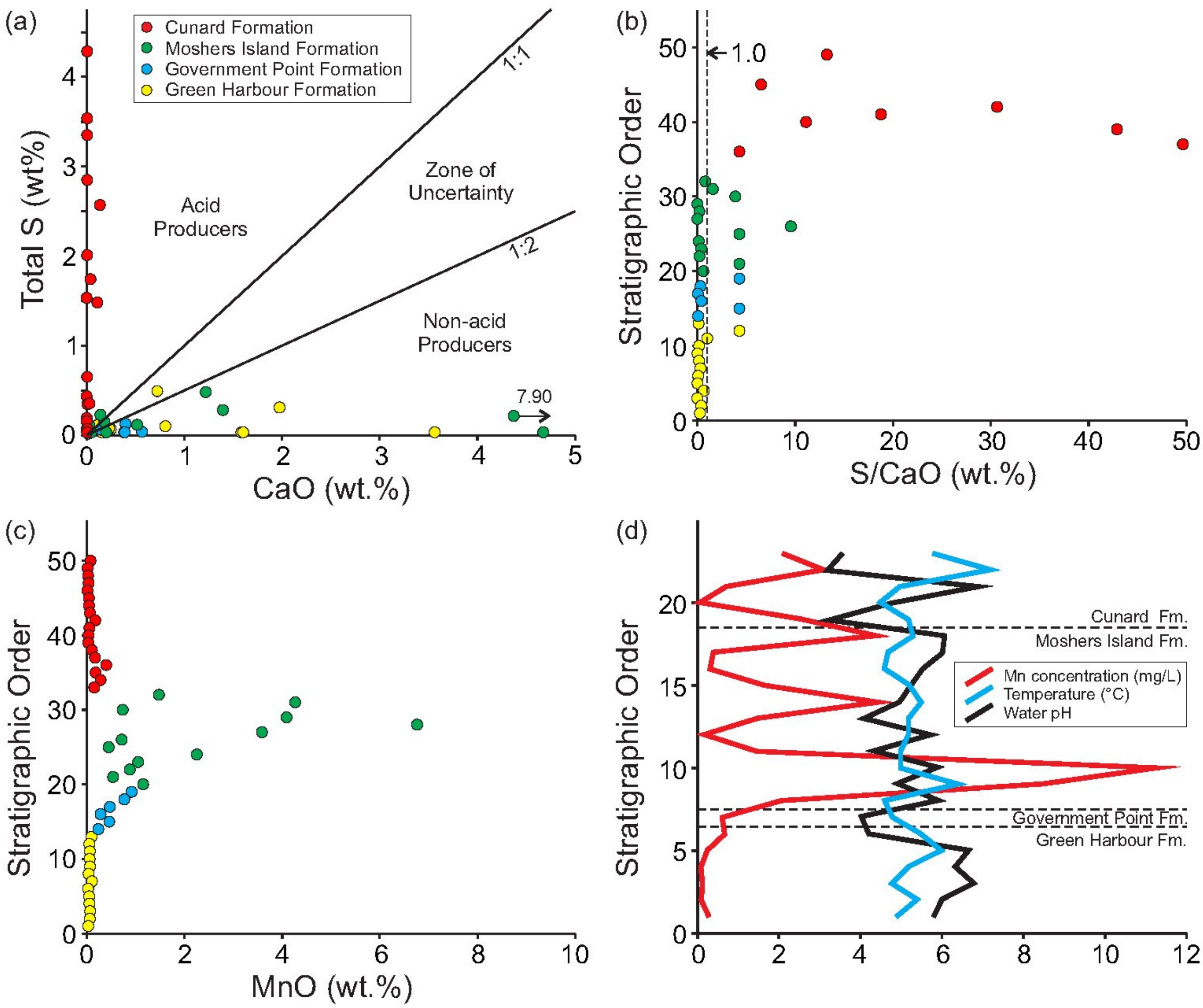

Figure 3. Geochemical data from the portable XRF. (a) Plot of total S against CaO. (b) Plot of acid-potential (S/CaO) against stratigraphic position. Note that most (10) of the samples from the Cunard Formation plot off scale to the right in this diagram. Samples to the right of the dashed vertical line are acid producers. (c) Plot of MnO (wt.%) against stratigraphic position. (d) Plot of stratigraphic position against Mn (mg/L) concentrations in water (red line); temperature (°C) (blue); and pH water data (black).

water facilities. There are currently 1545 registered facilities and NSE analyzed available data from 53% of these facilities. The data identified that 43% exceed an AO of 0.02 mg/L, with 22% exceeding a MAC of 0.10 mg/L. NSE also regulates 83 municipal drinking water facilities and recent data identify three facilities exceeding MAC and 14 facilities exceeding an AO of 0.02 mg/L in treated water (Health Canada, 2016). NSE does not regulate water quality at private residences and, therefore, it is not possible to provide a true determination of the impact of manganese in water with any certainty in these situations.

Summary

The greatest acid-producing potential in rocks around the watershed supplying the town of Bridgewater's drinking water are from slate, metasiltstone, and metasandstone in the Cunard and Moshers Island formations. The presence of abundant sulphide-bearing minerals, such as pyrite and pyrrhotite, coupled with a lack of Ca to neutralize the acid is the major problem. This is also reflected in the low pH of water samples. In contrast, the relative high CaO and low S contents in metasandstone of the Government Point and

Table 2. Locations of water samples collected for this study.

SO[1]	Sample	Setting	Underlying Lithology	Formation	UTM[2] Easting	UTM[2] Northing	T (°C)	pH	Mn (mg/L)
23	17BW-23	slow moving ditch water	slate	Cunard	377484	4916530	5.8	3.56	2.089
22	17BW-22	slow moving ditch water	metasiltstone	Cunard	377004	4916151	7.2	3.21	3.091
21	17BW-21	fast flowing stream	metasandstone	Cunard	376749	4915194	5.0	6.89	0.714
20	17BW-20	moderately flowing stream	slate	Cunard	373778	4913853	4.5	4.78	0.078
19	17BW-16	shallow pond in quarry	slate	Cunard	373344	4913696	5.2	3.24	2.520
18	17BW-15	still water pond off river	Mn-rich metasiltstone	Moshers Island	376965	4912179	5.3	6.06	4.375
17	17BW-14	fast flowing river	Mn-rich metasiltstone	Moshers Island	376925	4912141	4.7	6.02	0.399
16	17BW-13	standing ditch water	Mn-rich metasiltstone	Moshers Island	376858	4911707	4.6	5.70-6.13	0.313
15	17BW-12	standing ditch water	Mn-rich metasiltstone	Moshers Island	376527	4911134	5.2	5.26	1.655
14	17BW-11	standing ditch water	Mn-rich metasiltstone	Moshers Island	376231	4910653	5.5	4.97	4.420
13	17BW-10	standing ditch water	Mn-rich metasiltstone	Moshers Island	375806	4909924	5.2	4.10	1.486
12	17BW-09	standing ditch water	metasiltstone	Moshers Island	375485	4909376	5.2	5.72	0.185
11	17BW-08	standing ditch water	Mn-rich metasiltstone	Moshers Island	375287	4909043	5.0	4.35	1.464
10	17BW-07	standing ditch water	Mn-rich metasiltstone	Moshers Island	375168	4908870	5.0	5.88	11.270
9	17BW-06	standing ditch water	Mn-rich metasiltstone	Moshers Island	375037	4908477	6.4	4.91	8.489
8	17BW-19	fast flowing stream	Mn-rich metasiltstone	Moshers Island	373012	4913235	4.6	5.92	2.072
7	17BW-05	slow flowing stream	metasiltstone	Government Point	373991	4909132	4.8	4.04	0.613
6	17BW-18	pond	metasandstone	Green Harbour	371471	4911761	5.5	4.20	0.677
5	17BW-17	standing ditch water	metasandstone	Green Harbour	369904	4910700	6.0	6.65	0.242
4	17BW-04	lake	metasandstone	Green Harbour	372531	4908655	5.2	6.34	0.096
3	17BW-02	lake	metasandstone	Green Harbour	371868	4908401	4.8	6.78	0.132
2	17BW-01	moderately flowing stream	metasandstone	Green Harbour	371629	4908409	5.4	6.00	0.099
1	17BW-03	lake	metasandstone	Green Harbour	370776	4908688	4.9	5.80	0.275

Notes: [1] SO = stratigraphic order from oldest (1) to youngest (23); [2] UTM = NAD83, Zone 20

Green Harbour formation show that this unit has little risk of producing acid; hence, the moderate pH measurements in the overlying water samples. As noted in previous studies, development projects in or near the Cunard Formation should be aware of the risks associated with potential ARD generation.

Levels of manganese in water samples are extremely elevated, especially over the Moshers Island Formation, with most of the concentrations well above the proposed MAC and AO guidelines (Health Canada, 2016). Although NSE regulates water quality at municipal and registered public drinking water facilities, it does not regulate water quality at private residences. Based on the data provided here, coupled with data from previous studies (e.g. Health Canada, 2016), it is clear that knowledge of local geology is critical prior to developing sites for municipal drinking water. This is especially true for the 70,000 ‘unserviced areas’ where private drinking water supplies may be negatively impacted.

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